INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI®

Bell & Howell Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

The Study of poly(Divinylbenzene-*co*-Ethylvinylbenzene) and Modifications to the Pendant Vinylbenzene Groups

K. Lise Hubbard

Department of Chemistry
McGill University
Montreal, Canada.

June 1997

A Thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of the requirements of the degree of
Doctor of Philosophy

National Library
of Canada

Acquisitions and
Bibliographic Services

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque nationale
du Canada

Acquisitions et
services bibliographiques

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

Our file Notre référence

0-612-36984-6

Canada

Abstract

Cross-linked resins of poly(divinylbenzene-*co*-ethylvinylbenzene) were characterized and modified by a variety of reactions with the pendant vinylbenzene groups. Laboratory-prepared resins of a known composition were compared and contrasted to a commercial version with regard to surface area, porosity, and vinylbenzene content. The commercial resin, Amberlite XAD-4 (Rohm and Haas Company), had a higher surface area (831 m^2/g), porosity (1.18 mL/g), and accessible vinylbenzene groups (2.5 mmol/g, degree of functionalization 33%). Modifications of both resins by radical addition of a variety of thiols led to higher conversions (of vinylbenzene groups to modified groups) with use of the commercial resin (as high as 76%). Further modifications were done strictly with XAD-4. Some thiol additions to XAD-4 were done with water as the solvent, with conversions as high as 43%. Disulfides were added across the vinylbenzene groups of XAD-4 with iodine catalysis, with conversions as high as 55%. This simple one-step reaction has never been done with a polymer system before. XAD-4 was completely epoxidized using a solution of dimethyldioxirane in acetone, and completely brominated to form a resin with (1,2-dibromoethyl)benzene groups (3.76 mmol Br/g). Resins with (1-hydroxy-2-bromoethyl)benzene groups (1.5 mmol/g) were prepared by reaction of XAD-4 with *N*-bromosuccinimide and water, with 73% conversion. Resins with thiol groups (2.5 mmol S/g) were prepared by a one-pot reaction of brominated XAD-4 with *N*,*N*-dimethylthioformamide followed by methanolysis. From one commercially-available resin, several polymers with a variety of functional groups have thus been prepared by simple one- to three-step modifications.

Résumé

Des résines réticulées de poly-divinylbènzene-*co*-éthylvinylbènzene ont été charactérisées et modifiées par diverses réactions sur les groupes vinylbènzenes latéraux. Les résines de composition connue, préparées au laboratoire, ont été comparées et opposées à une résine commerciale du point de vue de la surface unitaire, la porosité et la proportion de vinylbènzene. La résine commerciale, l'Amberlite XAD-4 (de la Compagnie Rohm et Hass), possède une plus grande surface unitaire (831 m^2/g), une plus grande porosité (1.18 mL/g) ainsi que des groupes vinylbènzene plus accessibles (2.5 mmol/g, le degré de fonctionnalisation étant de 33%). Les modifications des deux résines par l'addition radicalaire de divers thiols ont conduit à un nombre plus important de conversions (des groupes vinylbènzenes en groupes modifiés) avec la résine commerciale (jusqu'à 76%). D'autres modifications ont été effectuées sur la résine XAD-4 seulement. Des additions de thiols sur la résine XAD-4 en solution dans l'eau ont donné jusqu'à 43% de conversions. Des disulfides ont été ajoutés le long des groupes vinylbènzene de la résine XAD-4 et catalysés par de l'iode, ce qui a mené à des taux de conversion de 55%. Cette simple réaction en une étape n'a jamais été réalisée auparavant sur un système polymérique. La résine XAD-4 a été complètement époxidée par une solution de diméthyldioxirane dans l'acétone et complètement brominée pour aboutir à une résine contenant des groupes 1,2-dibromoéthylbènzene (3.76 mmol Br/g). Des résines comprenant des groupes 1-hydroxy-2-bromoéthylbènzene (1.5 mmol/g) ont été préparées par réaction de *N*-bromosuccinimide et d'eau sur la résine XAD-4, ce qui a mené à des conversions de 73%. Des résines avec des groupes thiols (2.5 mmol S/g) ont été obtenues grâce à une réaction de la résine XAD-4 brominée, avec du *N,N*-diméthylthioformamide, puis d'une méthanolyse, ces réactions ont été effectuées dans une solution unique. À partir d'une résine commerciale, plusieurs polymères avec divers groupes fonctionnels ont été ainsi préparés au cours de simples réactions de modifications d'une à trois étapes.

Forward

In accordance with McGill University's Faculty of Graduate Studies and Research "Guidelines for Thesis Preparation", the following text must appear in the preface of a manuscript-based thesis:

> Candidates have the option of including, as part of the thesis, the text of one or more papers submitted or to be submitted for publication, or the clearly-duplicated text of one or more published papers. These texts must be bound as an integral part of the thesis.
>
> If this option is chosen, **connecting texts that provide logical bridges between the different papers are mandatory**. The thesis must be written in such a way that it is more than a mere collection of manuscripts; in other words, results of a series of papers must be integrated.
>
> The thesis must still conform to all other requirements of the "Guidelines for Thesis Preparation". **The thesis must include:** A Table of Contents, an abstract in English and French, an introduction which clearly states the rationale and objectives of the study, a review of the literature, a final conclusion and summary, and a thorough bibliography or reference list.
>
> Additional material must be provided where appropriate (e.g. in appendices) and in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis.
>
> In the case of manuscripts co-authored by the candidate and others, **the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent**. Supervisors must attest to the accuracy of such statements at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to make perfectly clear the responsibilities of all the authors of the co-authored papers.

List of papers comprising the thesis

The following chapters of the thesis are based on papers submitted, or soon to be submitted, to the journal Reactive and Functional Polymers. The co-authors for all papers were: K. Lise Hubbard, Dr. James A. Finch and Dr. Graham D. Darling.

Chapter 2. A Review of the Preparation, Characteristics and Modifications of Polymers with Pendant Vinyl Groups Including poly(Divinylbenzene-*co*-Ethylvinylbenzene) and Related Resins. (submitted April 1997)

Chapter 3. The Preparation and Characteristics of poly(Divinylbenzene-*co*-Ethylvinylbenzene), including Amberlite XAD-4. Styrenic Resins with Pendant Vinylbenzene Groups. (submitted April 1997)

Chapter 4. Thiol Addition to the Pendant Vinylbenzene Groups of poly(Divinylbenzene-*co*-Ethylvinylbenzene), including Amberlite XAD-4. Modification in Organic and Aqueous Solvents. (submitted May 1997)

Chapter 5. Disulfide Addition to the Pendant Vinylbenzene Groups of Commercial poly(Divinylbenzene-*co*-Ethylvinylbenzene). Modification with Alkyl and Aryl Disulfides. (submitted May 1997)

Chapter 6. Epoxidation of the Pendant Vinylbenzene Groups of Commercial poly(Divinylbenzene-*co*-Ethylvinylbenzene). (to be submitted June 1997)

Chapter 7. Bromohydration and Bromination of the Pendant Vinylbenzene Groups of Commercial poly(Divinylbenzene-*co*-Ethylvinylbenzene) Resins. Further Reactions of the (1,2-Dibromoethyl)benzene Groups with Thiourea, and with *N,N*-Dimethylthioformamide with Subsequent Methanolysis to Produce Thiol-Containing Styrenic Resins. (submitted May 1997)

Chapter 8. Modifications to the Pendant (1,2-Dibromoethyl)benzene Groups of Brominated Commercial poly(Divinylbenzene-*co*-Ethylvinylbenzene). Reaction with Amines. (to be submitted June 1997)

Appendix 1 is comprised of the following paper: Screening Ligands for Metallurgical Applications by the Determination of pH of Complexation with Metals" by K. Lise Hubbard, Dr. Graham D. Darling and Dr. James A. Finch published in Minerals Engineering, 10 (1), 41-54 (1997).

K.L. Hubbard did all experimental work with exceptions noted in the following acknowledgements, and prepared the initial drafts of each paper. Dr. G.D. Darling and Dr. J.A. Finch were co-supervisors of the thesis project.

The co-authors, and the publishers of any papers published by the date of submission of the thesis, have given permission to include these papers in the thesis (as follows).

Since this thesis is comprised of a collection of papers, there is some repetition of necessary information in each chapter.

Permission of co-authors

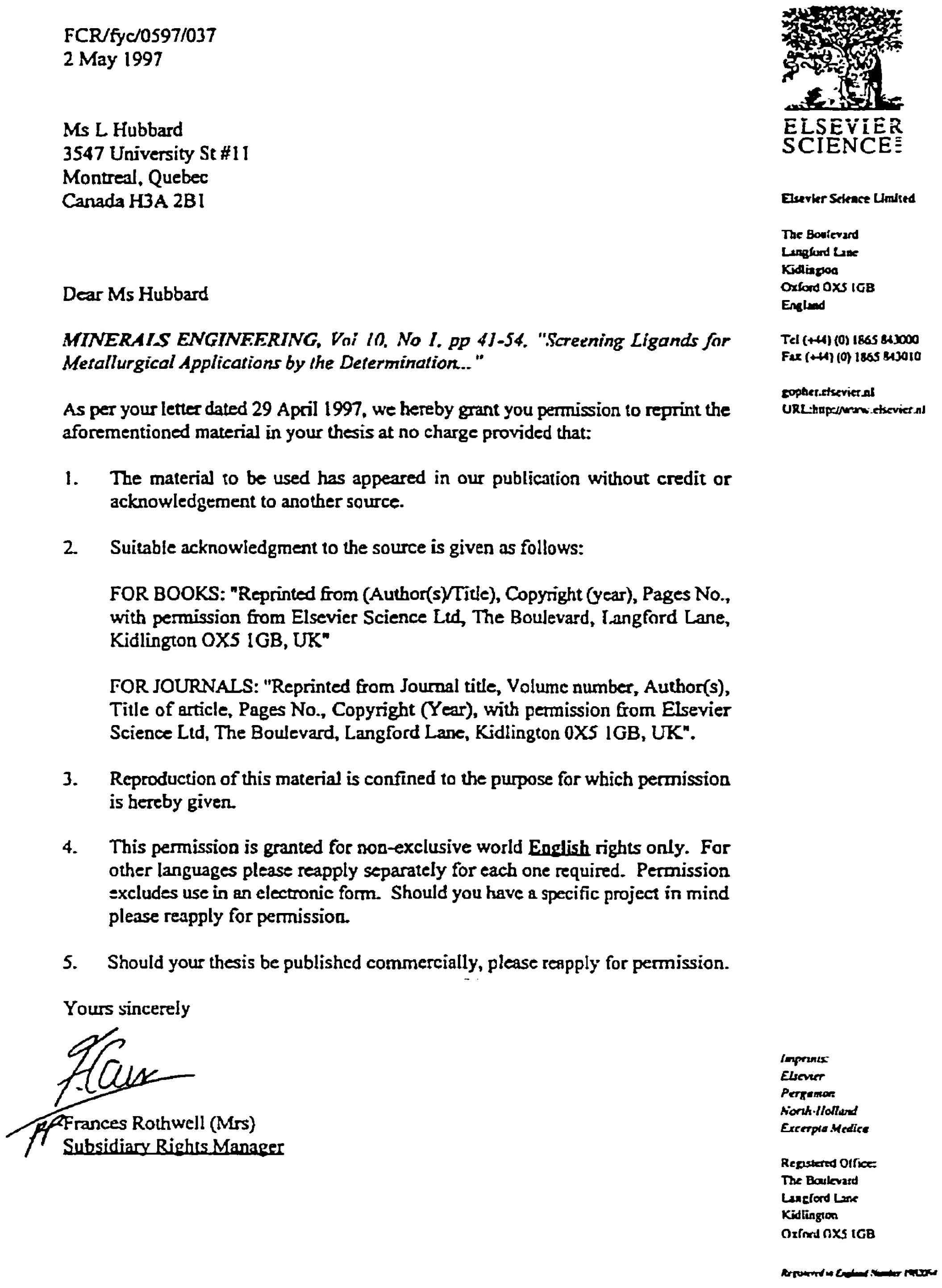
We, the undersigned, as co-authors with K. Lise Hubbard of papers previously published or submitted for publication, give permission to include in her thesis the full contents of these papers. The list of the papers is included in the previous section.

Graham Darling 1997.08.15

Graham D. Darling Date

James A. Finch Date

Copyright waiver of publisher



FCR/fyc/0597/037
2 May 1997

Ms L Hubbard
3547 University St #11
Montreal, Quebec
Canada H3A 2B1

ELSEVIER
SCIENCE

Elsevier Science Limited

The Boulevard
Langford Lane
Kidlington
Oxford OX5 1GB
England

Tel (+44) (0) 1865 843000
Fax (+44) (0) 1865 843010

gopher.elsevier.nl
URL:http://www.elsevier.nl

Dear Ms Hubbard

MINERALS ENGINEERING, Vol 10, No 1, pp 41-54, "Screening Ligands for Metallurgical Applications by the Determination..."

As per your letter dated 29 April 1997, we hereby grant you permission to reprint the aforementioned material in your thesis at no charge provided that:

1. The material to be used has appeared in our publication without credit or acknowledgement to another source.

2. Suitable acknowledgment to the source is given as follows:

   FOR BOOKS: "Reprinted from (Author(s)/Title), Copyright (year), Pages No., with permission from Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington OX5 1GB, UK"

   FOR JOURNALS: "Reprinted from Journal title, Volume number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington 0X5 1GB, UK".

3. Reproduction of this material is confined to the purpose for which permission is hereby given.

4. This permission is granted for non-exclusive world <u>English</u> rights only. For other languages please reapply separately for each one required. Permission excludes use in an electronic form. Should you have a specific project in mind please reapply for permission.

5. Should your thesis be published commercially, please reapply for permission.

Yours sincerely

pp Frances Rothwell (Mrs)
Subsidiary Rights Manager

Imprints:
Elsevier
Pergamon
North-Holland
Excerpta Medica

Registered Office:
The Boulevard
Langford Lane
Kidlington
Oxford OX5 1GB

Registered in England Number [illegible]

Acknowledgements

This work could not have been completed without the assistance of many people. I would like to thank the following people for helping to complete the research.

The following people provided services which were financially compensated:

- BET surface area and porosity: Lab group of Dr. J. Zhu, of the Department of Chemistry, University of Montreal
- ^{13}C NMR spectroscopy: Dr. F. Morin, of the Department of Chemistry, McGill University
- X-ray microprobe analysis: samples were prepared by G. Panagiotidis, analysis was done by G. Poirier, of the Department of Earth and Planetary Sciences, McGill University
- M. Soon, of the Department of Ocenography at the University of British Columbia, did hundreds of elemental analyses

Some of the lab work was done by the following undergraduate students under my direction and training, in the Department of Chemistry, McGill University (financially compensated):

- some infrared spectra were taken by K. Schantz, M. Ruzicka, and N. Walicki
- some repeats of polymer modifications were performed by J. Dracopoulos (chapter 4)
- some polymer modifications were done by S. Pierre (chapter 5)
- some titrations done by G. Prevost, R. Wada, and K. Schantz (appendix 1)
- K. Schantz helped compile titration curves and finish tables, organized data (appendix 1)

Acknowledgements (continued)

Thanks to the following people for helpful suggestions and contributions:

- Dr. G.D. Darling and Dr. J.A. Finch, who co-supervised the project
- Dr. R. Gehr who was involved in the early stages of the project
- Dr. D.N. Harpp, Dr. R.B. Lennox and Dr. D.S. Argyropoulos helped supervise the work upon Dr. G.D. Darling's departure from the university
- Dr. D.N. Harpp for the use of his laboratory for part of the research
- L. Desbaumes translated the abstract into French
- B. Stranix for teaching me the polymer preparation and some modification methodologies used in chapters 3 and 4
- M. Petrucci, E. Schultz, and Dr. F. Sauriol helped obtain liquid state ^1H and ^{13}C NMR spectra (chapter 5)
- B. Stranix and Dr. D.S. Argyropoulos independantly suggested the use of dimethyldioxirane to oxidize the resin (chapter 6)
- P. Hurst suggested the use of titrations to screen ligands (appendix 1)

I would like to thank the my friends and family for their friendship, support and encouragement during these past 5 years.

Funding for this project was provided by a Natural Sciences and Engineering Research Council of Canada Strategic Grant and MEND (Mine Environment Neutral Drainage) grant (Government of Canada). Four of the undergraduate students' salaries were compensated by the McGill Univeristy Work-Study program in conjunction with the McGill University Undergraduate Students' Science Society.

Table of Contents

Abstract ii
Résumé iii
Forward iv
  List of papers comprising the thesis v
  Permission of co-authors vi
  Copyright waiver of publisher vii
  Acknowledgements viii
Table of Contents x
List of Tables xix
List of Figures xxii
List of Schemes xxiv
Glossary of Symbols and Abbreviations xxv

Chapter 1 1
  1.1. Overview of research 1
  1.2. References 2

Chapter 2 3
  Forward to Chapter 2 3
  Abstract 4
  2.1. Introduction 4
  2.2. Non-Styrenic Polymers with Vinyl Groups 4
  2.3. Styrenic Polymers with Vinyl Groups 6
    2.3.1 Preparation by modification of preformed matrices 6
    2.3.2 Preparation of poly(divinylbenzene) and related polymers by polymerization of suitable monomers 8
      2.3.2.1 Linear poly(divinylbenzene) and related polymers 8
      2.3.2.2 Cross-linked poly(divinylbenzene) and related polymers 10
      2.3.2.3 Commercial divinylbenzene polymers 13
    2.3.3 Characteristics of Amberlite resins, poly(divinylbenzene) and related polymers 14
  2.4. Modification of Amberlite Resins 18
  2.5. Modification to Vinyl Groups of Styrenic, including Amberlite, Resins 20
  2.6. Discussion 22

2.7. Conclusions 23
2.8. Acknowledgements 23
2.9. References 24

Chapter 3 28
Forward to Chapter 3 28
Abstract 29
3.1. Introduction 29
3.2. Experimental 31
3.2.1 Materials 31
3.2.2 Preparation of poly(divinylbenzene-*co*-ethylvinylbenzene) 31
3.2.3 Bromination of XAD-4 31
3.2.4 Characterization 32
3.2.4.1 Infrared spectroscopy 32
3.2.4.2 Raman spectroscopy 32
3.2.4.3 ^{13}C NMR spectroscopy 32
3.2.4.4 Surface area and pore size measurements 32
3.2.4.5 Particle size 33
3.2.4.6 Electron microprobe analysis of brominated XAD-4 33
3.3. Results and Discussion 33
3.3.1 Calculation of vinyl content from FTIR absorbance spectra 33
3.3.2 Bromination of XAD-4 and calculation of degree of functionalization 38
3.3.3 Raman spectroscopy 39
3.3.4 ^{13}C NMR spectroscopy 42
3.3.5 Surface area, pore size and particle size distribution 44
3.3.6 X-Ray microprobe analysis to measure bromine distribution 47
3.4. Conclusions 52
3.5. Acknowledgements 52
3.6. References 53

Chapter 4 55
Forward to Chapter 4 55
Abstract 56
4.1. Introduction 56

4.1.1 Review of poly(divinylbenzene-*co*-ethylvinylbenzene), including XAD-4 56
4.1.2 Review of thiol addition to vinyl-containing polymers 57
4.1.3 Review of thiol addition to halogen-containing polymers 59
4.1.4 Addition of thiols to poly(divinylbenzene-*co*-ethylvinylbenzene) 59
4.2. Experimental 60
4.2.1 Materials 60
4.2.2 Preparation of poly(divinylbenzene-*co*-ethylvinylbenzene) 61
4.2.3 Anti-Markovnikov addition of thiols to pendant vinylbenzene groups 61
4.2.4 Characterization 63
4.2.4.1 Elemental analysis 63
4.2.4.2 Infrared spectroscopy 63
4.2.4.3 Raman spectroscopy 63
4.2.4.4 ^{13}C NMR spectroscopy 63
4.2.4.5 Surface area and pore size measurements 64
4.2.4.6 Electron microprobe analysis of mercaptoethanol-modified XAD-4 64
4.3. Results and Discussion 64
4.3.1 Characteristics of starting materials 64
4.3.2 Modification of XAD-4 by addition of thiols 65
4.3.2.1 Calculation of the degree of functionalization 65
4.3.2.2 Comparison of modification of resins using various organic solvents 66
4.3.2.3 Comparison of modification of XAD-4 and polyDVB-55 70
4.3.2.4 Comparison of modification of resins using organic solvents and water 71
4.3.3 X-Ray microprobe analysis to measure sulfur and oxygen distribution 74
4.3.4 Spectroscopic characterization 75
4.3.4.1 Infrared spectroscopy 75
4.3.4.2 Raman spectroscopy 84
4.3.4.3 ^{13}C NMR spectroscopy 90
4.3.5 Potential applications of thiol-modified resins 93
4.4. Conclusions 95
4.5. Acknowledgements 95

4.6. References 96

Chapter 5 99
Forward to Chapter 5 99
Abstract 100
5.1. Introduction 100
5.1.1 Review of poly(divinylbenzene-*co*-ethylvinylbenzene), including XAD-4 100
5.1.2 Review of disulfide chemistry, including thermal and radical reactions with alkenes 101
5.1.3 Review of reactions of styrene with disulfides 102
5.1.4 Iodine-catalyzed addition of disulfides to alkenes 104
5.1.5 Other catalyzed additions of disulfides to alkenes 106
5.1.5 Addition of disulfides to poly(divinylbenzene-*co*-ethylvinylbenzene) .. 106
5.2. Experimental 107
5.2.1 Materials 107
5.2.2 Addition of disulfides to pendant vinylbenzene groups 107
5.2.2.1 Iodine-catalyzed addition 108
5.2.2.2 Boron trifluoride-diethyl etherate-catalyzed addition 109
5.2.2.3 AIBN initiated radical addition 109
5.2.2.4 Ultraviolet-light initiated radical addition 110
5.2.3 Addition of analogous thiols to pendant vinylbenzene groups 110
5.2.4 Addition of analogous thiols to pendant (1,2-dibromoethyl)benzene groups 110
5.2.5 Preparation of model compounds 111
5.2.5.1 Preparation of 2-(4-methylphenylthio)ethylbenzene 111
5.2.5.2 Di-1,2-(4-methylphenylthio)ethylbenzene prepared by iodine-catalyzed addition of *p*-tolyl disulfide to styrene 111
5.2.6 Characterization 112
5.2.6.1 Elemental analysis 112
5.2.6.2 Infrared spectroscopy 112
5.2.6.3 Raman spectroscopy 112
5.2.6.4 ^{1}H and ^{13}C NMR spectroscopy 112
5.3. Results and Discussion 113
5.3.1 Characteristics of starting materials 113
5.3.2 Modification of XAD-4 by addition of thiols and disulfides 113

5.3.2.1 Calculation of the degree of functionalization 113
5.3.2.2 Results of disulfide addition using various solvents with iodine 114
5.3.2.3 Comparison of catalysts or initiators used 116
5.3.2.4 Comparison of thiol and disulfide addition to XAD-4 119
5.3.2.5 Comparison of disulfide addition to XAD-4 with thiol modification of brominated XAD-4 121
5.3.3 Model compounds 122
5.3.4 Spectroscopic characterization 123
5.3.4.1 Infrared spectroscopy 123
5.3.4.2 Raman spectroscopy 132
5.3.4.3 ^{13}C NMR spectroscopy 132
5.3.5 Potential applications of modified resins and suggestions for further investigations 137
5.4. Conclusions 138
5.5. Acknowledgements 138
5.6. References 139

Chapter 6 142
Forward to Chapter 6 142
Abstract 143
6.1. Introduction 143
6.1.1 Commercial poly(divinylbenzene-*co*-ethylvinylbenzene) 143
6.1.2 Introduction of epoxy groups into polymeric substrates, and subsequent reactions 144
6.1.3 Introduction of thiirane groups into polymeric substrates 147
6.2. Experimental 147
6.2.1 Materials 147
6.2.2 Epoxidation of pendant vinylbenzene groups 148
6.2.2.1 Epoxidation with hydrogen peroxide and acetonitrile, benzonitrile, or trichloroacetonitrile 148
6.2.2.2 Epoxidation with hydrogen peroxide and ethyl chloroformate 148
6.2.2.3 Epoxidation with hydrogen peroxide and methyltrioctylammonium tetrakis(diperoxotungsten)phosphate (3-) 149
6.2.2.4 Epoxidation with *m*-chloroperbenzoic acid (*m*CPBA) 149
6.2.2.5 Epoxidation with magnesium monoperoxyphthalate (MMPP) 150
6.2.2.6 Epoxidation with peracetic acid 150

6.2.2.7 Epoxidation with dimethyldioxirane (DMD) ... 150
6.2.3 Acid-catalyzed reaction of epoxy groups with *N*,*N*-dimethylthioformamide ... 151
6.2.4 Characterization ... 152
6.2.4.1 Elemental analysis ... 152
6.2.4.2 Infrared spectroscopy ... 152
6.2.4.3 Raman spectroscopy ... 152
6.2.4.4 ^{1}H and ^{13}C NMR spectroscopy ... 152
6.3. Results and Discussion ... 153
6.3.1 Characteristics of starting materials ... 153
6.3.2 Epoxidation of XAD-4 ... 153
6.3.2.1 Comparison of epoxidation techniques ... 153
6.3.2.2 Attempted conversion of epoxide to episulfide ... 156
6.3.3 Spectroscopic characterization ... 157
6.3.3.1 Infrared spectroscopy ... 157
6.3.3.2 Raman spectroscopy ... 160
6.3.2.3 ^{13}C NMR spectroscopy ... 163
6.3.4 Potential applications of modified resins and suggestions for further investigations ... 166
6.4. Conclusions ... 167
6.5 Acknowledgements ... 167
6.6 References ... 168

Chapter 7 ... 171
Forward to Chapter 7 ... 171
Abstract ... 172
7.1. Introduction ... 172
7.1.1 Review of our previous work, including characterization of XAD-4 ... 172
7.1.2 Review of bromohydrin preparation ... 173
7.1.3 Review of bromination of polymers ... 174
7.1.4 Modifications of resins with thiourea ... 175
7.1.5 Thiol-containing resins ... 176
7.1.6 Modifications of commercial poly(divinylbenzene-*co*-ethylvinylbenzene) in this paper ... 178
7.2. Experimental ... 179
7.2.1 Materials and methods ... 179

7.2.2 Bromohydration of XAD-4 179
7.2.3 Bromination of XAD-4 180
7.2.4 Reactions of brominated XAD-4 180
7.2.4.1. Addition of thiourea to (1,2-dibromoethyl)benzene groups 180
7.2.4.2. Addition of *N,N*-dimethylthioformamide to (1,2-dibromoethyl)benzene groups and methanolysis 180
7.2.5 Characterization 181
7.2.5.1 Elemental analysis 181
7.2.5.2 Infrared spectroscopy 181
7.2.5.3 Raman spectroscopy 181
7.2.5.4 ^{13}C NMR spectroscopy 182
7.3. Results and Discussion 182
7.3.1 Characteristics of starting materials 182
7.3.2 Modification of XAD-4 183
7.3.2.1 Calculation of the degree of functionalization 183
7.3.2.2 Bromohydration of XAD-4 183
7.3.2.3 Bromination of XAD-4 185
7.3.2.4 Reaction of brominated XAD-4 with thiourea 186
7.3.2.5 Addition of *N,N*-dimethylthioformamide to brominated XAD-4 and methanolysis 187
7.3.3 Spectroscopic characterization 191
7.3.3.1 Infrared spectroscopy 191
7.3.3.2 Raman spectroscopy 194
7.3.3.3 ^{13}C NMR spectroscopy 197
7.3.4 Potential applications of modified resins and suggestions for further work 198
7.4. Conclusions 200
7.5. Acknowledgements 200
7.6. References 201

Chapter 8 204
Forward to Chapter 8 204
Abstract 205
8.1. Introduction 205
8.1.1 Review of previous modifications of poly(divinylbenzene-*co*-ethylvinylbenzene) 205

8.1.2 Review of poly(divinylbenzene-*co*-ethylvinylbenzene), including XAD-4 206
8.1.3 Review of modifications of resins with amines 206
8.1.4 Addition of amines to (1,2-dibromoethyl)benzene groups of brominated poly(divinylbenzene-*co*-ethylvinylbenzene) 208
8.2. Experimental 209
8.2.1 Materials and methods 209
8.2.3 Bromination of XAD-4 209
8.2.4 Addition of amines to brominated XAD-4 210
8.2.5 Characterization 210
8.2.5.1 Elemental analysis 210
8.2.5.2 Infrared spectroscopy 211
8.2.5.3 Raman spectroscopy 211
8.2.5.4 ^{13}C NMR spectroscopy 211
8.3. Results and Discussion 212
8.3.1 Characteristics of starting materials 212
8.3.2 Modification of XAD-4 212
8.3.2.1 Bromination of XAD-4 212
8.3.2.1.1 Calculation of the degree of functionalization of brominated XAD-4 212
8.3.2.1.2 Results of bromination of XAD-4 212
8.3.2.3 Reaction of brominated XAD-4 with amines 213
8.3.3 Spectroscopic characterization 215
8.3.3.1 Infrared spectroscopy 215
8.3.3.2 Raman spectroscopy 218
8.3.3.3 ^{13}C NMR spectroscopy 219
8.3.4 Potential applications of modified resins and suggestions for further work 221
8.4. Conclusions 222
8.5 Acknowledgements 222
8.6 References 222

Chapter 9 225
9.1. Modifications of the pendant vinylbenzene groups of commercial poly(divinylbenzene-co-ethylvinylbenzene) 225
9.2. Contributions to knowledge 225

9.3. Suggestions for further work 229

Appendix 1 230
  Forward to Appendix 1 230
  Abstract 231
  A1.1. Introduction 231
  A1.2. Experimental work 232
    A1.2.1 Materials 232
    A1.2.2 Equipment 232
    A1.2.3 Method 232
  A1.3. Results and Discussion 235
  A1.4. Conclusions 251
  A1.5. Acknowledgements 251
  A1.6. References 251

Appendix 2 253

List of Tables

Table 2.1. Characteristics of Amberlite XAD polyaromatic adsorbent resins 15
Table 2.2. Raman peak assignments for Amberlite XAD-2 16
Table 2.3. Infrared peak assignments for divinylbenzene copolymers 17
Table 2.4. Solvent uptake for Amberlite XAD-1 and XAD-2 (g solvent per g resin) 18
Table 3.1. Infrared peak assignments for divinylbenzene copolymers 34
Table 3.2. Vinyl contents of divinylbenzene copolymers 36
Table 3.3. Raman peak assignments for XAD-4 39
Table 3.4. ^{13}C NMR peak assignments for XAD-4 42
Table 3.5. Surface areas and pore sizes of divinylbenzene copolymers 44
Table 3.6. Characteristics of commercial divinylbenzene copolymers 45
Table 3.7. Particle size distribution 46
Table 4.1. Thiols used in modification of pendant vinylbenzene groups 62
Table 4.2. Vinyl contents of divinylbenzene copolymers 65
Table 4.3. Surface areas and porosities of divinylbenzene copolymers 65
Table 4.4. Solubilities of thiols at room temperature 67
Table 4.5. Degree of functionalization ($C_{2\text{-SR}}$ (mmol SR/g), $X_{2\text{-SR}}$) and percent conversion (Φ) by thiol modification of vinylbenzene groups in organic solvents .. 69
Table 4.6. Comparison of modification of XAD-4 using organic solvents or water 73
Table 4.7. Results of modification of XAD-4 with varying amounts of mercaptoethanol 74
Table 4.8. Infrared peak assignments for thiol-modified resins 76
Table 4.9. ^{13}C CP-MAS-DD NMR peak assignments for thiol-modified XAD-4 .. 91
Table 5.1. Relative reactivities of disulfides compared to CCl_4 in reaction with phenyl radicals 102
Table 5.2. Chain transfer constants of disulfides 103
Table 5.3. Results of iodine-catalyzed addition of aryl disulfides to styrene derivatives 105
Table 5.4. Thiols and disulfides used in modification of vinylbenzene groups 108
Table 5.5. Solubilities of reagents 109
Table 5.6. Characteristics of XAD-4 113
Table 5.7. Degree of functionalization ($C_{1,2\text{-SR}}$ (mmol fg/g), $X_{1,2\text{-SR}}$) and percent conversion (Φ) by disulfide addition 117

Table 5.8. Comparison of percent conversion to solvent polarity for various solvents used in the iodine-catalyzed addition of *n*-propyl disulfide to the pendant vinylbenzene groups of XAD-4 119
Table 5.9. Comparison of the degree of functionalization and conversion (Φ) of modified XAD-4 by thiol addition ($C_{2\text{-SR}}$ (mmol fg/g), $X_{2\text{-SR}}$) to best disulfide results ($C_{1,2\text{-SR}}$ (mmol fg/g and mmol SR/g), $X_{1,2\text{-SR}}$) 120
Table 5.10. Comparison of percent conversion of thiol and disulfide addition to the pendant vinylbenzene groups of XAD-4, in order of yield 121
Table 5.11. Degree of functionalization (C_{fg} (mmol SR/g) for the modification of (1,2-dibromoethyl)benzene groups with analogous thiols 122
Table 5.12. Results of preparation of model compounds 122
Table 5.13a. Infrared peak assignments for thiol and disulfide-modified resins 123
Table 5.13b. Infrared peak assignments for thiol and disulfide-modified resins 124
Table 5.14. ^{13}C CP-MAS-DD NMR peak assignments for modified XAD-4 133
Table 6.1. Characteristics of XAD-4 153
Table 6.2. Methods which gave reductions of vinylbenzene groups 154
Table 6.3. Elemental contents of resins **7** and **8** 156
Table 6.4a. Infrared peak assignments for modified resins (**1-5**) 158
Table 6.4b. Infrared peak assignments for modified resins (**6-8**) 159
Table 6.5. ^{13}C CP-MAS NMR peak assignments for modified XAD-4 164
Table 7.1. Characteristics of XAD-4 182
Table 7.2. Results of bromohydration of XAD-4 with *N*-bromosuccinimide 184
Table 7.3. Results of bromination of XAD-4 185
Table 7.4. Results of reaction of brominated XAD-4 with thiourea 187
Table 7.5. Results of reaction of brominated XAD-4 with *N,N*-dimethylthioformamide with subsequent methanolysis 188
Table 7.6. Comparison of method of introduction of thiol-containing groups onto various polymers 190
Table 7.7. ^{13}C CP-MAS NMR peak assignments for modified XAD-4 197
Table 8.1. Results of reaction of chloromethylated polystyrene with amines 207
Table 8.2. Amines used in modification of brominated XAD-4 210
Table 8.3. Characteristics of XAD-4 212
Table 8.4. Result of bromination of XAD-4 213
Table 8.5. Results of reaction of brominated XAD-4 with amines 214
Table 8.6. Infrared peak assignments for amine-modified resins 216

Table 8.7. Possible functional groups of amine-modified brominated XAD-4 218
Table 8.8. ^{13}C NMR peak assignments for modified XAD-4 220
Table A1.1. Thiol-Containing Ligands Studied 234
Table A1.2. Amine-Containing Ligands Studied 235
Table A1.3: pH of Complexation of Ni^{+2} with Various Thiol Ligands 239
Table A1.4. Cited Stability Constants (pK_1) of Complexation of Ni^{+2} with Various Thiol Ligands 240
Table A1.5. pH of Complexation of Cu^{+2} with Various Thiol Ligands 241
Table A1.6. Cited Stability Constants (pK_1) of Complexation of Cu^{+2} with Various Thiol Ligands 242
Table A1.7. pH of Complexation of Zn^{+2} with Various Thiol Ligands 243
Table A1.8. Cited Stability Constants (pK_1) of Complexation of Zn^{+2} with Various Thiol Ligands 244
Table A1.9. pH of Complexation of Ni^{+2} with Various Amine Ligands 245
Table A1.10. Cited Stability Constants (pK_1) of Complexation of Ni^{+2} with Various Amine Ligands 246
Table A1.11. pH of Complexation of Cu^{+2} with Various Amine Ligands 247
Table A1.12. Cited Stability Constants (pK_1) of Complexation of Cu^{+2} with Various Amine Ligands 248
Table A1.13. pH of Complexation of Zn^{+2} with Various Amine Ligands 249
Table A1.14. Cited Stability Constants (pK_1) of Complexation of Zn^{+2} with Various Amine Ligands 250

List of Figures

Fig. 2.1. BMO-CO_2 copolymer..5
Fig. 2.2. Relative reactivities of of monomers..9
Fig. 2.3. Structure of linear poly(divinylbenzene)..10
Fig. 2.4. Structure of poly(1,4-phenylenevinylene)..10
Fig. 2.5. Structure of poly(divinylbenzene-*co*-ethylvinylbenzene)..11
Fig. 3.1. Structure of poly(divinylbenzene-*co*-ethylvinylbenzene)..30
Fig. 3.2. FTIR absorbance spectra of divinylbenzene copolymers..37
Fig. 3.3. FTIR absorbance spectra of XAD-4 and brominated XAD-4..40
Fig. 3.4. Raman spectrum of XAD-4..41
Fig. 3.5. Solid-phase ^{13}C NMR spectra of XAD-4..43
Fig. 3.6. Bromine distribution profile of brominated XAD-4 embedded in Epo-Tek-301 (Bead A)..50
Fig. 3.7. Bromine distribution profile of brominated XAD-4 embedded in Epo-Tek-377 (Bead B)..50
Fig. 3.8. Secondary electron micrographs of bead cross-sections of brominated XAD-4 embedded in Epo-Tek-301 (Bead A) and Epo-Tek-377 (Bead B)..51
Fig. 3.9. Backscatter electron micrographs of bead cross-sections of brominated XAD-4 embedded in Epo-Tek-301 (Bead A) and Epo-Tek-377 (Bead B)..51
Fig. 4.1. Structure of poly(divinylbenzene-*co*-ethylvinylbenzene)..57
Fig. 4.2. Sulfur and oxygen distribution profiles of **9a**, mercaptoethanol-modified XAD-4..75
Fig. 4.3a. FTIR absorbance spectra of XAD-4 and thiol-modified resins..78
Fig. 4.3b. FTIR absorbance spectra of XAD-4 and thiol-modified resins..79
Fig. 4.3c. FTIR absorbance spectra of XAD-4 and thiol-modified resins..80
Fig. 4.3d. FTIR absorbance spectra of XAD-4 and thiol-modified resins..82
Fig. 4.3e. FTIR absorbance spectra of XAD-4 and thiol-modified resins..83
Fig. 4.4a. Raman spectra of XAD-4 and thiol-modified resins..85
Fig. 4.4b. Raman spectra of XAD-4 and thiol-modified resins..86
Fig. 4.4c. Raman spectra of XAD-4 and thiol-modified resins..87
Fig. 4.4d. Raman spectra of XAD-4 and thiol-modified resins..88
Fig. 4.4e. Raman spectra of XAD-4 and thiol-modified resins..89
Fig. 4.5a. ^{13}C CP-MAS NMR spectra of XAD-4 and thiol-modified XAD-4..92
Fig. 4.5b. ^{13}C CP-MAS-DD NMR spectra of XAD-4 and thiol-modified XAD-4. 92

Fig. 5.1. Structure of poly(divinylbenzene-*co*-ethylvinylbenzene) 101

Fig. 5.2a. FTIR absorbance spectra of XAD-4 and modified resins. 127

Fig. 5.2b. FTIR absorbance spectra of XAD-4 and modified resins 128

Fig. 5.2c. FTIR absorbance spectra of XAD-4 and modified resins. 129

Fig. 5.2d. FTIR absorbance spectra of XAD-4 and modified resins 130

Fig. 5.2e. FTIR absorbance spectra of XAD-4-Br and thiol-modified XAD-4-Br. 131

Fig. 5.3a. ^{13}C CP-MAS NMR spectra of XAD-4 and modified XAD-4. 134

Fig. 5.3b. ^{13}C CP-MAS-DD NMR spectra of XAD-4 and modified XAD-4. 134

Fig. 5.4a. ^{13}C CP-MAS NMR spectra of XAD-4 and modified XAD-4. 135

Fig. 5.4b. ^{13}C CP-MAS-DD NMR spectra of XAD-4 and modified XAD-4. 135

Fig. 5.5a. ^{13}C CP-MAS NMR spectra of brominated XAD-4 and thiol-modified XAD-4-Br 136

Fig. 5.5b. ^{13}C CP-MAS-DD NMR spectra of brominated XAD-4 and thiol-modified XAD-4-Br 136

Fig. 6.1. Structure of poly(divinylbenzene-*co*-ethylvinylbenzene) 144

Fig. 6.2. FTIR absorbance spectra of XAD-4 and modified resins (**1-8**) 161

Fig. 6.3. Raman spectra of XAD-4 and modified resins (**7** and **8**) 162

Fig. 6.4. ^{13}C CP-MAS NMR spectra of XAD-4 and modified resins (**1-8**) 165

Fig. 7.1. Structure of poly(divinylbenzene-*co*-ethylvinylbenzene) 173

Fig. 7.2. FTIR absorbance spectra of XAD-4 and modified resins 192

Fig. 7.3. FTIR absorbance spectra of XAD-4-Br and modified XAD-4-Br. 195

Fig. 7.4. Raman spectra of XAD-4 and modified resins. 196

Fig. 7.5a. ^{13}C CP-MAS NMR spectra of XAD-4 and modified resins. 199

Fig. 7.5b. ^{13}C CP-MAS-DD NMR spectra of XAD-4 and modified resins 199

Fig. 8.1. Structure of poly(divinylbenzene-*co*-ethylvinylbenzene) 206

Fig. 8.2. FTIR absorbance spectra of brominated XAD-4 and modified resins 217

Fig. A1.1. Titration curves of Ni^{+2} (A), 2-aminoethanethiol hydrochloride (L, curve B), and Ni^{+2} in the presence of one (C) and two (D) equivalents of 2-aminoethanethiol hydrochloride. 238

List of Schemes

Scheme 1.1. Modifications of poly(divinylbenzene-*co*-ethylvinylbenzene) 2
Scheme 4.1. Anti-Markovnikov thiol addition to vinylbenzene groups of poly(divinylbenzene-*co*-ethylvinylbenzene) 62
Scheme 5.1. Proposed steps of iodine-catalyzed addition of disulfides to styrene .. 105
Scheme 5.2. Thiol and disulfide addition to vinylbenzene groups of poly(divinylbenzene-*co*-ethylvinylbenzene) 107
Scheme 5.3. Preparation of monosubstituted model compound 111
Scheme 5.4. Preparation of disubstituted model compound 111
Scheme 6.1. Preparation of styrenic resin with epoxy groups 145
Scheme 6.2. Epoxidation of vinylbenzene groups of XAD-4 with dimethyldioxirane 147
Scheme 7.1. Interconversion of isothiourea groups and isothiouronium groups 175
Scheme 7.2. Modifications to poly(divinylbenzene-*co*-ethylvinylbenzene) 179
Scheme 8.1. Modifications to poly(divinylbenzene-*co*-ethylvinylbenzene) 209
Scheme A2.1. Modification of poly(divinylbenzene-*co*-ethylvinylbenzene) 253

Glossary of Symbols and Abbreviations

AIBN	2,2'-azobis(isobutyronitrile)
avg MW	average molecular weight per repeat unit (mmol/g or mol/g)
BET	Brunauer-Emmett-Teller
bz	benzene
C_{epox}	functional capacity of epoxidized resins (mmol fg/g)
C_{fg}	functional capacity (see mmol fg/g)
$C_{1,2\text{-}Br}$	functional capacity of resins modified with bromine (mmol fg/g)
$C_{1,2\text{-}OHBr}$	functional capacity of resins with bromohydrin groups (mmol fg/g)
$C_{2\text{-}SR}$	functional capacity of resins modified with thiols (mmol SR/g)
$C_{1,2\text{-}SR}$	functional capacity of resins modified with disulfides (mmol fg/g)
CL	cross-linked
CP-MAS	cross polarization-magic angle spinning
CP-MAS-DD	cross polarization-magic angle spinning-dipolar dephased
DMD	dimethyldioxirane
DMF	*N,N*-dimethylformamide
DMSO	dimethyl sulfoxide
DVB	divinylbenzene
EB	ethylbenzene
EDAX	energy dispersive analysis of X-rays
EtOH	ethanol
equiv	equivalent(s)
EVB	ethylvinylbenzene
fg	functional group
FTIR	Fourier transform infrared
HSR	thiol
M	molar (mol/L)
*m*CPBA	*m*-chloroperbenzoic acid
MeOH	methanol
mmol fg/g	millimoles functional group per gram, functional capacity
MMPP	magnesium monoperoxyphthalate
mol fg/g	moles functional group per gram, functional capacity
mol %	mole percent
MW	molecular weight

MW fg	molecular weight of functional group
NBS	*N*-bromosuccinimide
NEt_3	triethylamine
NMP	*N*-methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
PEG-600	poly(ethylene glycol), molecular weight 600
polyDVB-55	poly(divinylbenzene-*co*-ethylvinylbenzene) prepared from 55 wt % technical grade divinylbenzene
polyDVB-80	poly(divinylbenzene-*co*-ethylvinylbenzene), prepared from 80 wt % technical grade divinylbenzene
rpm	revolutions per minute
RSSR	disulfide
SEM	scanning electron microscopy
str.	stretch
TDMF	*N*,*N*-dimethylthioformamide
THF	tetrahydrofuran
TU	thiourea
UV	ultraviolet
VB	vinylbenzene
wt %	weight percent
X_{CL}	degree of functionalization of cross-linked groups (as percent, %)
X_{EB}	degree of functionalization of ethylbenzene groups (as %)
X_{epox}	degree of functionalization of epoxidized resins (as %)
X_{fg}	degree of functionalization of functional groups (as %)
$X_{1,2\text{-Br}}$	degree of functionalization of resins modified with bromine (as %)
$X_{1,2\text{-OHBr}}$	degree of functionalization of resins with bromohydrin groups (as %)
$X_{2\text{-SR}}$	degree of functionalization of resins modified with thiols (as %)
$X_{1,2\text{-SR}}$	degree of functionalization of resins modified with disulfides (as %)
X_{VB}	degree of functionalization of vinylbenzene groups (as %)
Φ	percent conversion of vinylbenzene groups to functional groups

Chapter 1

Introduction to the Study of poly(Divinylbenzene-*co*-Ethylvinylbenzene) and Modifications to the Pendant Vinylbenzene Groups

1.1. Overview of research

The modification of styrenic resins can lead to a variety of functional polymers. Traditional methods include chloromethylation with subsequent reactions, sulfonation, nitration, and amination [1]. This work demonstrates simple alternatives to these methods, all of which stem from the modifications of the pendant vinylbenzene (or vinyl) groups in cross-linked poly(divinylbenzene-*co*-ethylvinylbenzene). This resin is commercially available as Amberlite XAD-4 (Rohm and Haas Company), and was the starting matrix in the majority of the modifications.

Chapter 2, a survey of the available literature, reviews the occurrence and introduction of vinyl groups in polymers, modifications to these polymers (including to the vinyl groups), and the XAD series of commercial resins. One of the objectives of this thesis was to compile information on XAD resins, with the main focus on XAD-4. Chapter 3 further examines XAD-4 and related commercial resins, with comparison to laboratory-made analogues.

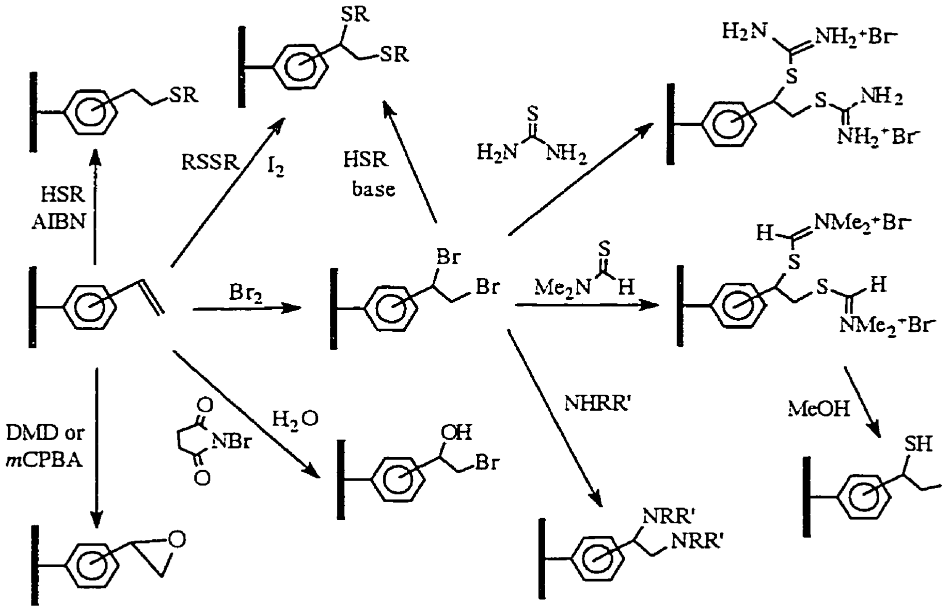
The remaining chapters (4-8) study the exploitation of the vinylbenzene groups in a series of one- to three-step modifications, as illustrated in scheme 1.1. Some of these modifications have never been performed on a polymer substrate before; none have previously been done to the vinylbenzene groups of commercial poly(divinylbenzene-*co*-ethylvinylbenzene). All of these methods are transferable to other vinyl-containing polymers. In total, slightly more than 350 polymer modifications were carried out. The calculations of percent conversions (Φ) of vinylbenzene groups to modified groups were based on elemental analyses.

Characterization by infrared, Raman, and ^{13}C NMR spectroscopy verified the structures of the functional groups of the modified resins.

One of the initial goals of this project was to develop coordinating and ion exchange resins. This work led to the development of a methodology to screen the complexing ability of ligands with metals by simple pH titration, as featured in appendix 1.

The objectives which were met for this work include a thorough characterization of commercial poly(divinylbenzene-*co*-ethylvinylbenzene), development of alternate methods of polymer modification, adaptation of small molecule reactions not previously done with macromolecules, the introduction of specific functional groups onto a polymer matrix, and modifications done entirely by reaction(s) with the vinylbenzene groups initially present in the resin.

The vinylbenzene groups were modified to prepare resins with thioether groups linked through a dimethylene spacer to the resin, as well as with vicinal groups such as 1,2-dithioether, 1,2-dibromo, 1,2-dithiol, and bromohydrin groups. Functional intermediates included resins with epoxide, bromohydrin, or dibromo groups, which could be used for further modifications (scheme 1.1).



Scheme 1.1. Modifications of poly(divinylbenzene-*co*-ethylvinylbenzene)

1.2. References

[1] J.M.J. Frechet and M.J. Farrall, in S.S. Labana (Editor), Chemistry and Properties of Crosslinked Polymers, Academic Press, New York, 1977, p. 59.

Chapter 2

A Review of the Preparation, Characteristics and Modifications of Polymers with Pendant Vinyl Groups, including poly(Divinylbenzene-*co*-Ethylvinylbenzene) and Related Resins

Forward to Chapter 2

The content of the following section is comprised of a paper with the same title which was submitted to the journal Reactive and Functional Polymers (K.L. Hubbard, G.D. Darling and J.A. Finch, submitted April 1997).

This chapter reviews information on polymers which have unsaturated groups, particularly styrenic resins having pendant vinylbenzene (also called vinyl) groups. This is the first review which compiles information about divinylbenzene copolymers, including the commercially-available crosslinked resin. Topics include the preparation, characteristics, spectral data available, and modifications to these polymers.

The main purposes for preparing this review were to compile available information about the commercial resin Amberlite XAD-4 (poly(divinylbenzene-*co*-ethylvinylbenzene)), and to review modifications of this resin, including those of its pendant vinylbenzene groups.

Abstract

This paper reviews polymers with pendant vinyl functionalities focusing on their preparations, characteristics and modifications. Of particular interest are poly(divinylbenzene-*co*-ethylvinylbenzene) and related cross-linked resins, including some of the commercially-available Amberlite resins. Styrenic resins are excellent substrates for the preparation of functional polymers. Modification through the vinyl functionality is generally underutilized and further research in this area as an alternate to more traditional polymer modification techniques such as chloromethylation is encouraged.

Keywords: pendant vinyl groups, Amberlite XAD-2, Amberlite XAD-4, poly(divinylbenzene-*co*-ethylvinylbenzene), divinylbenzene copolymers

2.1. Introduction

This review concerns resins and related polymers with pendant vinyl groups and modifications to these polymers. The emphasis is on polystyrene-like matrices and their functionalization, including those of their pendant vinylbenzene groups. The physical characteristics of these polymers will also be examined with particular attention to commercial resins such as Amberlite XAD-2 and XAD-4 (Rohm and Haas). Styrenic resins are regularly used as solid supports for the preparation of functional polymers; however, the information with regard to the presence of residual vinyl groups and any modifications involved has not been reviewed. One of the primary goals of this review is to compile the available information on these resins. Many researchers use styrenic resins to prepare functional polymers without regard to the vinyl content or consequences of their presence on modification side-products and side-reactions. Few researchers have actually taken advantage of the presence of vinyl groups.

2.2. Non-Styrenic Polymers with Vinyl Groups

Although this review concentrates on polystyrene-like resins, other polymers which have vinyl groups will first be introduced. There are several papers which cover the rubber family of polymers and only a brief mention of them is made.

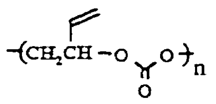
Pinazzi and co-workers extensively discussed the modification of polydienes[1]. They compared the reactivity of the 1,2- and 3,4- units of polybutadiene and the 1,4-units of polyisoprene in reactions such as cyclization, epoxidation, hydroboration and reactions with maleic anhydride and trichlorosilane. The order of reactivity varied with reaction conditions and mechanisms. Their conclusion was that polymers with vinyl groups are excellent reactive polymers and precursors for functional polymers.

Golub and co-workers discussed the photorearrangements of polymers with internal and/or pendant vinyl groups such as polybutadiene, polyisoprene, and other related polydienes [2]. They compared their photorearrangements to thermal rearrangements and discussed cis-trans isomerization and [2 + 2] cycloaddition.

A review on the chemistry of unsaturated polymers by Schultz and co-workers covers reactions of the polydienes and some other unsaturated polymers [3]. Topics included hydrogenation, halogenation, hydrohalogenation, cyclization, cis-trans isomerization, epoxidation and other reactions to the vinyl groups.

Of particular interest to the authors is the work by Boutevin and co-workers [4]. They modified the vinyl groups of carboxytelechelic polybutadiene by the radical addition of mercaptoacetic acid, yielding a polymer with pendant carboxylic acid functionalities linked via a thioether to the backbone.

Yoshida and co-workers prepared and modified a polycarbonate having pendant vinyl groups (figure 2.1) [5]. The polymer was prepared by the copolymerization of carbon dioxide with butadiene monoxide (BMO), using a diethylzinc-water catalytic system. They modified the vinyl groups by either bromination or reaction with a platinum(II) complex.



$$-\!\left(\mathrm{CH_2\underset{}{\overset{CH=CH_2}{CH}}-O-\underset{\underset{O}{\|}}{C}-O}\right)\!-_n$$

Fig. 2.1. BMO-CO_2 copolymer [5].

Taking advantage of residual unsaturation in polyethylene and poly(vinyl chloride), Bergbreiter and co-workers showed that grafting chemistry can be applied to these systems [6]. They performed hydroboration followed by grafting of various monomers.

Samarkandy modified polymers, referred to as inner olefins, by reaction with residual double bonds [7]. He focused on the attachment of acetylacetone in order to produce a polymer-chelate-metal complex.

Percec and Auman prepared polymers with pendant vinyl or ethynyl groups [8]. Their method involved a multi-step preparation from poly(ether sulfone) or poly(oxy-2,6-dimethyl-1,4-phenylene). The polymers were first chloromethylated, followed by conversion into their phosphonium salts and then into vinyl groups by a Wittig reaction. Bromination, followed by dehydrobromination, converted the vinyl groups into ethynyl groups. Alternately, the methyl groups of poly(oxy-2,6-dimethyl-1,4-phenylene) were monobrominated and then converted to the vinyl groups using the same methods as for the chloromethyl groups.

In order for a polymer to be successful as a functional polymer, it needs to have certain characteristics which make it suitable for the intended application. Use of functional polymers in columns or other systems, generally requires mechanical strength and integrity. Polystyrene-based resins are superior with regard to these features and are commonly used because of this. The modifications to the vinyl groups of polymers mentioned in this section equally apply to styrenic resins having vinyl functionalities.

2.3. Styrenic Polymers with Vinyl Groups

There are two main routes to prepare polystyrene-based polymers with vinylbenzene groups (also called pendant vinyl groups, the entire repeat unit is called the vinylstyrene unit). The first route is the modification of a preformed polystyrene-like matrix and the second route is the polymerization of suitable monomers with possible further modification to form the pendant vinyl groups.

2.3.1 Preparation by modification of preformed matrices

One popular route to prepare polystyrene-based resins with pendant vinyl groups is by the multi-step conversion of the styrene unit to the vinylstyrene unit by chloromethylation, followed by conversion into their phosphonium salts and finally by a Wittig vinylation. Neumann and Peterseim prepared poly(*para*-vinylstyrene) from various commercial macroporous resins using this method [9]. The vinyl groups were then hydrostannylated and modified further. The vinyl group content was determined by conversion to the dibromo group and then performing bromine analysis. The degree of functionalization of vinyl groups was between 6 and 41%. The vinyl content was dependent on which resin was used and which method of chloromethylation was used. After complete conversion of the vinyl groups to the tin-containing functionality, it was stated that the tin was homogeneously distributed across the beads. This was determined by the use of energy-dispersive analysis of X-rays (EDAX) in conjunction with scanning electron microscopy (SEM) to plot the tin and chlorine distribution across the internal cross-section of a halved bead. Thus, by inference, they concluded that the vinyl groups were evenly distributed throughout the resin. It should be noted that the experimental details did not mention the resolution of the EDAX linescans.

Hodge and Waterhouse also worked on the conversion of chloromethylated polystyrene to various vinyl-containing resins by a Wittig synthesis using a variety of aldehydes, including formaldehyde and a ferrocene complex [10]. The resin with pendant vinyl groups had a degree of functionalization of only 6%.

To prepare polystyrene with pendant vinyl groups, Farrall and co-workers started with soluble polystyrene and used either of two routes [11]. The first was the chloromethylation, a Wittig reaction pathway, and the second involved lithiation, conversion to the aldehyde by reaction with *N,N*-dimethylformamide, followed by reaction with methyltriphenylphosphonium bromide and potassium *tert*-butoxide to form the vinyl groups. The vinyl content was found by conversion to the dibromide, followed by bromine analysis. The degree of functionalizations were 12% and 36% for the chloromethylation route (done twice) and 29% for the aldehyde route. For all three polymers, the percent conversion to the vinyl group from the chloromethyl group or the aldehyde was between 86% and 92%.

Frechet and Schuerch prepared polystyrene matrices with pendant allyl acid, allyl ester and allyl alcohol groups from the conversion of chloromethylated polystyrene to the aldehyde group with further subsequent reactions [12]. The Wittig reaction was used to convert the chloromethyl groups to allyl chloride groups by addition of chloroacetaldehyde to the phosphonium salt.

Frechet did further work on preparing polystyrene with pendant *para*-vinylbenzene groups using phase-transfer conditions [13]. The method of conversion was the Wittig reaction to chloromethylated groups. Bromination of the vinyl groups, followed by bromine analysis, gave a degree of functionalization of 42%.

Frechet and co-workers also prepared polystyrene resins with pendent sulfone groups including one with an allyl group ($P\text{-}SO_2CH_2CH{=}CH_2$) [14].

An alternative to working with chloromethylated polystyrene was the use of *meta*-(1,2-dibromoethyl)styrene as a monomer which was then copolymerized with styrene or *meta*-divinylbenzene [15]. The monomer was prepared by selectively brominating one vinyl group of *meta*-divinylbenzene using pyridinium hydrobromide perbromide. The dibromoethyl groups of the copolymers formed were then converted to vinyl groups by heating in the presence of sodium iodide to eliminate bromine. They reported that the copolymer with styrene as co-monomer had 1.34 mmol vinyl/g, and the copolymer with divinylbenzene as co-monomer had 1.77 mmol vinyl/g. However, they did not mention the percent conversion of the dibromoethyl groups to vinyl groups, or whether any dibromoethyl groups were still present.

In the preparation of resins with vinyl groups from preformed matrices, side-reactions and incomplete conversions in each step can lead to a mixture of functional groups. Further modifications to the polymer with vinyl groups could then also cause side-reactions, leading to more side-products. The presence of undesired functional groups may change the resin characteristics and create difficulties in analysis of the functionalized resin.

2.3.2 Preparation of poly(divinylbenzene) and related polymers by polymerization of suitable monomers

This methodology tends to be the preferred route due to the minimization of side-products which can occur in the multi-step procedures mentioned in the previous section. Depending on polymerization methodologies, either linear or crosslinked polymers or copolymers of divinylbenzene can be prepared. Many use commercial (technical grade) divinylbenzene, which contains meta- and para-isomers of DVB and ethylvinylbenzene (EVB), usually composed of 50 to 80 weight percent DVB.

2.3.2.1 Linear poly(divinylbenzene) and related polymers

The most popular method of forming linear poly(divinylbenzene) is by using anionic polymerization techniques. In 1968, Aso and co-workers anionically polymerized *ortho*-divinylbenzene [16]. They used organolithium and alkali metal-naphthalene catalysts in various ethers. The extent of cyclization for anionic polymerization was found to be less than for cationic or free-radical polymerizations.

In 1978, Nitadori and Tsuruta polymerized *meta*-divinylbenzene, as well as *para*-divinylbenzene, using lithium diisopropylamide (LDA) or butyl lithium as initiators [17]. It was found that the para-isomer polymerized more readily than the meta-isomer. They varied the quantities of diisopropylamine and butyl lithium used, as well as the choice of solvent. The best reaction conditions to produce a linear polymer involved the use of LDA as initiator and tetrahydrofuran as solvent. When benzene was used as the solvent, or, when butyl lithium was used as initiator, either alone or with only a small amount of diisopropylamine, a gel or oligomer was produced. The relative reactivities of each unit were determined (figure 2.2). This demonstrated that the pendant vinyl group has a lower reactivity than DVB, hence the absence of cross-linking.

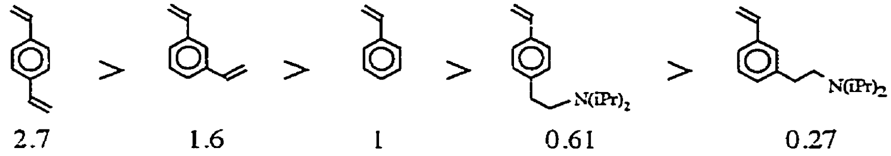


Fig. 2.2. Relative reactivities of monomers [17].

In 1985, Tsuruta prepared soluble poly(*para*-divinylbenzene) of varying molecular weights (MW) by anionic polymerization methods [18]. Extensive studies, including the use of ^{13}C NMR spectroscopy, were done to compare monomer reactivities and degree of functionalization. For a polymer of MW 18000, there were 98.1 vinyl units per 100 repeat units; whereas for a polymer of MW 32000, there were 95.6 vinyl units per 100 repeat units. The remaining repeat units were branched groups. Further work to study the reaction mechanism was presented in 1986 and the ^{13}C NMR spectral peak assignments for linear poly(*para*-divinylbenzene) were given [19].

Further work on the anionic polymerization of divinylbenzene was carried out by Bates and Cohen [20]. They used technical grade divinylbenzene (60% DVB, 40% EVB, 75% meta-, 25% para-isomers for both monomers), and either *n*-butyl lithium or *sec*-butyl lithium. They were able to produce homogeneous gels of divinylbenzene-ethylvinylbenzene having pendant vinyl groups. The presence of THF or dioxane with benzene as co-solvent gave clear homogeneous gels; whereas the use of benzene alone created opaque inhomogeneous powders.

The use of divinylbenzene to form linear polymers where the vinyl groups were in the backbone of the polymer instead of existing as pendant vinylbenzene groups was discussed in two papers.

Hasegawa and Higashimura cationically polymerized a mixture of *meta-* and *para*-divinylbenzenes (meta:para, 70:30) using oxo acids such as CF_3SO_3H,

$AcClO_4$, p-$CH_3C_6H_4SO_3H$ or BF_3-OEt_2 as catalytic initiators, and either benzene or 1,2-dichloroethane as solvent [21]. Except for the system using BF_3-OEt_2 and dichloroethane, linear polymers were formed. The best systems used benzene as the solvent, either CF_3SO_3H, $AcClO_4$ or p-$CH_3C_6H_4SO_3H$ as catalyst, and low monomer concentrations. For high molecular weight linear polymers, sequential monomer addition was done to keep the monomer concentration low. Molecular weights of up to 25000 were attained and that polymer was still soluble in various solvents. Its structure consisted of trans olefinic and phenyl groups in the main chain with vinyl groups at both ends (figure 2.3).

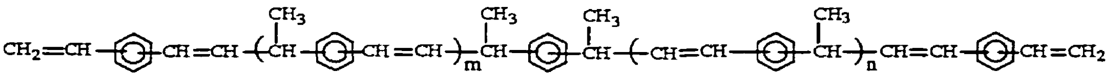


Fig. 2.3. Structure of linear poly(divinylbenzene) [21].

Poly(1,4-phenylenevinylene) was prepared by metathesis of *para*-divinylbenzene (figure 2.4) [22]. A metal-carbene complex reacted with one of the vinyl groups to form a new metal-carbene complex, followed by reaction with another monomer and elimination of the metal-carbene. For each monomer added to the chain, one molecule of ethylene was evolved in the process. No solvent was used in this process, which produced a yellow powder. It was calculated that the number-average degree of polymerization (n) was between 5 and 8.

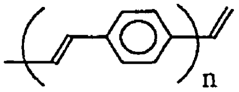


Fig. 2.4. Structure of poly(1,4-phenylenevinylene) [22].

2.3.2.2 Cross-linked poly(divinylbenzene) and related polymers

The general structure of a cross-linked divinylbenzene-ethylvinylbenzene random copolymer such as could be prepared from commercial DVB is shown in figure 2.5. These copolymers have a cross-linked structure with pendant vinylbenzene and ethylbenzene groups. The degrees of functionalization are indicated by the symbols X_{CL}, X_{VB}, and X_{EB}, (CL for cross-linked, VB for vinylbenzene, and EB for ethylbenzene). In this example, the monomers are meta- and para-disubstituted.

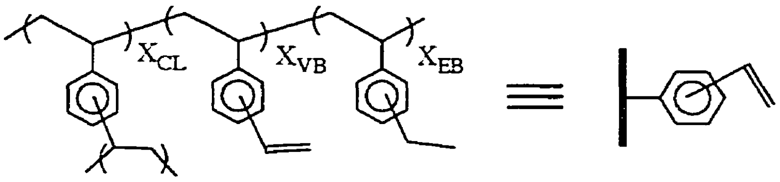


Fig. 2.5. Structure of poly(divinylbenzene-*co*-ethylvinylbenzene).

Much work on the preparation of reactive microgels by polymerization of divinylbenzene was done by Funke [23-31]. Crosslinked microgel particles (having diameters of 5-10 nm [31]) with pendant vinylbenzene groups were prepared by emulsion polymerization of DVB. Monomers used included *para*-DVB, commercial DVB, and mixtures of DVB and styrene. The vinylbenzene groups were homogeneously distributed throughout the polymer. The microgels were modified by the radical addition of potassium persulfate to the pendant vinylbenzene groups to form sulfate groups, creating a hydrophilic polymer [29]. Funke suggested, but did not actually do, other modifications to the vinyl groups including the addition of hydrogen bromide, epoxidation, formation of hydroxyl end groups, and formation of carboxyl end groups [31].

Commercial divinylbenzene was used in the preparation of microgels [32]. The copolymer poly(*p*-DVB-*co*-*m*-DVB-*co*-*p*-EVB-*co*-*m*-EVB) was characterized using infrared spectroscopy. The vinyl group content was calculated from the IR spectra, as well as by bromination. Over 50% of the pendant vinyl groups were consumed in cyclization and cross-linking. The rates of incorporation of each type of monomer were different from each other due to differences in reactivities. *para*-DVB was found to be twice as reactive as *meta*-DVB; while *meta*-EVB was only slightly more reactive than *para*-EVB. The overall order of reactivity was: *para*-DVB >> *meta*-DVB > *meta*-EVB > *para*-EVB. Due to the much higher reactivity of *para*-DVB, the proportion of DVB groups to EVB groups in the polymer was much higher than in the monomer mixture.

Using a seeded polymerization technique, Okubo and Nakagawa prepared micron-size monodisperse polymers with pendant vinyl groups [33]. The seed particles were polystyrene and produced by dispersion polymerization. The seed polymerization step used divinylbenzene, which swelled the polystyrene seeds, and ran for 24 hours.

Macroporous resins can be formed using high proportions of divinylbenzene. Suspension (or bead) polymerization is the preferred method to produce beads which could have applications as solid supports. This technique has previously been reviewed [34].

Using solution polymerization methods, commercial divinylbenzene was polymerized in a mixture of toluene and *n*-butanol, and the resulting polymer powdered [35]. Surface areas were as high as 600 m^2/g [35]. The highest surface area was produced when the non-solvent (*n*-butanol) to solvent (toluene) volume ratio was 1 to 3. Commercial DVB was also suspension copolymerized with styrene (90 wt % DVB to 10 wt % styrene) to form beads with surface areas as large as 500 m^2/g. The suspension polymerization used toluene, polyvinyl alcohol, water and *n*-butanol, and ran for 6 hours at 80 °C, stirring at 550 rpm. In all these polymerizations, 2,2'-azobis(isobutyronitrile) (AIBN) was used as the radical initiator. For both methods, it was found that when the toluene content was less than 25% (rest *n*-butanol), the vinyl group content tended to be higher, and when toluene content was higher than 25%, the vinyl content levelled out. The absolute values of the vinyl contents were not calculated; instead, a ratio technique compared the infrared absorption spectral peaks of the vinyl peak (1630 cm^{-1}) to a characteristic polystyrene peak (1600 cm^{-1}). As well, the average pore diameters increased with decreasing toluene content. The proportions of meta- and para-isomers of DVB and EVB units were almost the same as for the monomer mixture.

Gao and co-workers also produced macroporous beads by the suspension polymerization of commercial grade divinylbenzene (55 wt % DVB, 45 wt % ethylvinylbenzene) [36]. The reaction mixture, consisting of water, toluene, AIBN, monomer and cellulose ether, was stirred under nitrogen at 1000 rpm for 2 hours at 70 °C. The resulting white beads were characterized using infrared spectroscopic analysis to measure the vinyl group content. The degree of functionalization was between 25 and 30% vinyl groups. ^{13}C CP-MAS (cross-polarization magic angle spinning) and ^{13}C CP-MAS-DD (DD is dipolar dephasing) NMR spectra were taken. The ^{13}C NMR peak assignments were as follows: 144 ppm was due to phenyl C, 137 ppm was due to $CH{=}CH_2$, 129 ppm was due to phenyl CH, 114 ppm was from $CH{=}CH_2$, 41 ppm was due to the CH_2 and CH units of the backbone, and 30 ppm and 16 ppm were due to the CH_2 and CH_3 of the pendant ethyl groups from the ethylvinylbenzene repeat unit.

Other researchers have done similar work on the preparation of macroporous styrene-divinylbenzene copolymers with pendant vinyl groups [37]. They varied reaction time, temperature and proportions of initiator and porogen to control surface area and vinyl content.

2.3.2.3 Commercial divinylbenzene polymers

Commercial copolymers based on large proportions of divinylbenzene and little or no styrene have been available from Rohm and Haas Company for many years. This section will review some of the available information on these macroporous resins.

In 1962, Rohm and Haas announced the preparation of macroreticular (macroporous) resins [38]. They used suspension polymerization techniques, and modified the resins to form anion or cation exchange resins.

In 1967, the first of the Amberlite adsorbents became commercially-available. The styrenic-based ones were developed as high surface area non-polar adsorbents with applications in the pharmaceutical and water treatment industries [39]. One of the most frequently used resins is Amberlite XAD-4 [40]. Characteristics of the styrenic Amberlite adsorbents are given in Rohm and Haas product literature [41]. They do not, however, disclose the monomer compositions of any of their products.

The preparation of this group of resins is covered by a United States patent [42]. The method involves suspension polymerization of various monomers in varying proportions including technical grades of divinylbenzene (between 55 and 80% DVB). Various solvents (called precipitants) which act as a solvent for the monomers, but do not induce any solvent action on the polymer (i.e. nonswelling), were used in this method. Examples of solvents used as precipitants include *tert*-amyl alcohol, *n*-butanol and *sec*-butanol. It was also desired to have precipitants which have low solubility in water, a factor which could be decreased by the addition of salts. The precipitant caused phase separation; the copolymer separated from the monomer phase as it formed. During polymerization, the precipitant was squeezed out of the copolymer, forming microscopic channels. These channels were larger than the micropores which typically are found in cross-linked resins. This effect was enhanced by the presence of larger than usual amounts of cross-linking agent (8 to 25 wt % of monomer mixture). For aromatic monomers, such as styrene and DVB, the preferred precipitants were either C_4 to C_{10} alkanols or higher saturated hydrocarbons (heptane or isooctane, etc.), used in amounts of 30 to 50% of the total weight of the monomer mixture and precipitant. Due to higher amounts of cross-linking, these resins tended to be more resistant to physical stresses, such as osmotic shock. Ion-exchange resins prepared from these copolymers had an increased resistance to oxidative degradation.

This patent mentions applications for the resins, such as adsorbents, or for further modification including sulfonation, nitration, chloromethylation, formation of quaternary anion exchangers, and so on. It does not, however, mention the presence of pendant vinyl groups or modifications to the vinyl functionality.

While the exact monomer compositions or preparations for the Amberlite series are not revealed, there are a few sources which give some indication of their composition. The United States Food and Drug Administration states that a divinylbenzene copolymer is "derived by the polymerization of a grade of divinylbenzene which comprises at least 79 weight percent divinylbenzene, 15 to 20 weight percent ethylvinylbenzene, and no more than 4 weight percent nonpolymerizable impurities" [43]. Amberlite XAD-4 is mentioned in this reference.

2.3.3 Characteristics of Amberlite resins, poly(divinylbenzene) and related polymers

This section covers the sources of information which provide physical characteristics and reveal the presence of vinyl groups or monomer content in these commercial resins. Some references to other data available will also be given. Modifications to the commercial resins, including to their vinyl groups as well as those of related polymers, will then be considered.

Researchers have frequently used two of the Amberlite resins, XAD-2 and XAD-4, as the matrix for the preparation of functional resins. Much of the work treated these resins as standard polystyrene resins, with no mention of the presence of vinyl groups. Very little work has been reported on the modification of these commercial resins by reaction of their residual (or pendant) vinyl groups. As well, only scattered information on their characteristics is available.

Since the physical characteristics of the Amberlite resins are available from Rohm and Haas product literature, and are also published in other reviews, only a brief mention of them will be made. The pore size and surface area are the important physical characteristics for most applications. This information is given in table 2.1 [44]. Only XAD-4, XAD-16 and XAD-1180 were commercially available as of February 1996 [45].

Table 2.1. Characteristics of Amberlite XAD polyaromatic adsorbent resins (reproduced in part from [44])

Resin	Approx. Pore Volume (mL/g)	True Wet Density (g/mL)	Skeletal Density (g/mL)	Mean Surface Area (m^2/g)	Mean Pore Diameter (Å)	Mesh Size
XAD-2	0.65	1.02	1.07	300	90	20-60
XAD-4	0.98	1.02	1.08	725	40	20-60
XAD-16	1.82	1.02	1.08	800	100	20-60
XAD-1180	1.68	1.01	1.04	600	300	20-60
XAD-2000	0.64	–	1.09	580	42	20-60
XAD-2010	1.80	–	1.09	660	280	20-60

In 1981, de Munck and co-workers conducted extensive research on Amberlite XAD-2 and XAD-4 [46]. Using Raman spectroscopy, they revealed the presence of vinyl groups. They calculated the vinyl group content by addition of iodine chloride across the vinyl groups, followed by elemental analysis (iodine and chlorine). They mentioned that the monomer content of the reaction mixture for both of these commercial resins was 20% *p*-DVB as a 50% solution in *p*-EVB, mixed in a 1:3 ratio with styrene. However, the reference that they cited did not actually contain this information. There was no mention of the presence of meta-disubstituted monomers. The Raman spectrum for XAD-2 only was given, and their peak assignments are given in table 2.2. This group also gave the BET surface area and pore size information for these resins. The adsorption and desorption isotherms of nitrogen for XAD-4, given in the paper, showed a hysteresis loop indicating the presence of ink-bottle type cavities. The surface area for XAD-4 was calculated to be 788 m^2/g.

Another research group performed Raman spectroscopy on a copolymer of commercial divinylbenzene [47]. Their peak assignments were similar to those in table 2.2, with the notable exception of the peak at 800 cm^{-1} which they assigned to the meta-disubstituted phenyl groups.

Other researchers have also discussed the presence of vinyl groups in XAD-2 [48]. Infrared spectroscopy gave characteristic vinyl peaks at 1633, 1410, 990 and 905 cm^{-1}.

Table 2.2. Raman peak assignments for Amberlite XAD-2 (reproduced from [46])

Band (cm^{-1})	Assignment
645, 800	para-disubstitution
1006	breathing vibration of benzene ring
1190, 1240	para-disubstitution
1320	bending vibrations of CH_2 and CH_3
1410, 1450	disubstitution
1590, 1612	C-C stretch vibrations of benzene ring
1636	C=C stretch vibrations of vinyl group
2910	C-H stretch vibrations
3006, 3060	C-H stretch vibrations of benzene ring

A comprehensive review published in 1986 by Albright of Rohm and Haas discussed the physical characteristics of many Amberlite resins, including XAD-2 and XAD-4 [49]. It does not mention, however, the presence of vinyl groups. The review revealed that XAD-4 is a copolymer of divinylbenzene and ethylvinylbenzene, with a glass transition temperature of 90 °C. Heating this resin at 130 °C for 3 hours did not significantly change the pore size distribution. Sulfonation of XAD-4 to form Amberlyst XN-1010 caused a slight decrease in pore size. The surface areas of XAD-4, XAD-16 and XN-1010 were: 841-860 m^2/g, 942 m^2/g, and 401 m^2/g, respectively. Other properties mentioned included porosity, which was 55 to 61% for XAD-4 (1.1 to 1.4 mL/g), and the cross-linking density, in weight percent of divinylbenzene, for XN-1010 (made from XAD-4) was 85%. Consequently, the monomer content of XAD-4 seems to be 85% DVB and 15% ethylvinylbenzene.

Periyasamy and co-workers performed ^{13}C NMR studies on divinylbenzene-based resins including Amberlite XAD-1, XAD-2 and XAD-4 [50]. Isotopically labelled poly(*para*-divinylbenzene-*co*-styrene) resins were prepared. Analysis included bromination to measure vinyl content. The peak assignments were the same as by Gao and co-workers, mentioned previously [36]. The ^{13}C CP-MAS NMR spectra for XAD-2 and XAD-4 were shown and were like that for poly(divinylbenzene-*co*-ethylvinylbenzene) [36]. No dipolar-dephased spectra were taken. It was reported that the DVB content of XAD-1, XAD-2, and XAD-4 were 20, 50 and 80 weight percent respectively, however no reference was given.

A method for the determination of vinyl group content for divinylbenzene copolymers using infrared spectrometry has been reported [51]. Using absorbance mode, an extinction coefficient was calculated for each relevant peak. By comparison of the peak heights multiplied by their coefficients, the vinyl group content could be calculated using a ratio technique. The infrared peak assignments are given in table 2.3 [51]. This method has not previously been used to quantitatively determine the vinyl content of the Amberlite resins.

Table 2.3. Infrared peak assignments for divinylbenzene copolymers [51]

Band (cm^{-1})	Assignment
1630, 1410, 1015, 990	vinyl group
1510	para-disubstituted phenyl ring
1493, 1028, 760	monosubstituted phenyl ring
905	mixed band, weak monosubstituted phenyl ring, medium to weak disubstituted phenyl ring and strong vinyl group
838	mixed band, weak monosubstituted phenyl ring and strong para-disubstituted phenyl ring
795	meta-disubstituted phenyl ring

Faber and co-workers modified XAD-2 and XAD-4 [52]. They found by transmittance infrared spectroscopy that XAD-2 was composed of styrene, divinylbenzene and ethylvinylbenzene, whereas XAD-4 was composed of divinylbenzene and ethylvinylbenzene. The IR spectrum of XAD-4 was shown. Addition of HBr to the pendant vinyl groups gave 0.95 mmol Br/g for XAD-2 and 1.95 mmol Br/g for XAD-4. This would have meant that the degree of functionalization of vinyl groups was 13.5% for XAD-2 and 30.2% for XAD-4. They mentioned that the vinyl content was 0.7 mmol/g for XAD-2 and 1.95 mmol/g for XAD-4; however, based on the bromine content, the vinyl contents are calculated to be closer to 1.0 mmol/g and 2.3 mmol/g, respectively. (Calculated by dividing the degree of functionalization by the average molecular weight per repeat unit).

Two papers discussed solvent uptake and wetting of resins, including some of the XAD resins [53, 54]. The solvent uptakes for XAD-1 and XAD-2 are given in table 2.4 [53]. The wetting behavior and adsorption of polar organic solvents of XAD-2 and XAD-4 were studied by Rixey and King [54].

Table 2.4. Solvent uptake for Amberlite XAD-1 and XAD-2 (g solvent per g resin) (reproduced in part from [53])

Solvent	XAD-1	XAD-2	Solvent	XAD-1	XAD-2
water	0.061	0.072	dioxane	1.21	0.960
methanol	0.488	0.699	ethyl acetate	0.907	0.816
ethanol	0.507	0.719	acetic acid	1.872	1.00
n-propanol	0.535	0.757	chloroform	1.59	1.22
isopropanol	0.509	0.721	carbon tetrachloride	1.64	1.35
n-butanol	0.527	0.758	benzene	0.993	0.779
acetonitrile	0.688	0.743	hexane	0.515	0.540
nitromethane	1.00	0.872	cyclohexane	0.728	0.656
tetrahydrofuran	1.05	0.736	isobutyl methyl ketone	0.818	0.745

2.4. Modification of Amberlite Resins

Many researchers have used XAD-4 and related resins to prepare functional resins. Unless otherwise noted, the following researchers did not mention the presence of pendant vinyl groups.

Zuo and Muhammed used XAD-2 and XAD-4, and other styrenic resins to prepare coordinating resins [55]. The styrene units were chloromethylated, aminated with hexamethylenetetramine and then converted to the polymer-bound thiourea functionality by reaction with NH_4SCN. The introduction of spacer groups was accomplished by modification with either 1,2-diaminoethane or 1,3-diaminopropane, instead of by amination.

Fritz and co-workers used XAD-4 as a matrix for the preparation of many modified resins [56-60]. One modification involved first acetylation, followed by hydrolysis to the benzyl alcohol functionality, then esterification with thioglycolic acid to produce a resin with thioglycoloylmethyl groups [56]. The infrared spectra were shown for the resins, and vinyl peaks were visible in the spectrum for the starting material, XAD-4. In the spectrum for the modified resin, weak peaks between 2600-2700 cm^{-1} may be attributed to the presence of thiol groups, although this was not mentioned in the paper. Reduction of the vinyl peaks in the spectra for the modified resins was also not noted, nor the presence of side-products attributed to reactions with vinyl groups.

XAD-4 has been used to prepare anion-exchange resins [57]. It was chloromethylated and then aminated with trimethylamine.

Various hydroxamic acid resins have been prepared from XAD-4 [58, 59]. The first step involved acetylation, followed by oxidation of the acetophenone groups to carboxylic acid groups. The carboxy groups were then converted to acid chloride (chloroformyl) groups by reaction with thionyl chloride. The addition of various hydroxyl amines to the acid chloride groups formed hydroxamic acid groups.

The surface characteristics of XAD-4 were also altered by modification [60]. Functional groups added, using Friedel-Crafts methods, included: $-C(CH_3)_3$, $-CH_2OH$, $-COCH_3$, $-COCH_2CH_2COOH$, and $-CH_2CN$. The modified resins showed differences as chromatographic materials due to differences in their hydrophilicity.

Armer studied the effects on sorptive properties by modification of XAD-4 [61, 62]. Functional groups which were incorporated included: alkanes, ketones, amines, sulfonamides, fluorocarbons, polyglycols with or without methyl-capping, benzyl alcohol, chloromethyl, bromo, pentafluorophenyl, and phosphonic acid. Established polymer modification techniques, such as chloromethylation, were used. The content of XAD-4 was incorrectly stated as being poly(styrene-*co*-2% divinylbenzene). The research focused on applications of the functional resins, and no spectral data to characterize these resins were given. It was not indicated whether XAD-4 had pendant vinyl groups.

XAD-2 has been brominated in the presence of ferric chloride [63, 64]. The only structure shown was: XAD-2–CH_2CH_2Br [64]. This structure is questionable because the reaction conditions used would form aryl bromide groups, but there was no structural information given in the papers. No characterization details were included, and there was no mention of pendant vinyl or ethyl groups.

XAD-4 and related resins have been used as substrates to immobilize functional groups by physical adsorption because of their high surface areas and porosities. For example, zerovalent palladium catalysts were created by the impregnation of lipophilic palladium complexes into XAD-2 and XAD-4, followed by reduction with hydrazine to Pd(0) [65].

Immobilization of various functional chemicals by adsorption into XAD-4 has been done by several researchers to prepare functional substrates. Lipophilic tetraaza macrocycles were impregnated into XAD-4 by adsorption from organic solutions [66]. These resins were tested for trace metal uptake from seawater.

Solvent extraction reagents, such as dihexyl *N,N*-diethylcarbamoylmethylphosphonate [67, 68], di(2-ethylhexyl)phosphoric acid [69], and di(2-ethylhexyl)dithiophosphoric acid [70], were physically adsorbed into XAD-4 to form solvent-impregnated resins. These were tested for metal uptake ability.

Functional groups have been bonded to XAD-4 through long spacer groups [71]. Using Friedel-Crafts methods, the acid chloride of a monoalkyl ester of an alkanedioic acid was attached to the styrene units. The polymer-bound keto group was converted to tosylhydrazone followed by selective reduction to either retain the ester functionality or to convert it to an alcohol group. The ester group was also further converted into carboxylic acid, amide, and hydroxamic acid functionalities.

De Munck and co-workers modified XAD-2 and XAD-4 by chloromethylation, phosphination, and chlorophosphination, in order to couple a rhodium complex to the resin [46]. They noted that the presence of vinyl groups contributed to undesired side-reactions. They also suggested that it may be possible to couple the rhodium complex to the resin through the vinyl groups.

Likewise, Bootsma and co-workers found that the presence of vinyl groups caused side-reactions in chloromethylation of XAD-2 [48]. They suggested that chloromethyl methyl ether had added across the vinyl groups to form a less reactive aliphatic chloride towards nucleophilic addition in comparison to the benzylchloride group.

2.5. Modification to Vinyl Groups of Styrenic, including Amberlite, Resins

There is a broad spectrum of the type of reactions which can involve vinyl groups. As with the non-styrenic polymers discussed previously, many modifications have been done to vinyl groups present in styrenic resins, some of which have been briefly mentioned.

Macroporous styrenic resins with pendant vinyl groups have been modified by graft polymerization. Schutten and co-workers grafted *N*-vinyl-tertbutylcarbamate by radical addition to the vinyl groups [35]. Hydrolysis converted the grafted carbamates to amines. Cobalt-containing catalysts were then fixed to the resins by interaction with the amine groups.

Brunelet and co-workers also grafted various monomers to the pendant vinyl groups of styrenic resins [72]. The resins were swollen with monomer overnight before grafting. Depending on the starting resin and reaction conditions used, the porous structure was either retained or filled in by grafted polymer.

In some cases, it is undesirable to have residual unsaturation in styrenic polymers. The Dow Chemical Company developed a method to reduce the pyrolytic behaviour of divinylbenzene copolymers by either hydrogenation, halogenation or hydrohalogenation [73].

Using *m*CPBA (*m*-chloroperbenzoic acid), Frechet and Eichler epoxidized pendant vinyl groups of a styrenic resin [13]. Some ring-opening of the epoxide occurred.

As outlined in the section on non-styrenic polymers, Boutevin and co-workers modified a butadiene polymer by the radical addition of mercaptoacetic acid to the vinyl groups [4]. Similarly, Gao and co-workers modified poly(divinylbenzene-*co*-ethylvinylbenzene) by the anti-Markovnikov radical addition of thiols to the pendant vinyl groups [36]. The thiols they used were: benzenethiol, mercaptoethanol, *n*-butanethiol, *tert*-butyl mercaptan, mercaptoacetic acid, 1,2-ethanedithiol, 1,3-propanedithiol, 1,4-butanedithiol, and 3-mercaptopropionic acid. The one-step modification involved stirring polymer, excess thiol and AIBN in toluene at 70 °C under nitrogen for 1-2 days.

Only two papers were found that described the functionalization of the commercial Amberlite XAD resins by modification to pendant vinyl groups [52, 74]. In both cases, the aim was to prepare polymer-supported catalysts.

Faber and co-workers modified the vinyl groups of XAD-2 and XAD-4 to prepare solid-phase catalysts for the benzoin condensation [52]. Anti-Markovnikov and Markovnikov hydrobrominations were performed; the first method used radical addition of hydrogen bromide (HBr) to form $-CH_2CH_2Br$ groups, and the second method used electrophilic addition of HBr to form $-CHBrCH_3$ groups. 5-Hydroxyethyl-4-methylthiazole was immobilized by reaction with the $-CH_2CH_2Br$ groups, joining it through a dimethylene spacer to the polymer backbone. The bromine distribution profile for anti-Markovnikov hydrobrominated XAD-4 was determined using electron probe X-ray microanalysis. It was found that the distribution of bromine was homogeneous, inferring that the vinyl group distribution is also homogenous throughout the bead. It should be noted that the bromine distribution shown was only for 1/3 of the diameter (300 μm of a 900 μm bead) with 6 data points at approximately 42 μm spacing. The distribution was on the micron-scale and it was noted that at the submicron scale, the distribution of vinyl groups was inhomogeneous, they being situated primarily in the cores of the resin microspheres.

The vinyl groups of XAD-2 and XAD-4 have been used as graft sites for the addition of poly(methylhydrosiloxane) using a platinum catalyst [74]. The Si-H groups were further modified to prepare chiral catalysts containing the ephedrine group.

2.6. Discussion

The preparation of styrenic resins having pendant vinyl groups has been successful either by modification of a preformed polystyrene matrix, or by polymerization of divinylbenzene in various proportions with other optional monomers, such as ethylvinylbenzene.

Researchers utilizing the first route have prepared resins with vinyl contents ranging from 6 to 42%, depending on preparative conditions [9-11, 13]. Unfortunately, many involved time-consuming, costly multi-step reactions. It is important to minimize the presence of other functionalities, which means that each step should have complete conversion; this is unrealistic in most cases.

The preparation of linear polyDVB can create polymers with 95 to 98% vinyl content, but the preparation involves very stringent and hazardous reaction conditions and requires very pure reagents. For the preparation of functional resins, these polymers would not have the proper structural characteristics, such as porosity, high surface area and structural integrity.

The best route to prepare a structurally-ideal styrenic matrix with pendant vinyl groups is by the polymerization of technical grades of divinylbenzene, preferably with the highest possible amount of DVB (i.e. 80 wt % DVB is commercially-available). Gao and co-workers prepared such a resin from 55 wt % DVB (45 wt % EVB) [36]. They found that the vinyl content ranged from 25 to 30%. However, they did not measure the surface area and porosity.

The Amberlite resins, including XAD-2 and XAD-4, are ideal for the preparation of functional resins based on their porosity and surface areas (table 2.1, [44]). From the data of Faber and co-workers, the vinyl content was calculated to be 13.5% for XAD-2, and 30.2% for XAD-4 [52]. They were able to completely convert the vinyl groups to the hydrobrominated groups ($-CH_2CH_2Br$), indicating accessibility of the vinyl groups to reagents. The other advantage is that XAD-4 is commercially-available, so the focus can be on the modification of the resin, not its preparation. Complete spectral characterization of XAD-4 or comparison to a polymer of known composition have not yet been done. There are no published

Raman or ^{13}C CP-MAS-DD NMR spectra. The method using FTIR spectrometry to measure vinyl content [51] has also not yet been used for XAD-4 or related Amberlite resins.

One question which arises is the composition of resins prepared from large proportions of DVB. When commercial divinylbenzene was used in the preparation of microgels, it was found that the polymer was richer in DVB than the monomer mixture [32]. The relative monomer reactivities were: *p*-DVB >> *m*-DVB > *m*-EVB > *p*-EVB, which accounted for the higher DVB content.

Conversely, when suspension polymerization methods were used to polymerize commercial divinylbenzene to prepare macroporous beads, the proportions of meta- and para-isomers of DVB and ethylvinylbenzene units were almost the same as for the monomer mixture [35]. This contradicts the expected composition based on the relative reactivities of the monomers. However, as DVB is consumed during the reaction, more ethylvinylbenzene may be incorporated towards the end of the polymerization. Within a polymer, portions will most likely be higher in one monomer, with varying compositions throughout the polymer. As seen by these two different studies, it would seem that reaction conditions, including time of reaction, probably play a significant role in monomer incorporation.

2.7. Conclusions

Amberlite XAD-4, a styrenic copolymer of meta- and para-isomers of divinylbenzene (80-85 wt %) and ethylvinylbenzene (15-20 wt %), is an ideal matrix for preparing functionalized resins. It has high surface area, porosity, structural integrity, pendant vinyl groups which can act as sites for modification, and has the advantage of being commercially-available. Modification to these pendant vinyl groups has thus so far been underutilized in favour of more traditional polymer modification techniques such as chloromethylation.

2.8. Acknowledgements

The authors would like to thank both Rohm and Haas Company and Dr. J. Snow of Millipore Corporation for providing some of the information used in this paper. Thanks also go to the following people for helpful suggestions during the preparation of this paper: Dr. D.S. Argyropoulos, Dr. D.N. Harpp and

Dr. B.R. Lennox. Funding was provided by a Natural Sciences and Engineering Research Council of Canada Strategic Grant.

2.9. References

[1] C. Pinazzi, J.C. Brosse. A. Pleurdeau and D. Reyx, Appl. Polym. Symp., 26 (1975), 73.

[2] M.A. Golub and M.L. Rosenberg, J. Polym. Sci., Polym. Chem. Ed., 18 (1980), 2543.

[3] D.N. Schultz, S.R. Turner and M.A. Golub, Rubber Chem. Technol., 55 (1982), 809.

[4] B. Boutevin, E. Fleury, J.P. Parisi and Y. Pietrasana, Makromol. Chem., 190 (1989), 2363 (in French).

[5] Y. Yoshida, A. Nishiyama and S. Inoue, Polym. J., 14 (1982), 327.

[6] D.E. Bergbreiter, G.F. Xu and C. Zapata Jr., Macromolecules, 27 (1994), 1597.

[7] A.R.A. Samarkandy, Ph.D. Thesis, University of Washington, Diss. Abstr. Int. B 49 (4) (1988), 1203; Chem. Abstr. 110 (1989), 76243s.

[8] V. Percec and B.C. Auman, Makromol. Chem., 185 (1984), 2319.

[9] W.P. Neumann and M. Peterseim, React. Polym., 20 (1993), 189.

[10] P. Hodge and J. Waterhouse, Polymer, 22 (1981), 1153.

[11] M.J. Farrall, M. Alexis and M. Trecarten, Polymer, 24 (1983), 114.

[12] J.M. Frechet and C. Schuerch, J. Am. Chem. Soc., 93 (1971), 492.

[13] J.M.J. Frechet and E. Eichler, Polym. Bull. (Berlin), 7 (1982), 345.

[14] A.J. Hagen, M.J. Farrall and J.M.J. Frechet, Polym. Bull. (Berlin), 5 (1981), 111.

[15] T. Yamamizu, M. Akiyama and K. Takeda, React. Polym., 3 (1985), 173.

[16] C. Aso, T. Kunitake and Y. Imaizumi, Makromol. Chem., 116 (1968), 14.

[17] Y. Nitadori and T. Tsuruta, Makromol. Chem., 179 (1978), 2069.

[18] T. Tsuruta, Makromol. Chem., Suppl., 13 (1985), 33.

[19] Y. Nagasaki, H. Ito and T. Tsuruta, Makromol. Chem., 187 (1986), 23.

[20] F.S. Bates and R.E. Cohen, Macromolecules, 14 (1981), 881.

[21] H. Hasegawa and T. Higashimura, Macromolecules, 13 (1980), 1350.

[22] A. Kumar and B.E. Eichinger, Makromol. Chem., Rapid Commun., 13 (1992), 311.

[23] V.D. Kuhnle and W. Funke, Makromol. Chem., 139 (1971), 255.

[24] D. Kuhnle and W. Funke, Makromol. Chem., 158 (1972), 135.

[25] W. Obrecht, U. Seitz and W. Funke, Angew. Chem., Int. Ed. Engl., 13 (1974), 414; Chem. Abstr. 82 (1975), 17294q.

[26] W. Obrecht, U. Seitz and W. Funke, Makromol. Chem., 175 (1974), 3587; Chem. Abstr. 82 (1975), 44141u.

[27] W. Obrecht, U. Seitz and W. Funke, Makromol. Chem., 176 (1975), 2771; Chem. Abstr. 84 (1976), 5429r.

[28] W. Obrecht, U. Seitz and W. Funke, Makromol. Chem., 177 (1976), 1877; Chem. Abstr. 85 (1976), 63367a.

[29] W. Obrecht, U. Seitz and W. Funke, Makromol. Chem., 177 (1976), 2235; Chem. Abstr. 85 (1976), 124440t.

[30] W. Obrecht, U. Seitz and W. Funke, ACS Symp. Ser., 24 (1976), 92; Chem. Abstr. 85 (1976), 21898u.

[31] W. Funke, J. Oil Col. Chem. Assoc., 60 (1977), 438.

[32] B. Walczynski, B.N. Kolarz and H. Galina, Polym. Commun., 26 (1985), 276.

[33] M. Okubo and T. Nakagawa, Colloid Polym. Sci., 270 (1982), 853.

[34] R. Arshady and A. Ledwith, React. Polym., 1 (1983), 159.

[35] J.H. Schutten, C.H. van Hastenberg, P. Piet and A.L. German, Angew. Makromol. Chem., 89 (1980), 201.

[36] J.P. Gao, F.G. Morin and G.D. Darling, Macromolecules, 26 (1993), 1196.

[37] X. Jin, Z. Zhang, H. Li, B. He and P. Wang, Lizi Jiaohuan Yu Xifu, 8 (1992), 508 (in Chinese); Chem. Abstr. 121 (1994), 36712q.

[38] R. Kunin, E. Meitzner and N. Bortnick, J. Am. Chem. Soc., 84 (1962), 305.

[39] C.T. Dickert, Amberhilites (produced by Rohm and Haas Co.), Number 185 (winter 1989).

[40] R. Kunin, Amberhilites (produced by Rohm and Haas Co.), Number 161 (spring 1979).

[41] R. Kunin, Amberhilites (produced by Rohm and Haas Co.), Number 163 (winter 1980).

[42] E.F. Meitzner and J.A. Oline, U.S. Patent 4,382,124, issued May 3, 1983.

[43] Code of Federal Regulations, 21, Food and Drugs. 173.65, page 100 in Parts 170 to 199. Food and Drug Administration, U.S. Government Printing Office, Washington, D.C. Revised April 1, 1994.

[44] Supelco Product Catalogue, 1995, page 264.

[45] B. Kinch, Rohm and Haas Company, personal communication, February 1996.

[46] N.A. de Munck, M.W. Verbruggen and J.J.F. Scholten, J. Mol. Catal., 10 (1981), 313.

[47] M. Bacquet, C. Caze, J. Laureyns and C. Bremard, React. Polym., 9 (1988), 147.

[48] J.P.C. Bootsma, B. Eling and G. Challa, React. Polym., 3 (1984), 17.

[49] R.L. Albright, React. Polym., 4 (1986), 155.

[50] M Periyasamy, W.T. Ford and F.J. McEnroe, J. Polym. Sci., Polym. Chem. Ed., 27 (1989), 2357.

[51] M. Bartholin, G. Boissier and J. Dubois, Makromol. Chem., 182 (1981), 2075.

[52] M.C. Faber, H.J. van den Berg, G. Challa and U.K. Pandit, React. Polym., 11 (1989), 117.

[53] D.J. Pietrzyk, Talanta, 16 (1969), 169.

[54] W.G. Rixey and C.J. King, J. Coll. Interface Sci., 131 (1989), 320.

[55] G. Zuo and M. Muhammed, React. Polym., 24 (1995), 165.

[56] R.J. Phillips and J.S. Fritz, Anal. Chem., 50 (1978), 1504.

[57] J.J. Richard and J.S. Fritz, J. Chromatogr. Sci, 18 (1980), 35.

[58] R.J. Phillips and J.S. Fritz, Anal. Chim. Acta, 121 (1980), 225.

[59] R.J. Phillips and J.S. Fritz, Anal. Chim. Acta, 139 (1982), 237.

[60] J.J. Sun and J.S. Fritz, J. Chromatogr., 522 (1990), 95.

[61] D.M. McPhillips, T.A. Armer and D.R. Owen, J. Biomed. Mater. Res., 17 (1983), 993.

[62] T.A. Armer, Ph.D. Thesis, Tulane University, Diss. Abstr. Int. B 43 (6) (1982), 1910; Chem. Abstr. 98 (1983), 35435w.

[63] M. Martinez, J. Aracil, F. Addo-Yobo and C.N. Kenney, DECHEMA Biotechnology Conferences, 2 (Bioreactors, Downstream Processing, Process and Reactor Modelling, Bioprocesses), (1988), 83; Chem. Abstr. 112 (1990), 18539y.

[64] J.L. Casillas, J.L. Garrido, J. Aracil, M. Martinez, F. Addo-Yobo and C.N. Kenney, Separations for Biotechnology, 2 (Papers presented at the International Symposium on Separations for Biotechnology), 2nd (1990), 285; Chem. Abstr. 114 (1991), 183777y.

[65] G. Bar-Sela and A. Warshawsky, J. Polym. Sci., Polym. Chem. Ed., 28 (1990), 1303.

[66] S. Blain, P. Appriou and H. Handel, Analyst, 116 (1991), 815.

[67] T. Kimura and J. Akatsu, J. Radioanal. Nucl. Chem., 149 (1991), 13.

[68] J. Akatsu and T. Kimura, J. Radioanal. Nucl. Chem., 149 (1991), 195.

[69] R.S. Juang and S.H. Lee, React. Funct. Polym., 29 (1996), 175.

[70] K. Jerabek, L. Hankova, A.G. Strikovsky and A. Warshawsky, React. Funct. Polym., 28 (1996), 201.

[71] S.V. Luis, M.I. Burguete and B. Altava, React. Funct. Polym., 26 (1995), 75.

[72] T. Brunelet, M Bartholin and A. Guyot, Angew. Makromol. Chem., 106 (1982), 79.

[73] J.C. Tou, U.S. Patent 4,727,115, issued February 23, 1988; Chem. Abstr. 108 (1988), 205793f.

[74] Z. Zhengpu, P. Hodge and P.W. Stratford, React. Polym., 15 (1991), 71.

Chapter 3

The Preparation and Characteristics of poly(Divinylbenzene-*co*-Ethylvinylbenzene), including Amberlite XAD-4.
Styrenic Resins with Pendant Vinylbenzene Groups.

Forward to Chapter 3

The content of the following section is comprised of a paper with the same title which was submitted to the journal Reactive and Functional Polymers (K.L. Hubbard, G.D. Darling and J.A. Finch, submitted April 1997).

Upon reviewing material on poly(divinylbenzene-*co*-ethylvinylbenzene), including the commercial resin Amberlite XAD-4, it was found that the available literature had incomplete information. This chapter will compare and contrast laboratory-prepared poly(divinylbenzene-*co*-ethylvinylbenzene) with XAD-4 with regard to physical features and monomer content. Comparison of XAD-4 to other related XAD resins is also made. Spectral information not previously available on XAD-4 is presented in this chapter. The location of vinylbenzene groups is mapped for beads of XAD-4. The goal of this chapter was to develop a better understanding of the features of XAD-4 since it is the starting matrix for the majority of the polymer modifications presented in this thesis.

Abstract

The preparation and characteristics of poly(divinylbenzene-*co*-ethylvinylbenzene), including the resin Amberlite XAD-4 available from Rohm and Haas Company, were studied. The monomer and vinylbenzene group content, surface area, and pore size of lab-made resins were compared to those of the commercial resin. Compared to lab-made resins, we have found that Amberlite XAD-4 has a much higher surface area and porosity, making it an ideal matrix for preparing functional resins by modification of pendant vinylbenzene groups. The degree of functionalization of vinylbenzene groups for XAD-4 ranged from 29 to 41%, approximately one-third of repeat units having a pendant vinyl group.

Keywords: Amberlite XAD-4, Amberlite XAD-16, Amberlite XAD-1180, pendant vinyl groups, poly(divinylbenzene-*co*-ethylvinylbenzene)

3.1. Introduction

This paper presents our work on the preparation of a polystyrene-like matrix with pendant vinylbenzene groups. The characteristics of these cross-linked resins are examined along with those of the commercial resin Amberlite XAD-4 (Rohm and Haas Company). Other related Amberlite resins, including XAD-2, XAD-16, and XAD-1180, are also briefly examined.

Styrenic resins are regularly used as solid supports for the preparation of functional polymers; in future work, we intend to take advantage of the presence of residual vinyl groups. We will discuss the method of preparation, the spectroscopic characterization, surface area and pore size measurements, and vinyl group content and distribution within the resin.

The literature has considerable information (some of it conflicting) with regard to the monomer content of Amberlite XAD-4. The literature on XAD-4 and related resins has recently been reviewed [1]. The key information follows.

Amberlite XAD-4 is a macroporous resin prepared from technical grade divinylbenzene (DVB), which is approximately 80 to 85 wt % DVB and 15 to 20 wt % ethylvinylbenzene (EVB) [2-6]. The monomers are meta- and para-isomers in a ratio of approximately 70:30 to 75:25. XAD-4 has a high surface area (725 to 860 m^2/g) and porosity [6-8]. Very little work has been done on characterizing this resin and the related XAD-2 with regard to vinyl group content; as well, only five other research groups have mentioned the presence of vinyl groups [8-12], and only two actually modified these resins by reaction with the vinyl functionality [11, 12]. The following spectra have been published elsewhere: the transmittance infrared spectrum of XAD-4 [11], the Raman spectrum of XAD-2 (but not XAD-4) [8], and the ^{13}C CP-MAS NMR spectra of XAD-2 and XAD-4 [10].

Here, we are the first to completely characterize XAD-4 spectroscopically and compare it to a polymer of known composition. This includes adapting a method that uses infrared spectrometry to measure vinyl content [13] for XAD-4 and related Amberlite resins.

Copolymers of divinylbenzene and ethylvinylbenzene, referred to as polyDVB henceforth, have a cross-linked structure with pendant vinylbenzene groups and ethylbenzene groups (figure 3.1). The degrees of functionalization are indicated by the symbols X_{CL}, X_{VB}, and X_{EB}, (CL for cross-linked, VB for vinylbenzene, and EB for ethylbenzene). Since the cross-linked and vinylbenzene groups result from the divinylbenzene monomer, X_{CL} plus X_{VB} will add to the monomer content (i.e. 55% for polyDVB prepared from 55% technical grade DVB, assuming monomer composition equals polymer composition). The monomers are meta- and para-disubstituted, giving a total of 6 randomly-occurring repeat units.

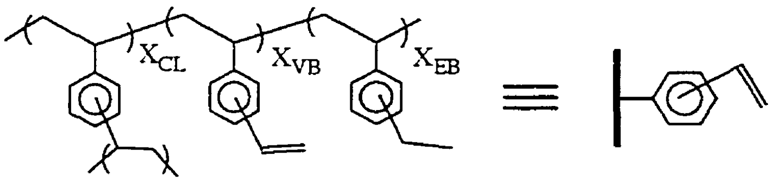


Fig. 3.1. Structure of poly(divinylbenzene-*co*-ethylvinylbenzene).

We wanted a resin with accessible pendant vinyl groups in order to modify these groups with various functionalities. We first prepared resins from two grades of commercial DVB (55% and 80% DVB, remainder ethylvinylbenzene). A comparison of the "lab-made" resins to the commercial resins was then made in terms of surface area, porosity, and monomer and vinyl group content. Further studies were also done on XAD-4, including Raman and ^{13}C NMR spectroscopy. The most important features are the vinyl group content and accessibility. We also attempted to determine the location of vinyl groups by bromination of XAD-4, and mapping the bromine distribution across bead cross-sections using electron microprobe analysis.

3.2. Experimental

3.2.1 Materials

Unless otherwise noted, all materials were purchased from Aldrich Chemical Company and used as received. Two grades of commercial divinylbenzene (DVB) were used. One had a monomer content of 55 weight percent DVB and 45 weight percent EVB, the other had a monomer content of 80 weight percent DVB and 20 weight percent EVB. The meta- to para-isomer ratio for all monomers was 70 to 30. Samples of different lots of Amberlite XAD resins were obtained from either Aldrich Chemical Co., Supelco Inc., Rohm and Haas Co., or Millipore Corp. All resins were pretreated by Soxhlet extraction with acetone for several days, followed by drying under vacuum overnight at 60 °C.

3.2.2 Preparation of poly(divinylbenzene-*co*-ethylvinylbenzene)

Using the methodology of Gao and co-workers, macroporous beads were produced by the suspension polymerization of commercial grade divinylbenzene [14]. A typical preparation follows.

To a 2 L 3-neck round bottom flask fitted with mechanical stirrer and condenser, commercial divinylbenzene (50 g, 385 mmol), 50 mL toluene, 500 mL distilled water, 0.25 g of cellulose ether (Dow Methocel K100LV) and a radical initiator, AIBN (2,2'-azobis(isobutyronitrile), 0.5 g, 3 mmol) were added. After stirring at 1000 rpm under nitrogen at 70 °C for 2 hours, the resin was filtered and washed with toluene, then acetone, purified for 2 or more days by Soxhlet extraction using acetone, and then dried under vacuum at 60 °C overnight.

3.2.3 Bromination of XAD-4

XAD-4 (lot #1090-7-1473) was brominated using a slight excess (1.1 equiv) of bromine. In a 1 L round bottom flask equipped with magnetic stirring bar, XAD-4 (50 g, 2.5 mmol vinyl/g) in 500 mL of carbon tetrachloride was cooled to 0 °C. Bromine (7 mL, 140 mmol) in 20 mL CCl_4 was added, and the reaction stirred in the dark at room temperature overnight. The resin was filtered and Soxhlet extracted for one day with dichloromethane, followed by drying under vacuum at 60 °C overnight. Samples were analyzed for bromine content (Robertson Microlit Laboratories, Inc., Madison, NJ).

3.2.4 Characterization

3.2.4.1 Infrared spectroscopy

The resins were characterized using infrared spectroscopic analysis to measure the vinyl group content [13]. Samples were ground into powder with FTIR-grade potassium bromide (KBr) and pressed into disks. Fourier transform infrared absorbance spectra were taken with a Bruker IFS 66 spectrometer, using a DTGS detector and 2 cm^{-1} resolution, with 120 to 200 scans.

3.2.4.2 Raman spectroscopy

Fourier transform Raman spectra were taken using a Bruker IFS 88 spectrometer with FRA-105 Raman module using a Nd^{+3}:YAG laser (1064.1 nm). Samples were ground into powder and packed lightly into an aluminum sample cup. The number of scans ranged from 250 to 5000, with a 4 cm^{-1} resolution.

3.2.4.3 ^{13}C NMR spectroscopy

Solid-phase ^{13}C NMR spectra were obtained with a Chemagnetics Inc. M-100 instrument. ^{13}C CP-MAS (cross polarization-magic angle spinning) NMR spectra were obtained at 25.1 MHz with contact time of 2 ms, pulse delay of 2 s, spinning rate of 3-4 kHz, and high-power proton decoupling during acquisition. The ^{13}C CP-MAS-DD (DD is dipolar dephased) NMR spectra had a dephasing time (τ) of 45 μs. Samples were referenced to hexamethylbenzene.

3.2.4.4 Surface area and pore size measurements

To determine the surface area and porosity, BET gas adsorption measurements were performed on a Coulter SA-3100 surface area and pore size analyzer (Coulter Scientific Instruments) with nitrogen.

3.2.4.5 Particle size

Samples were screened through a series of sieves of standard mesh size to determine particle size distributions.

3.2.4.6 Electron microprobe analysis of brominated XAD-4

Beads of the brominated XAD-4 were embedded in two different epoxy resins, Epo-Tek-301, and Epo-Tek-377, from Epoxy Technology Inc., Billerica, MA. The first epoxy had a diamine cure agent, while the second had an anhydride cure agent which necessitated a cure temperature of 70 °C. Polishing was done using diamond paste, and the samples were then coated in carbon. Cross sections of the beads were scanned for bromine (Br L_α) using a JEOL 8900 electron microprobe. The instrument parameters were: 15.0 kV accelerating voltage, 8 to 15 nA probe current, 5 μm beam diameter, 20 sec dwell time, and 15 μm distance between points.

3.3. Results and Discussion

3.3.1 Calculation of vinyl content from FTIR absorbance spectra

Table 3.1 gives the infrared spectral peak assignments for divinylbenzene copolymers [13]. Using some of these peaks, the vinyl content of several resins was calculated (table 3.2). The precision of this technique ranged from 2-10% standard deviation, with the majority of samples having less than 5% error. For our applications, a standard deviation of less than 5% is acceptable.

Since the resins studied contained no styrene, we modified the technique of Bartholin to calculate vinyl content [13]. The degree of functionalization of vinylbenzene groups (X_{VB}, percentage of double bonds) is calculated according to equation 3.1.

Equation 3.1 $$X_{VB} = \frac{(A+B)}{2(C+D)} \times 100\%$$

The peak heights multiplied by their various extinction coefficients give A, B, C, and D, for the vinyl peaks at 1630 cm^{-1} (A) and 990 cm^{-1} (B), and the para-

($1510\ cm^{-1}$, C) and meta-disubstituted ($795\ cm^{-1}$, D) peaks. C and D account for all of the repeat units in the polymer since all of the monomers were either para- or meta-disubstituted.

Table 3.1. Infrared peak assignments for divinylbenzene copolymers [13]

Band (cm^{-1})	Assignment
1630, 1410, 1015, 990	vinyl group
1510	para-disubstituted phenyl ring
1493, 1028, 760	monosubstituted phenyl ring
905	mixed band, weak monosubstituted phenyl ring, medium to weak disubstituted phenyl ring and strong vinyl group
838	mixed band, weak monosubstituted phenyl ring and strong para-disubstituted phenyl ring
795	meta-disubstituted phenyl ring

It is assumed that the monomer content of the polymer is similar to that of the starting monomer mixture. The relative reactivities of the various monomers are *p*-DVB >> *m*-DVB > *m*-EVB > *p*-EVB, and it was previously found that the proportion of DVB to EVB in a microgel of commercial DVB was much higher than in the monomer mixture [15]. Conversely, macroporous beads of DVB and EVB have been prepared by suspension polymerization having almost identical proportions of meta- and para-isomers of DVB and EVB as the monomer mixture [16]. There would probably be regions with varying monomer compositions within the overall polymer structure, with incorporation of mostly DVB at the beginning of polymerization, and with more of the less reactive monomers towards the end as the DVB concentrations decrease. It would seem that reaction conditions, including time of reaction (3 hours in [15], 8 hours in [16]), probably play a significant role in monomer incorporation. Whether the proportions in the resin are different from the monomer mixture or not, it should not affect the calculation of vinyl content since a ratio technique is used. However, it will affect the calculation of the degree of cross-linking, since the degree of cross-linking (X_{CL}) is the difference between the (assumed) divinylbenzene content (% DVB) and the (measured) vinyl content (X_{VB}) (equation 3.2).

Equation 3.2 $$X_{CL} = \%\,\mathrm{DVB} - X_{VB}$$

The vinylbenzene content in mmol/g is calculated from the X_{VB} and the average molecular weight per repeat unit (avg. MW) (equation 3.3). The average MW is the weighted average of the molecular weights of the monomer fractions. The molecular weights of the monomers are 130.2 g/mol for DVB, and 132.2 g/mol for ethylvinylbenzene. For a copolymer containing 80 mol % DVB, the average MW per repeat unit is 130.6 g/mol (0.8 x 130.2 + 0.2 x 132.2). (Note: commercial grades of DVB are supplied in weight %, but since the MW of DVB and EVB are similar, the mole fractions are almost the same as the weight fractions, i.e. 80% DVB is composed of 80.2 mol % DVB and 19.8 mol % EVB.) Likewise, for a copolymer containing 55 mol % DVB, the average MW per repeat unit is 131.1 g/mol. Again, the assumption is that the proportions remain the same in the polymer as in the monomer mixture.

Equation 3.3

$$\text{mmol VB / g} = \frac{X_{VB}}{\text{avg. MW}} \times 10$$

As can be seen from the data in table 3.2, the lab-made resins which were made using 80 mol % DVB (polyDVB-80) have a much higher vinyl content than the commercial resins. Of these, XAD-4 tended to have the highest X_{VB} (29-41%), followed by XAD-16 (30-31%), and lastly XAD-1180 (21-24%). With XAD-4 there was a 12% range in vinyl content from lot to lot. We also assumed that XAD-16 and XAD-1180 are composed of 80% DVB, as is XAD-4. We need resins which have high vinyl contents, but also other important features such as structural integrity and accessibility of the vinyl groups. As we will see later, the commercial resins are superior with regard to these requirements, even with lower vinyl contents.

Table 3.2. Vinyl contents of divinylbenzene copolymers

Resin & Lot	Degree of Functionalization (X_{VB}, %)	Degree of Cross-Linking (X_{CL}, %)	Vinyl Content (mmol/g)
polyDVB-55-a	20 ± 2	35 ± 3	1.5 ± 0.1
polyDVB-55-b	30 ± 3	25 ± 3	2.3 ± 0.2
polyDVB-55-c	24 ± 2	31 ± 3	1.8 ± 0.2
polyDVB-55-d	21 ± 2	34 ± 3	1.6 ± 0.1
polyDVB-80-a	47 ± 2	33 ± 2	3.6 ± 0.2
polyDVB-80-b	47 ± 3	33 ± 3	3.6 ± 0.2
polyDVB-80-c	58 ± 1	22 ± 1	4.5 ± 0.1
polyDVB-80-d	55 ± 3	25 ± 3	4.2 ± 0.2
XAD-4-a lot #2-0028	34 ± 1	46 ± 1	2.6 ± 0.1
XAD-4-b lot #00126BZ	29 ± 1	51 ± 2	2.2 ± 0.1
XAD-4-c lot #03803HF	41 ± 1	39 ± 1	3.1 ± 0.1
XAD-4-d lot #1090-7-1473	33 ± 1	47 ± 2	2.5 ± 0.1
XAD-16-a lot #013154	31 ± 2	49 ± 2	2.4 ± 0.2
XAD-16-b lot #62165CY	30 ± 1	50 ± 2	2.3 ± 0.1
XAD-1180-a lot #62157A3	21 ± 1	59 ± 1	1.6 ± 0.1
XAD-1180-b lot #62165CRA	24 ± 6	56 ± 6	1.8 ± 0.5

Figure 3.2 compares the FTIR spectra of the lab-made resins and the commercial resins. The lab-made resins, called polyDVB-55 and polyDVB-80, were prepared from 55 wt % and 80 wt % commercial DVB, respectively. The spectrum of polyDVB-80 resin has the most prominent vinyl peaks (1630, 1410, 1015, and 990 cm^{-1}). Otherwise, the spectra of the resins are identical, with the exception of XAD-2. The spectra for the other XAD resins are identical to that of the lab-made resins, indicating a monomer composition of DVB and EVB only. The spectrum of XAD-2 has peaks which are attributed to monosubstituted styrene (1028 and 760 cm^{-1}). Our results agree with those of Faber and co-workers who also found by IR spectroscopy that XAD-2 was composed of styrene, divinylbenzene and ethylvinylbenzene, and that XAD-4 was composed of divinylbenzene and ethylvinylbenzene [11].

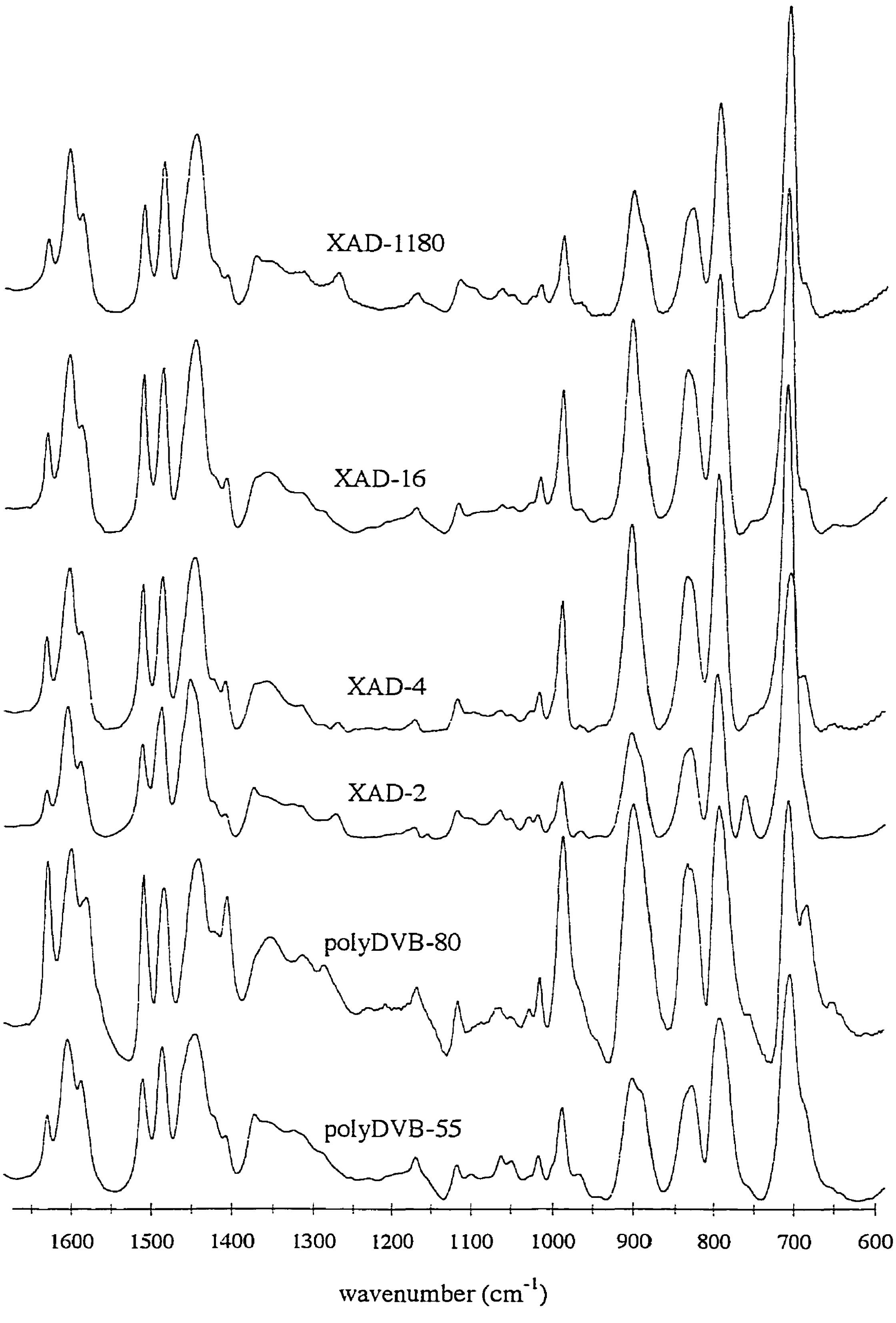


Fig. 3.2. FTIR absorbance spectra of divinylbenzene copolymers.

3.3.2 Bromination of XAD-4 and calculation of degree of functionalization

The general equation for calculating the degree of functionalization of modified XAD-4 (X_{fg}) is based on the average MW per repeat unit of unmodified resin (130.6 for 80% DVB content), the mole content of functional group (mol fg/g, calculated from elemental analysis), and the molecular weight (MW fg) of the modifying reagent (equation 3.4). The degree of functionalization of brominated XAD-4 ($X_{1,2\text{-}Br}$) was calculated based on the bromine content. Since each functional group contains two bromine atoms ($-CHBrCH_2Br$), the (mol fg/g) equals (mol Br/g ÷ 2) and the (MW fg) equals (MW Br x 2), simplifying equation 3.4 to equation 3.5.

Equation 3.4
$$X_{fg} = \frac{130.6 \times (\text{mol fg/g})}{1 - (\text{mol fg/g} \times \text{MW fg})} \times 100\%$$

Equation 3.5
$$X_{1,2\text{-Br}} = \frac{130.6\ \text{g/mol} \times (\text{mol Br/g} \div 2)}{1 - (\text{mol Br/g} \times \text{MW Br})} \times 100\%$$

The bromine content was 3.76 ± 0.02 mmol/g (1.88 ± 0.01 mmol fg/g), giving a degree of functionalization ($X_{1,2\text{-}Br}$) of 35.1 ± 0.2%. This was in close agreement to the vinyl content calculated using the FTIR spectroscopic technique of the starting XAD-4 (lot #1090-7-1473), X_{VB}, 33 ± 1 %. This would indicate that the vinylbenzene groups were converted entirely to (1,2-dibromoethyl)benzene groups without further cross-linking or any side-reactions. The FTIR absorbance spectra of XAD-4 and brominated XAD-4 (designated XAD-4-Br) are shown in figure 3.3. For the brominated XAD-4, the vinyl peaks (1630, 1410, 1015, and 990 cm^{-1}) are absent, and peaks due to the (1,2-dibromoethyl)benzene functionality are seen (1236, 1215, 1176, 1130, 602, and 571 cm^{-1}) [17]. The peak at 900 cm^{-1} is also reduced, with a second peak at 892 cm^{-1} visible.

Faber and co-workers modified XAD-2 and XAD-4 by anti-Markovnikov hydrobromination, using radical addition of hydrogen bromide (HBr), to form $-CH_2CH_2Br$ groups [11]. The bromine content was 0.95 mmol Br/g for XAD-2 and 1.95 mmol Br/g for XAD-4. Using our formula to calculate degree of functionalization, we find that the degree of functionalization of hydrobrominated groups, and thus vinyl groups, was 13.5% for XAD-2 and 30.2% for XAD-4. They mentioned that the vinyl content was 0.7 mmol/g for XAD-2 and 1.95 mmol/g for XAD-4; however, we calculate that the vinyl contents were closer to 1.0 mmol/g and 2.3 mmol/g respectively. The vinyl content of XAD-4 (from [11]) is comparable to our findings for XAD-4 (table 3.2).

3.3.3 Raman spectroscopy

Raman spectra taken with samples in glass melting point tubes had fluorescence due to the glass which obscured most peaks, so samples were packed into cups. Figure 3.4 shows the Raman spectrum of XAD-4 (lot #1090-7-1473). While the spectrum for the related Amberlite XAD-2 has been published [8], that for XAD-4 has not been. The resolution of the spectrum for XAD-4 (figure 3.4) is higher than that previously published for XAD-2 [8]. Although peaks were previously assigned for XAD-2, the researchers assumed only para-disubstitution [8]. Amberlite XAD-2 is composed of styrene and meta- and para-isomers of divinylbenzene and ethylvinylbenzene, whereas XAD-4 has no styrene [6, 10, 11]. Another research group did Raman spectroscopy on a copolymer of commercial divinylbenzene [18]. The peaks for XAD-4 are assigned in table 3.3.

Table 3.3. Raman peak assignments for XAD-4

Band (cm^{-1})	Assignment	Band (cm^{-1})	Assignment
3056, 3008	C-H stretch vibrations of benzene ring	2910	C-H stretch vibrations
1632	C=C stretch vibrations of vinyl group	1610	C-C stretch vibrations of benzene ring
1447	meta-disubstitution (ethylbenzene)	1409	meta-disubstitution (vinylbenzene)
1315	bend vibrations of CH_2 and CH_3	1232	para-disubstitution (ethylbenzene)
1209	para-disubstitution (vinylbenzene)	1181	para-disubstitution
1065	benzene ring C-H wagging	1001	breathing vibration of benzene ring
905	C-H out-of-plane	800	meta-disubstitution
734	C-H out-of-plane	643	para-disubstitution

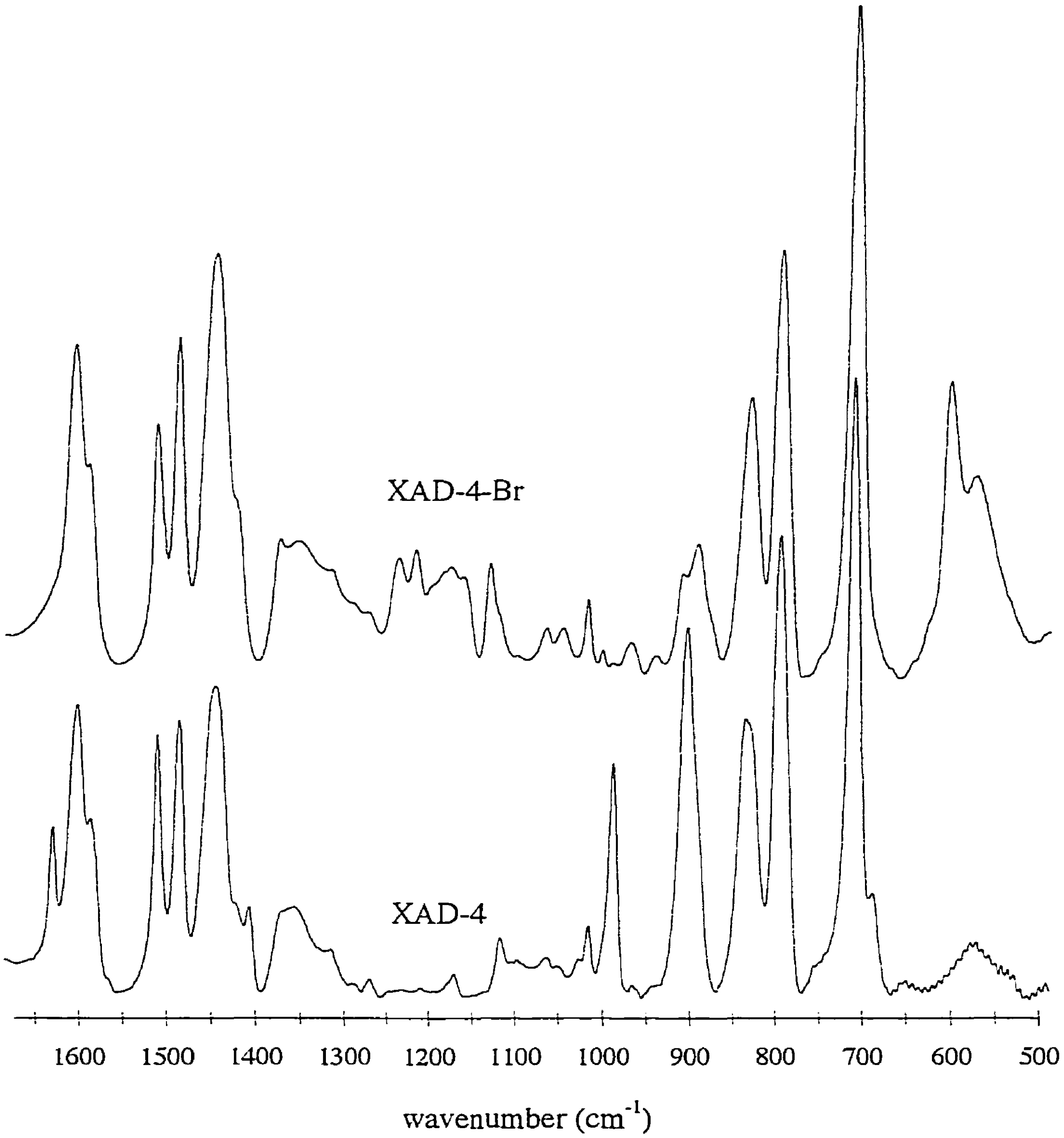


Fig. 3.3. FTIR absorbance spectra of XAD-4 and brominated XAD-4.

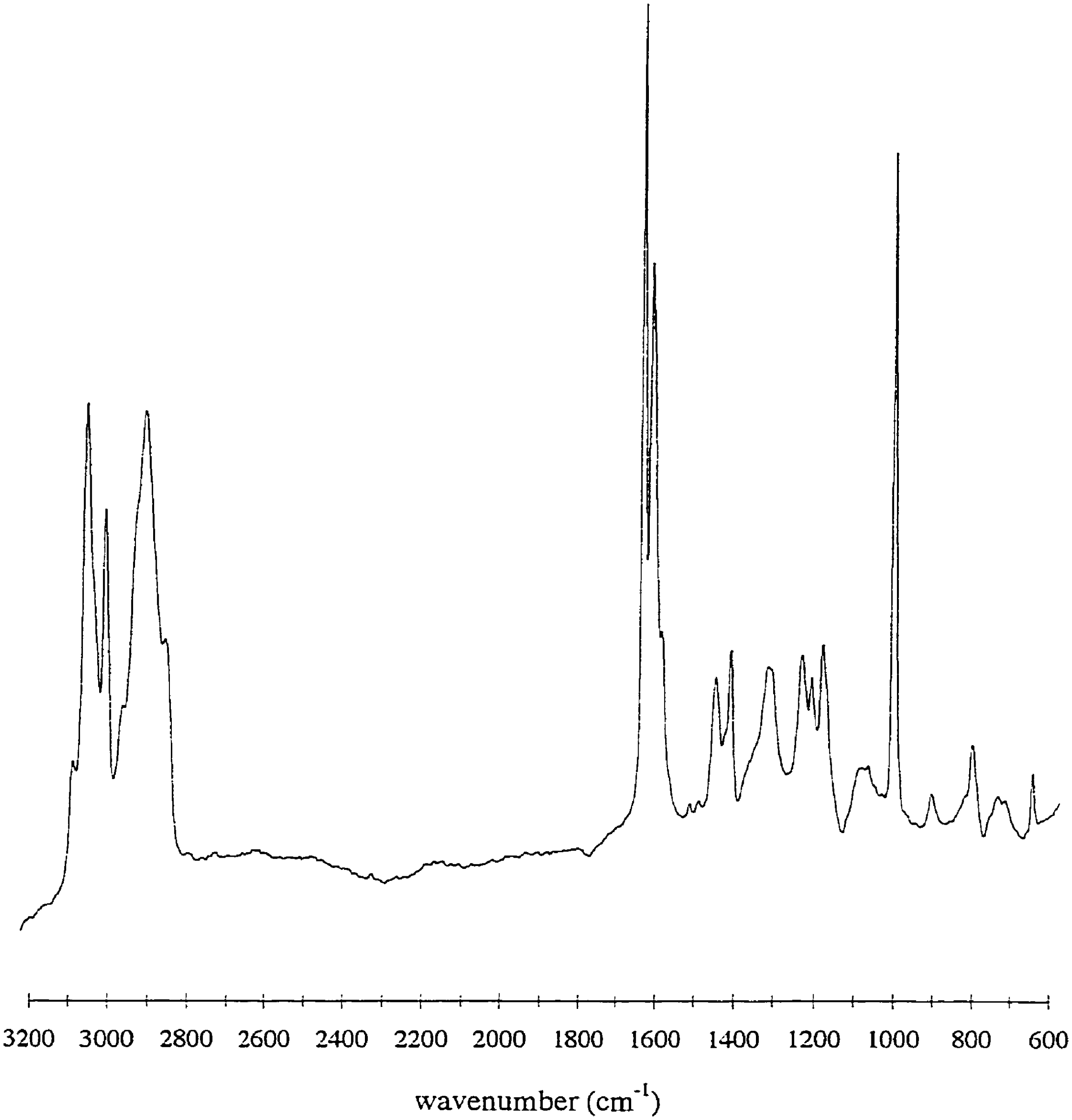


Fig. 3.4. Raman spectrum of XAD-4.

3.3.4 ^{13}C NMR spectroscopy

Figure 3.5 shows the solid-phase ^{13}C CP-MAS NMR and ^{13}C CP-MAS-DD NMR spectra for XAD-4 (lot #1090-7-1473). ^{13}C NMR peak assignments for model compounds such as styrene (137.54, 136.85*, 128.45*, 127.72*, 126.16*, 113.69 ppm, * denotes odd parity, i.e. CH or CH_3), and 1,3-diethylbenzene (144.17, 128.33*, 127.44*, 125.07*, 28.88, 15.61* ppm) aid in peak assignment for the resin [19].

Table 3.4 gives the ^{13}C NMR spectral peak assignments for XAD-4 [10, 14, 20]. Since dipolar dephasing eliminates immobile CH and CH_2 groups, the previous assignment of 137 ppm for $CH{=}CH_2$ is incomplete. This peak is also due to the phenyl C attached to the vinyl group. This can also be seen based on the peak assignments for styrene. The peak for the CH_2 units of the polymeric backbone may have been assigned to 30 ppm, if compared to the peaks of diethylbenzene as a model compound. However, this peak is much smaller than would be expected if attributed to the backbone contribution. Other researchers published the ^{13}C CP-MAS NMR spectra of XAD-2 and XAD-4, but not the dipolar-dephased spectra [10]. The peaks of the published ^{13}C CP-MAS NMR spectra are identical to those of the ^{13}C CP-MAS NMR spectrum in figure 3.5. Our spectra of XAD-4 are also the same as those of poly(divinylbenzene-*co*-ethylvinylbenzene) which appear in the work by Gao and co-workers [14]. We also took spectra of a sample of poly(divinylbenzene-*co*-ethylvinylbenzene) (polyDVB-55), with the same results as Gao and those of XAD-4. Peak height proportions varied for all samples due to differences in monomer and vinyl content.

Table 3.4. ^{13}C NMR peak assignments for XAD-4

Peak (ppm)	Assignment
144 ppm	phenyl C
137 ppm	$CH{=}CH_2$ and adjoining phenyl C
129 ppm	phenyl CH
114 ppm	$CH{=}CH_2$
41 ppm	CH_2 and CH units of the backbone
30 ppm	CH_2 of the pendant ethyl groups
16 ppm	CH_3 of the pendant ethyl groups

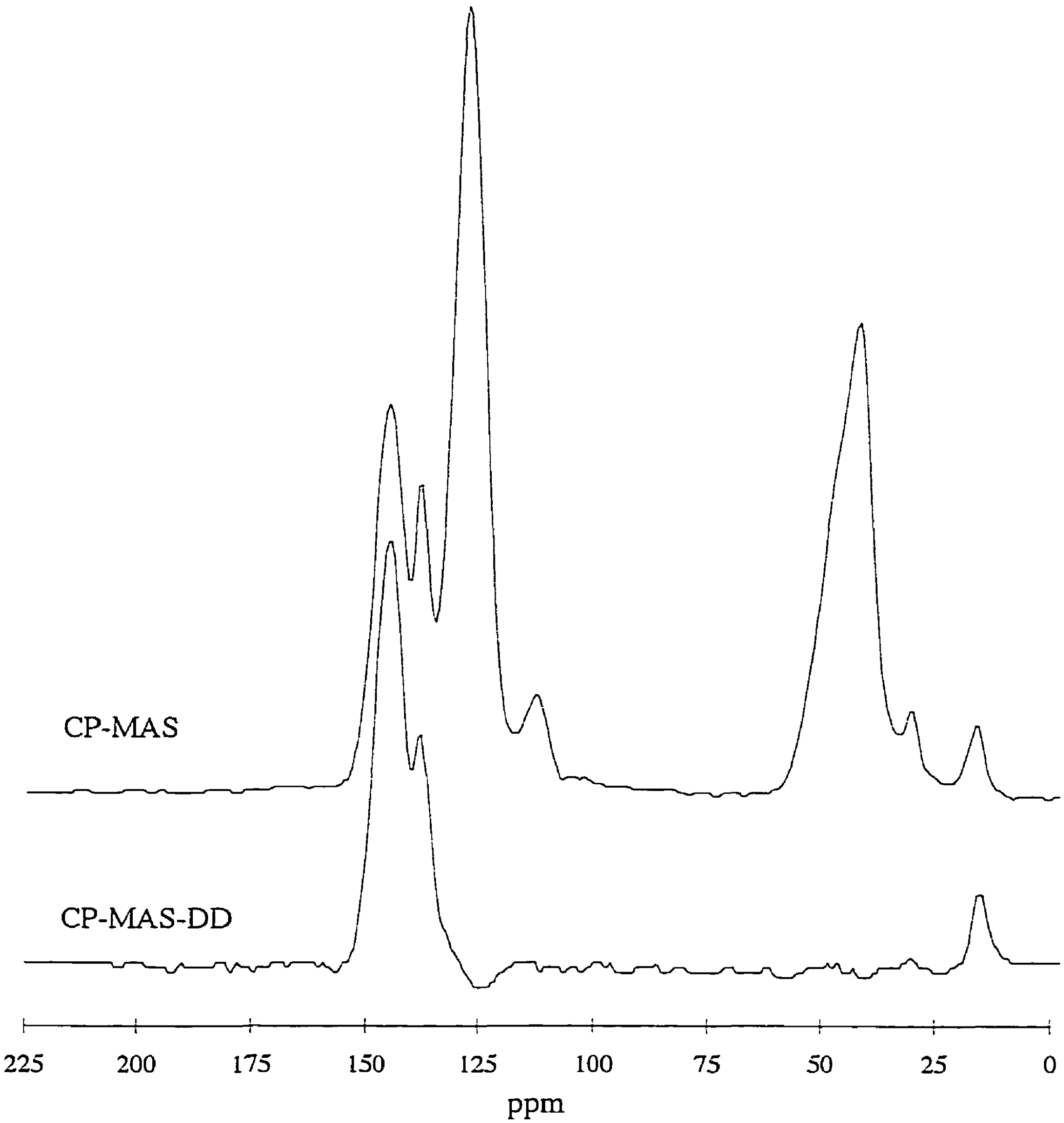


Fig. 3.5. Solid-phase ^{13}C NMR spectra of XAD-4.

3.3.5 Surface area, pore size and particle size distribution

Table 3.5 gives the results of BET (Brunauer-Emmett-Teller)[21a] surface area, total pore volume, and the desorption BJH (Barrett-Joyner-Halender)[21a] pore size distribution of several resins. The pore size distribution is based on the volume percentage of the total pore volume for pores with a given diameter. For example, 92.4% of the total pore volume exists as pores with less than 6 nm diameters for polyDVB-55-a. The adsorption and desorption isotherms for the polyDVB-55 resins and for XAD-4 gave a hysteresis loop, indicating the presence of ink-bottle type cavities [21b]. The polyDVB-80 resins did not have this. Our results for XAD-4 are similar to those of de Munck and co-workers, who published in 1981 the isotherm and pore size distribution [8]. Their sample of XAD-4 had a surface area of 788 m^2/g. In 1986, Albright determined the surface area of other samples of XAD-4 to be between 841-869 m^2/g [6]. Some samples of XAD-4, produced more recently (the 1990's), have an even higher surface area.

Although called macroporous resins, based on the measured pore sizes the commercial resins are actually mesoporous, according to a common classification of size: micropores < 2 nm, mesopores 2-50 nm, and macropores > 50 nm [21c].

Table 3.5. Surface areas and pore sizes of divinylbenzene copolymers

Resin	Surface Area (m^2/g)	Total Pore Volume (mL/g)	Pore Size (nm)
polyDVB-55-a	499	0.483	< 6 (92.4%)
polyDVB-55-b	58	0.046	< 6 (99.8%)
polyDVB-55-c	455	0.425	< 6 (87.7%) 6-12 (9.6%)
polyDVB-55-d	504	0.502	< 6 (92.4%)
polyDVB-80-a	0.08	0.0005	–
polyDVB-80-b	2.9	0.0067	< 6 (5.9%) 6-16 (84.5%)
polyDVB-80-c	0.16	0.0010	< 80 (94.6%)
polyDVB-80-d	0.25	0.0015	< 80 (97.1%)
XAD-4-d lot #1090-7-1473	831	1.181	< 6 (17.3%) 6-10 (20.5%) 10-20 (59.5%)
XAD-4-e lot #24023	1040	1.546	5.95 (average)
(Millipore results)	984	1.411	5.73 (average)

The physical characteristics of the XAD resins available in product literature, are given in table 3.6 [7]. Again, this data is a few years old, and as can be seen for XAD-4 the surface area seems to have increased recently when compared to the results in table 3.5. This may be due to changes in the manufacturing process. Although XAD-4, XAD-16 and XAD-1180 have similar surface areas, the mean pore diameter, pore volume, and amount of cross-linking is higher for XAD-16 and XAD-1180 than for XAD-4. Higher porosities are probably due to higher amounts of cross-linking which may be needed to form the more porous structure. XAD-1180 has the largest pores, highest amount of cross-linking, and consequently the lowest amount of vinyl groups; while XAD-4 has the smallest pores, least cross-linking, and highest amount of vinyl groups. Depending on the end-use of the XAD resins, and the types of chemicals used for modification, the porosity of XAD-4 is probably sufficient for the absorption of reagents to modify the vinyl groups.

Table 3.6. Characteristics of commercial divinylbenzene copolymers (reproduced in part from [7])

Resin	Approx. Pore Volume (mL/g)	True Wet Density (g/mL)	Skeletal Density (g/mL)	Mean Surface Area (m^2/g)	Mean Pore Diameter (nm)	Mesh Size
XAD-4	0.98	1.02	1.08	725	4	20-60
XAD-16	1.82	1.02	1.08	800	10	20-60
XAD-1180	1.68	1.01	1.04	600	30	20-60

In contrast to the lab-made resins, the commercial resins are higher in surface area and porosity. The polyDVB-80 resins had the highest amounts of vinyl groups, but almost no internal surface and almost no porosity. The polyDVB-55 resins had high surface areas, but much smaller pores than the commercial resins. It should be noted that our method of preparation was different than that for the commercial resins. The commercial resins are prepared in the presence of a solvent (called precipitant) which acts as a solvent for the monomers, but does not induce any solvent action on the polymer (i.e. is nonswelling) [4]. The result of using a precipitant is the formation of microscopic channels which are larger than the micropores which typically are found in cross-linked resins. This effect is enhanced by the presence of large amounts of cross-linking agent (8 to 25 wt % of the monomer mixture) [4]. Our suspension polymerization used toluene, which is a good solvent for both the monomer and polymer. But the overall trend seems to be a correlation between amount of cross-linking and porosity.

Table 3.7 gives the weight percentage of beads retained on each sieve when samples were dry sieved through a series of sieves for samples of polyDVB-55 (lots a, b, c, and d) and XAD-4 (b and c). The polyDVB beads were smaller, with a greater size range than XAD-4. The size distribution also varied greatly from lot to lot of polyDVB. Overall the majority of polyDVB beads were between 63 and 249 µm. The beads of the two lots of XAD-4, in contrast, were larger, with the majority of beads larger than 425 µm. The first sample, XAD-4-b had most of the beads in the 425 to 849 µm range, whereas the second sample, XAD-4-c had approximately half the beads greater than 850 µm, and the other half between 425 and 849 µm in size. Depending on the application, sieving of samples before use may be recommended. XAD-4 is in the size range used for many engineering applications (columns, etc.), while the smaller polyDVB beads may be unsuitable (i.e. due to a potential reduction in fluid pressure in columns).

Table 3.7. Particle size distribution

Mesh Size	Minimum Particle Size Retained (µm)	Weight % Retained for polyDVB-55				Weight % Retained for XAD-4	
		-a	-b	-c	-d	-b	-c
20	850	0.0	0.1	0.0	0.0	12.5	51.7
40	425	0.3	0.3	0.0	0.0	79.7	46.9
60	250	10.2	6.4	0.2	0.5	7.7	1.4
100	150	62.5	15.8	28.8	14.7	0.0	0.0
140	106	23.6	17.5	47.9	55.9	0.0	0.0
230	63	2.6	48.6	20.2	23.7	0.0	0.0
325	45	0.5	8.8	2.1	3.5	0.0	0.0
> 325	< 45	0.3	2.4	0.7	1.7	0.0	0.0

Overall, it would seem that XAD-4 is the best choice of resin for the preparation of functional resins by modification to the pendant vinyl groups based on its high surface area, porosity, particle size and vinyl group content.

3.3.6 X-Ray microprobe analysis to measure bromine distribution

Similar experiments to ours have been done to determine the distribution of functional groups within a resin. Polystyrene resins were sulfonated using a variety of methods, which affected the functional group distribution within the beads [22]. EDAX (energy dispersive analysis of X-rays) with scanning electron microscopy (SEM) was used to determine the sulfur and sodium (for salts of the sulfonic acid groups) distributions across a bead cross-section. Variation of reaction conditions led to either homogeneous, surface, or gradient distributions of functional groups. It was found that functionalization occurs from the surface and progresses successively inward [23]. Shell-progressive sulfonation into each microparticle also occurred. When a solvent, such as nitromethane, that could penetrate the matrix, was used in sulfonation, homogenous modification occurred. It was also noted that based on different reactivities of the monomers, the cross-linking density was inhomogeneous within the microparticles, higher in the centre and less at the surface of each microparticle [23]. Variations of porosity showed that the accessibility for modification varied with surface area, though longer reactions times could overcome any barriers to diffusion [23]. Unfortunately, no experimental details with regard to sample preparation for the EDAX-SEM work was included in either paper.

Commercial macroporous polystyrene resins were used to prepare resins with pendant vinyl groups by the multi-step conversion of the styrene unit to the vinylstyrene unit by chloromethylation, followed by conversion into their phosphonium salts and finally by a Wittig vinylation [24]. The vinyl groups were then hydrostannylated and modified further. Beads bearing the hydrostannyl group were halved with a microtome, and the tin and chlorine distributions across the internal cross-section were determined by the use of EDAX-SEM. It was stated that the tin and chlorine were homogeneously distributed within the beads, implying that the vinyl groups were evenly distributed throughout the resin. The difference with respect to our work is that they introduced the vinyl groups into a preformed matrix, whereas XAD-4 already has vinyl groups, so the vinyl groups distribution is not based on the modification of a resin, but the method of polymerization. It was not mentioned in the experimental whether the beads were embedded in any substrate for microtoming.

As mentioned earlier, Faber and co-workers modified the residual vinyl groups of XAD-4 [11]. The bromine distribution profile for anti-Markovnikov hydrobrominated XAD-4 was determined using electron probe X-ray microanalysis. It was found that the distribution of Br was homogeneous, implying that the vinyl group distribution was also homogenous across the bead. It should be noted that their data was restricted to only 1/3 of the diameter from the bead edge (~300 μm of a 930 μm bead), and only 6 data points at intervals of approximately 42 μm were collected. The sample width was on the micron-scale and it was noted that, at the submicron scale, the distribution of vinyl groups could be inhomogeneous, with vinyl groups situated primarily in the cores of the resin microspheres. They also did not give specific experimental details, such as the type of epoxy the beads were embedded in.

We did similar experiments with the brominated XAD-4 as a way to map the vinyl group distribution. However, we sampled every 15 μm across the entire bead diameter, to give as many as 70 data points. When an epoxy with an amine cure agent (Epo-Tek-301) was used, we found that the bromine concentration at the outer edges was approximately twice that of the centre, as seen in figure 3.6 (counts are proportional to concentration and the probe current, which was 15.6 nA). It was thought that the amine may have reacted with the bromine-containing functional groups, affecting the distribution. Indeed, the regions with higher bromine content became more smoothly polished, whereas the inner regions tended to be softer due to a lack of penetration of the epoxy and were consequently pitted slightly. The added depth in the inner region may have also contributed to the lower measured bromine content. We repeated the experiment on beads of the same sample of brominated resin using an epoxy which had an anhydride cure agent (Epo-Tek-377). This time, the epoxy fully penetrated the entire bead, leading to uniformly-polished surfaces. However, results were inconsistent for this case, as shown for one bead in figure 3.7. The probe current used, 8.3 nA, was approximately half of that used for the previous bead, resulting in proportionately lower bromine counts. The bromine distribution was not only inhomogeneous across the bead, but also varied significantly from bead to bead. The morphology of the beads may play a role, regions where lower bromine concentrations were measured, the structure may have been more porous.

Figure 3.8 shows the SEM secondary electron micrographs of the two beads for which bromine distribution profiles were shown in figures 3.6 and 3.7. The left image (3.8A) shows the bead embedded in Epo-Tek-301 (bead A henceforth), while the right image (3.8B) shows the bead embedded in Epo-Tek-377 (bead B henceforth). The diameters of bead A and bead B were 0.93

mm and 1.2 mm respectively, and the magnifications were 95X and 65X. The pitting in bead A is visible, the outer edge accounting for approximately 25% of the diameter. Bead B was polished much more uniformly. The bumps are due to dust particles on the sample surface. The points where the electron beam scanned the bead cross-sectional diameters are visible as a series of small dots along a line on each bead, approximately horizontally for bead A and vertically for bead B.

Figure 3.9 shows the SEM backscatter micrograph of the same two beads. As for figure 3.8, the left image shows bead A, while the right image shows bead B. The fluorescence varies with average atomic number and roughly indicates the variations in bromine content. The brighter areas, around the outer edges of the beads indicate higher levels of bromine, whereas the inner region gets darker towards the centre, indicating a lower bromine content. It would appear that the bromine seems more concentrated towards the outer region of the beads. This confirms that the outer parts of the beads are richer in vinyl groups.

Even though the bromine distribution profile for bead B was very inhomogeneous, the micrographs show an agreement in overall bromine distribution as for bead A. Although we cannot conclude with certainty whether the distribution of bromine (and thus vinyl groups) is more like that of bead A (figure 3.6) or bead B (figure 3.7), we can conclude that all the vinyl groups are accessible for modification since the vinyl groups were completely consumed by bromination as seen in the FTIR spectrum (figure 3.3), without further cross-linking, aryl or alkyl bromination (the bromine content was in close agreement to the vinyl content).

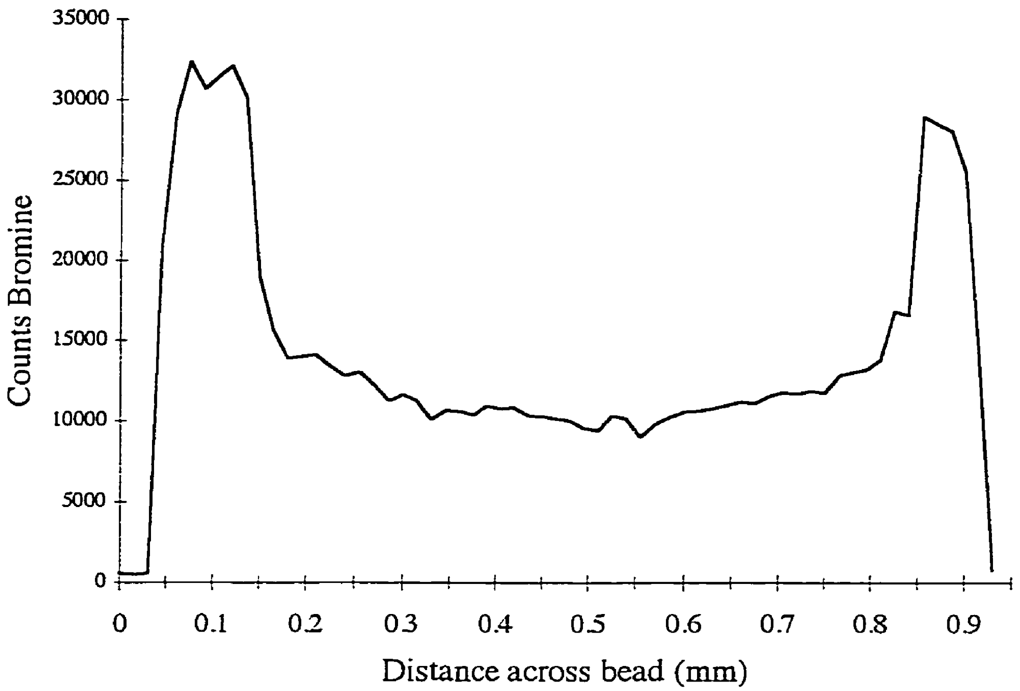


Fig. 3.6. Bromine distribution profile of brominated XAD-4 embedded in Epo-Tek-301 (Bead A).

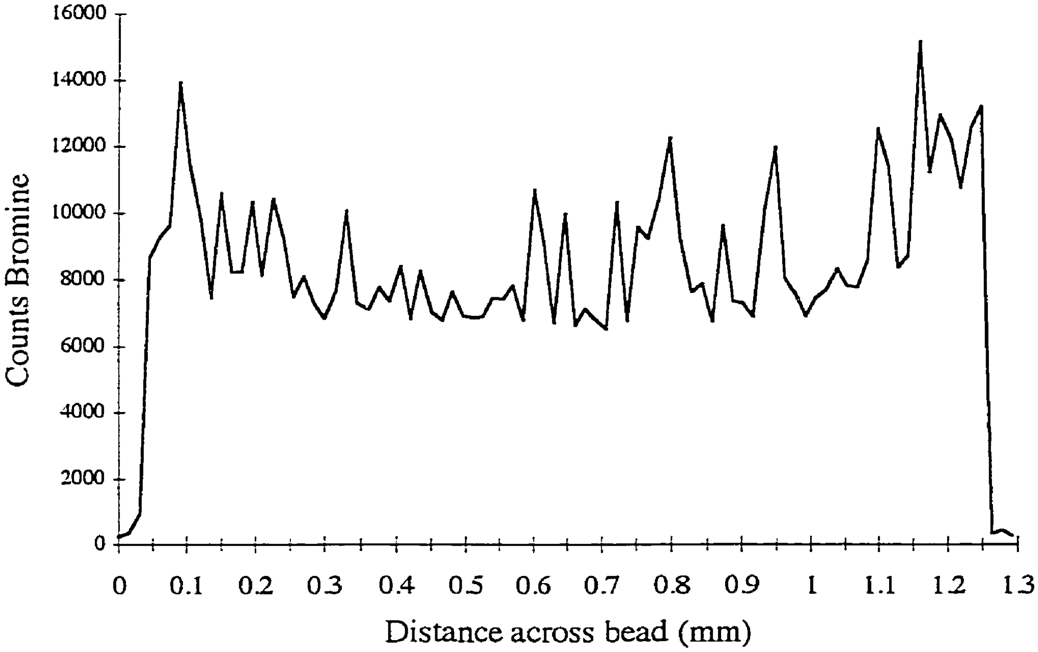


Fig. 3.7. Bromine distribution profile of brominated XAD-4 embedded in Epo-Tek-377 (Bead B).

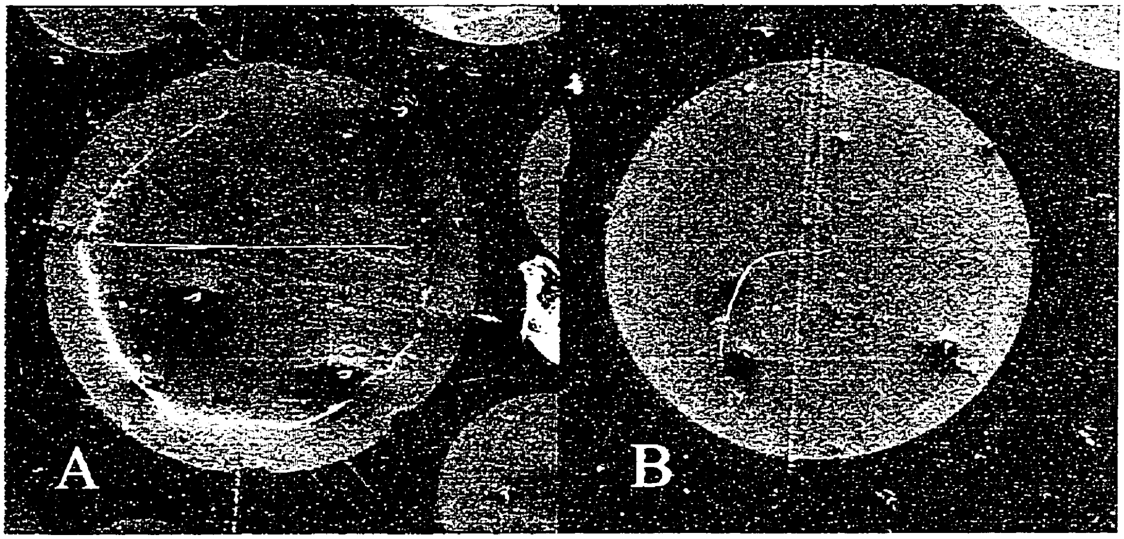


Fig. 3.8. Secondary electron micrographs of bead cross-sections of brominated XAD-4 embedded in Epo-Tek-301 (Bead A) and Epo-Tek-377 (Bead B).

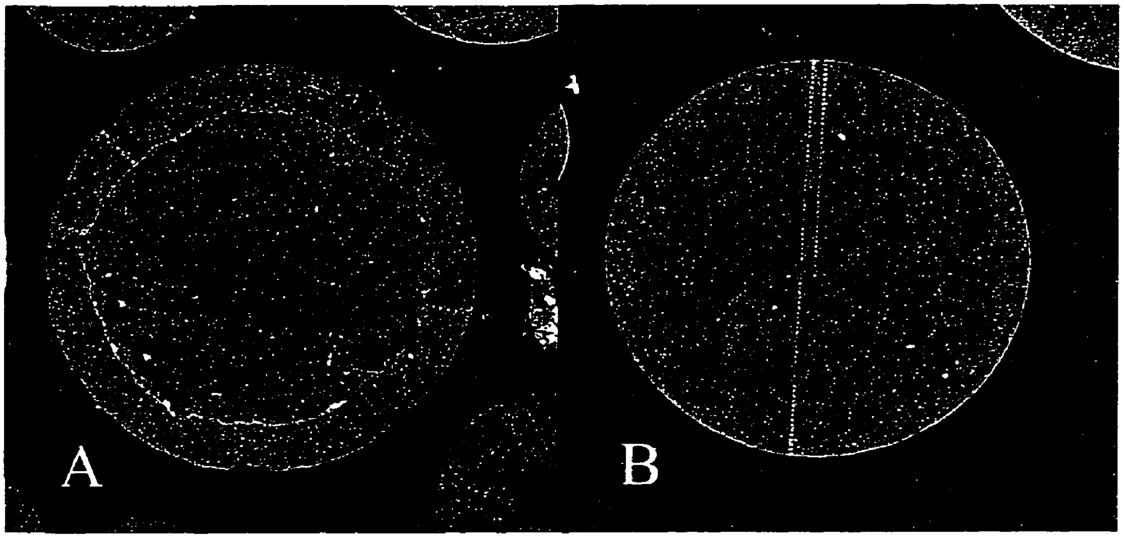


Fig. 3.9. Backscatter electron micrographs of bead cross-sections of brominated XAD-4 embedded in Epo-Tek-301 (Bead A) and Epo-Tek-377 (Bead B).

3.4. Conclusions

Amberlite XAD-4, a styrenic copolymer of meta- and para-isomers of divinylbenzene (80-85 wt %) and ethylvinylbenzene (15-20 wt %), is an ideal matrix for preparing functionalized resins. Since it is commercially-available, the need to prepare a matrix for the synthesis of functional resins is eliminated. It has high surface area, porosity, and accessible pendant vinyl groups which can act as sites for modification. Bromination of XAD-4 showed complete conversion of vinylbenzene groups to (1,2-dibromoethyl)benzene groups. XAD-4 has a vinyl content ranging from 29-41%, meaning that approximately one-third of repeat units provide sites for further modification.

3.5. Acknowledgements

We wish to thank Rohm and Haas Company for donation of 5 kg of Amberlite XAD-4 and other samples, and for providing some literature, and Dr. J. Snow of Millipore Corporation for providing some information and samples used in this paper. ^{13}C NMR spectra were taken by Dr. F.G. Morin of the Department of Chemistry, McGill University. Samples for X-ray microprobe analysis were prepared by G. Panagiotidis and analysis was done by G. Poirier, both of the Department of Earth and Planetary Sciences, McGill University. Surface areas and pore sizes were measured by the lab group of Dr. J. Zhu, University of Montreal. Thanks also go to Dr. R.B. Lennox, Dr. D.N. Harpp, and Dr. D.S. Argyropoulos for helpful discussion. Funding for this project was provided by a Natural Sciences and Engineering Research Council of Canada Strategic Grant.

3.6. References

[1] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted April 1997. Chapter 2 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[2] R. Kunin, Amberhilites (produced by Rohm and Haas Co.), Number 161 (spring 1979).

[3] R. Kunin, Amberhilites (produced by Rohm and Haas Co.), Number 163 (winter 1980).

[4] E.F. Meitzner and J.A. Oline, U.S. Patent 4,382,124, issued May 3, 1983.

[5] Food and Drug Administration, U.S. Government, 173.65, page 100 in "Code of Federal Regulations", 21, Food and Drugs. Parts 170 to 199, revised April 1, 1994.

[6] R.L. Albright, React. Polym., 4 (1986), 155.

[7] Supelco Product Catalogue, 1995, page 264.

[8] N.A. de Munck, M.W. Verbruggen and J.J.F. Scholten, J. Mol. Catal., 10 (1981), 313.

[9] J.P.C. Bootsma, B. Eling and G. Challa, React. Polym., 3 (1984), 17.

[10] M Periyasamy, W.T. Ford and F.J. McEnroe, J. Polym. Sci. Polym., Chem. Ed., 27 (1989), 2357.

[11] M.C. Faber, H.J. van den Berg, G. Challa and U.K. Pandit, React. Polym., 11 (1989), 117.

[12] Z. Zhengpu, P. Hodge and P.W. Stratford, React. Polym., 15 (1991), 71.

[13] M. Bartholin, G. Boissier and J. Dubois, Makromol. Chem., 182 (1981), 2075.

[14] J.P. Gao, F.G. Morin and G.D. Darling, Macromolecules, 26 (1993), 1196.

[15] B. Walczynski, B.N. Kolarz and H. Galina, Polym. Commun., 26 (1985), 276.

[16] J.H. Schutten, C.H. van Hastenberg, P. Piet and A.L. German, Angew. Makromol. Chem., 89 (1980), 201.

[17] C.J. Pouchert (Editor), The Aldrich Library of FT-IR Spectra, Edition 1. Aldrich Chemical Company, Inc., Milwaukee, 1985. Volume 1, page 974.

[18] M. Bacquet, C. Caze, J. Laureyns and C. Bremard, React. Polym., 9 (1988), 147.

[19] C.J. Pouchert and J. Behnke (Editors), The Aldrich Library of ^{13}C and ^{1}H FT-NMR Spectra, Edition 1. Aldrich Chemical Company, Inc., Milwaukee, 1993. Volume 2, pages 12, 23.

[20] Y. Nagasaki, H. Ito and T. Tsuruta, Makromol. Chem., 187 (1986), 23.

[21] S.J. Gregg and K.S.W. Sing, Adsorption, Surface Area, and Porosity. 2nd Ed. London: Academic Press, Inc. 1982. 21a. p. 3, 21b. p. 128, 21c. p. 25.

[22] J. Klein, H. Widdecke and N. Bothe, Makromol. Chem., Suppl. 6 (1984), 211.

[23] M. Struck and H. Widdecke, Angew. Makromol. Chem., 235 (1996), 131.

[24] W.P. Neumann and M. Peterseim, React. Polym., 20 (1993), 189.

Chapter 4

Thiol Addition to the Pendant Vinylbenzene Groups of poly(Divinylbenzene-*co*-Ethylvinylbenzene), Including Amberlite XAD-4. Modification in Organic and Aqueous Solvents.

Forward to Chapter 4

The content of the following section is comprised of a paper with the same title which was submitted to the journal Reactive and Functional Polymers (K.L. Hubbard, G.D. Darling and J.A. Finch, submitted May 1997).

The initial goal of this thesis was to modify laboratory-prepared poly(divinylbenzene-*co*-ethylvinylbenzene) by the radical anti-Markovnikov addition of thiols to the pendant vinylbenzene groups. Work on this topic was previously done in Dr. G.D. Darling's group by J.P. Gao and B. Stranix, and my work presented in this chapter expanded upon their methodology. The thiols used for modification had functional groups which could potentially render the modified resins useful for ion-exchange, metal coordination, or other applications. I discovered, while searching the literature, that poly(divinylbenzene-*co*-ethylvinylbenzene) was commercially-available as Amberlite XAD-4, and attention turned to modification of the commercial resin. This chapter expands on the choices of thiols used in modification of poly(divinylbenzene-*co*-ethylvinylbenzene), compares the modification of the laboratory-prepared and commercial forms of the resin, and explores on the use of various solvents, most notably water.

Abstract

Laboratory-prepared poly(divinylbenzene-*co*-ethylvinylbenzene) resin, and the commercial version, Amberlite XAD-4, were modified by the anti-Markovnikov addition of thiols to pendant vinylbenzene groups, linking functional groups through a thioether-dimethylene spacer to the resin. Depending on the thiol, different solvents and radical initiators were used to optimize functionalization. The most important factors for maximum modification were the solubility of the thiol and the accessibility of vinyl groups. Compared to lab-made resins, Amberlite XAD-4, which has a much higher surface area and porosity, could be modified to a greater extent. The degree of modification of vinyl groups for XAD-4 was as much as 25%, up to 76% of vinyl groups were converted to thioether groups.

Keywords: Amberlite XAD-4, poly(divinylbenzene-*co*-ethylvinylbenzene), pendant vinyl groups, thiol addition

4.1. Introduction

This paper discusses the modification of vinyl groups in a polystyrene-like matrix by the radical addition of thiols. We compare the use of lab-made and commercial resins as the starting material, as well as the variation of reaction conditions and thiols used. We have previously studied poly(divinylbenzene-*co*-ethylvinylbenzene), including the commercial resin Amberlite XAD-4 (Rohm and Haas Company) [1,2], and have found it to contain pendant vinylbenzene groups. This work presents the modification of this polymer by reaction with these groups.

4.1.1 Review of poly(divinylbenzene-*co*-ethylvinylbenzene), including XAD-4

Amberlite XAD-4 is a macroporous resin prepared from commercial grade divinylbenzene, approximately 80 to 85 wt % divinylbenzene and 15 to 20 wt % ethylvinylbenzene [1-7]. It is an ideal matrix for the preparation of functional resins based on its structural characteristics: XAD-4 has a high surface area (725 to 1040 m^2/g) and porosity (0.98 to 1.55 mL/g) [1, 2, 7-9]. The vinyl content ranges from 29 to 41% (2.2 to 3.1 mmol/g), depending on the lot [2]. Only five research groups have mentioned the presence of vinyl groups in XAD-4 [9-13], and of these, only two have actually modified the resin by reaction with the vinyl functionality [12, 13].

Copolymers of divinylbenzene and ethylvinylbenzene, referred to as polyDVB henceforth, have a cross-linked structure with pendant vinylbenzene and ethylbenzene groups (figure 4.1). The degrees of functionalization are indicated by the symbols X_{CL}, X_{VB}, and X_{EB}, (CL for cross-linked, VB for vinylbenzene, and EB for ethylbenzene). The monomers are meta- and para-disubstituted, giving a total of 6 randomly-occurring repeat units. The most important features of a resin are the vinyl group content and accessibility. Since commercial XAD-4 has a high surface area and porosity, vinyl groups should be accessible to chemicals used during modification.

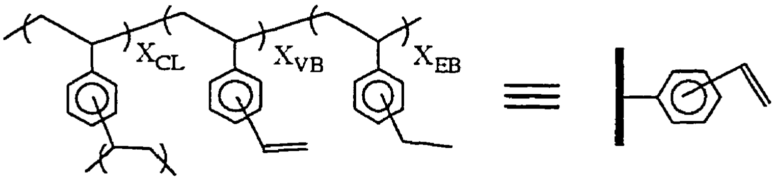


Fig. 4.1. Structure of poly(divinylbenzene-*co*-ethylvinylbenzene).

We intend to demonstrate that XAD-4 can be modified by the radical addition of thiols to its pendant vinylbenzene groups.

4.1.2 Review of thiol addition to vinyl-containing polymers

Researchers have previously modified polymers by the addition of thiols to form polymer-bound thioethers. Pendant allyl groups of hydrophilic polytriallylamine were reacted with bisulfite and some thiols [14]. Reactions of the resin as its hydrochloride salt were done in water, methanol, dimethyl sulfoxide (DMSO) with or without water, or *N,N*-dimethylformamide (DMF), with initiators being either air, benzoyl peroxide with *N,N*-dimethylaniline, ultraviolet (UV) light with acetone, hydrogen peroxide with ferrous ion (H_2O_2/Fe^{+2}), or azobisisobutyramidinium dihydrochloride. Although modification was attempted with many thiols, only two reacted quantitatively: mercaptoethanol and thioglycolic acid (done in water with either air or H_2O_2/Fe^{+2} as initiator). Thiophenol and thioacetic acid did not react under any conditions attempted. Hydrogen sulfide and methanethiol reacted with the polymer in water with H_2O_2/Fe^{+2} as initiator with 20% and 52% yields (percent conversion of vinyl groups to functional groups), respectively. 2-(*N,N*-Diethylamino)ethanethiol hydrochloride reacted with the polymer in as much as 32% yield using water and air initiation, whereas use of the azo initiator yielded only 5% conversion. The experimental conditions were not described in detail, so it is not known if radical reactions were done in the absence of oxygen. Higher yields were attributed to solubility of the thiols in water, which swells the polymer, as well as to steric factors.

Photochemical addition of thiols to linear polymers with pendant vinyl ether groups was done using benzophenone (BP) as a photosensitizer [15, 16]. The addition of methyl 3-mercaptopropionate was highest in benzene, toluene, and tetrahydrofuran (THF) (67 to 83% yield), followed by 1,4-dioxane (46%) and *N*-methyl-2-pyrrolidone (NMP) (18 to 43%). Reaction did not occur when DMSO was used [15]. Addition of ethyl 3-mercaptopropionate in benzene to the polymer gave 93% yield [15]. Addition of *N*-acetyl-L-cysteine in THF gave optically-active polymers with as much as 71% yield [15]. It was found that degradation of the polymer backbone occurred. The presence of a sensitizer such as benzophenone increased yields [15].

Further work with the same polymer was done using more thiols (benzenethiol, benzylmercaptan, 2-mercaptoacetic acid, ethyl 3-mercaptopropionate, *N*-acetyl-L-cysteine, oxy(dibenzenedithiol), and 1,4-phenylenedi(methylthiol)) [16]. The reactions were carried out in THF with benzophenone (BP). It was found that yields were dependent upon the molar ratio of thiol to vinyl group (maximum yield was with 3 equivalents benzenethiol), and the amount of photosensitizer added, with a maximum of 16 mol % for BP (with benzenethiol). Larger amounts of photosensitizer interfered with the penetration of UV light to the reacting system. Excess dithiol led to reaction of only one of the thiol groups with the polymer, leaving a soluble polymer bearing thiol groups, whereas lower amounts of dithiol led to cross-linking and less or no free thiols.

Octanethiol and 3-(trimethoxysilyl)-1-propanethiol were added free-radically to butadiene polymers [17, 18]. It was found that the 1,2-vinyl group was most reactive, followed by the 1,4-cis double bond. The 1,4-trans double bond was unreactive.

The vinyl groups of carboxytelechelic polybutadiene were modified by the radical addition of mercaptoacetic acid, yielding a polymer with pendant carboxylic acid functionalities linked via a thioether to the backbone [19]. Fluorinated thiols, of the formula $C_nF_{(2n+1)}CH_2CH_2SH$ (n = 6 to 8), were also grafted to the vinyl groups photochemically [20].

Polymers containing the norbornene moiety were modified by radical addition of thiols [21]. Mercaptoethanol and 1,2-ethanedithiol were added to the alkene groups by reaction in tetrahydrofuran at 80 °C for 18 hours with 2,2'-azobis(isobutyronitrile) (AIBN) as initiator. Conversions of alkene groups were high (90 to 100%); cross-linking occurred with the dithiol.

4.1.3 Review of thiol addition to halogen-containing polymers

Polymer-bound thioethers have also been prepared by Williamson-type (thio)ether synthesis from resins such as chloromethylated polystyrene [22]. Sodium salts of various thiols were formed in an ethanol-THF swelling mixture which was then refluxed with the resin for 8 to 90 hours. It was not mentioned whether the reactions were done under inert atmosphere. Purification of the beads involved washing with THF and water, followed by Soxhlet extraction with THF. Up to 95% of the chlorine was replaced, the best yields were attained with shorter thioethers (i.e. 1,2-ethanedithiol, 2-mercaptoethyl sulfide).

Chloromethylated polystyrene was modified with 2,3-dimercaptopropanol using phase-transfer conditions and sodium hydroxide as base [23]. The modified resin had thiol and alcohol groups.

Linear poly(vinyl chloride) was modified by reaction with 1,3,4-thiadiazole-2,5-dithiol in *N,N*-dimethylformamide at 97 °C for 10 hours with triethylamine as base [24]. Some cross-linking occurred, and less than approximately one-third of the chlorine was replaced with the thioether functionality, yielding (by our deduction from their data) 3.4 mmol/g functional groups.

The same methodology was used to modify chloromethylated polystyrene with 1,3,4-thiadiazole-2-amino-5-thiol [25]. The reaction was carried out at 85 °C for 2 hours, yielding a resin with 3.4 mmol/g of functional groups.

4.1.4 Addition of thiols to poly(divinylbenzene-*co*-ethylvinylbenzene)

Previously, our group modified lab-made poly(divinylbenzene-*co*-ethylvinylbenzene) (polyDVB-55) by the anti-Markovnikov radical addition of a few simple thiols to the pendant vinyl groups [26]. The thiols used included benzenethiol, mercaptoethanol, *n*-butanethiol, *tert*-butyl mercaptan, mercaptoacetic acid, 1,2-ethanedithiol, 1,3-propanedithiol, 1,4-butanedithiol, and 3-mercaptopropionic acid. These one-step modifications involved stirring polymer, excess thiol and AIBN in toluene at 70 °C under nitrogen for 1-2 days. Excess reagent was removed by Soxhlet extraction with acetone. Degrees of functionalization of the modified resins were between 25 and 30%.

We are the first to take advantage of the ideal characteristics of commercial poly(divinylbenzene-*co*-ethylvinylbenzene) (XAD-4) to prepare functional resins by modification of the vinyl groups through the addition of thiols. We will present our results on modifying XAD-4 with a variety of thiols and reaction conditions, and also compare the degree of modification of XAD-4 to that of the lab-made analogous resin (polyDVB-55). For some water-soluble thiols, we will compare the extent of modification when either water or organic solvents were used. We will also study the distribution of modified groups within the beads for resins modified with two amounts of mercaptoethanol.

One advantage of using this method to prepare functional resins is that only a one-step modification of a commercially-available preformed matrix is needed. The reaction conditions are straightforward, of short duration, and no side-products are formed. Purification of the modified resin is done simply by Soxhlet extraction with suitable solvents. Introduction of a wide range of functionalities is possible, with the only restriction being that the modifying chemical has to have a thiol to form the thioether linkage to the resin.

4.2. Experimental

4.2.1 Materials

Unless otherwise noted, all materials were purchased from Aldrich Chemical Company and used as received. Samples of different lots of Amberlite XAD-4 were obtained from either Aldrich Chemical Co. or Rohm and Haas Co. XAD-4 comes imbibed with sodium chloride and sodium carbonate to retard bacterial growth [27]. Unless otherwise noted, all unmodified resins were pretreated by Soxhlet extraction with acetone for several days, followed by drying under vacuum overnight at 60 °C. Two initiators were used, one soluble in organic solvents and the other soluble in water: AIBN (2,2'-azobis(isobutyronitrile), CAS registry number [78-67-1]) and Wako V-50 ((2,2'-azobis(2-amidinopropane) dihydrochloride, CAS registry number [2997-92-4], Wako Pure Chemical Industries). AIBN is soluble in solvents such as toluene, ethanol and methanol, while V-50 is very soluble in water and sparingly soluble in methanol, ethanol, acetone, dioxane and dimethyl sulfoxide (DMSO) [28].

4.2.2 Preparation of poly(divinylbenzene-*co*-ethylvinylbenzene)

Macroporous beads (polyDVB-55) were prepared by the suspension polymerization of commercial grade divinylbenzene (55 wt % DVB, 45 wt % ethylvinylbenzene), as previously reported [2, 26].

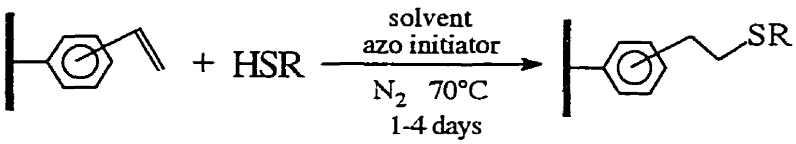
4.2.3 Anti-Markovnikov addition of thiols to pendant vinylbenzene groups

Addition of thiols to the vinylbenzene groups of the resin was done using a similar methodology as in previous work in our lab [26]. Typical experimental details follow.

In a 50 mL 2-neck round bottom flask equipped with condenser and magnetic stirring bar, 1 g of resin, 1.5 to 5 equivalents thiol, 25 mL of solvent, 1 to 2 wt % azo initiator, and optionally 10 wt % PEG-600 (poly(ethylene glycol), molecular weight of 600) were added. The stirring mixture was flushed with nitrogen, heated to 70 °C, and the reaction was allowed to run between 0.5 and 4 days. In some reactions, more solvent or initiator was added after one or more days. Afterwards, the resin was filtered, rinsed with various solvents, and Soxhlet extracted for several days with various solvents, generally with acetone as the last solvent. The purified resin was dried under vacuum (70 °C) for one day.

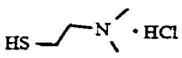
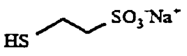
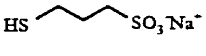
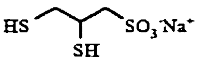
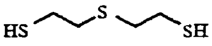
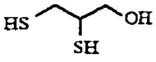
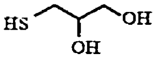
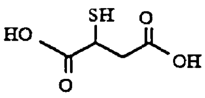
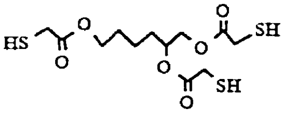
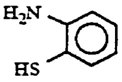
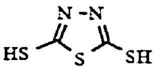
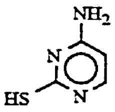
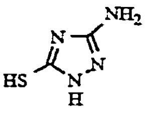
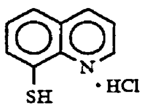
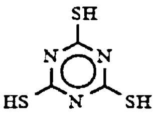
The solvents used for the reaction included toluene, dioxane, *N,N*-dimethylformamide (DMF), ethanol, *N*-methyl-2-pyrrolidone (NMP), or water with methanol or ethanol. The solvents used for Soxhlet extraction included dioxane, methanol, ethanol, tetrahydrofuran, dichloromethane, water or acetone.

Scheme 4.1 illustrates the reaction scheme for modification of the resins. The thiols used are listed in table 4.1. The IUPAC names and CAS registry numbers are included. The solubilities of these thiols in various solvents were qualitatively determined by adding a few milliliters of solvent (at room temperature) to a few milligrams of thiol in a test tube and shaking.



Scheme 4.1. Anti-Markovnikov thiol addition to vinylbenzene groups of poly(divinylbenzene-*co*-ethylvinylbenzene).

Table 4.1. Thiols used in modification of pendant vinylbenzene groups

Reagent Structure	IUPAC Name [CAS number]	Reagent Structure	IUPAC Name [CAS number]
 (1)	2-aminoethanethiol hydrochloride [156-57-0]	 (2)	2-dimethylaminoethanethiol hydrochloride [13242-44-9]
 (3)	2-mercaptoethanesulfonic acid (sodium salt) [19767-45-4]	 (4)	3-mercapto-1-propanesulfonic acid (sodium salt) [17636-10-1]
 (5)	2,3-dimercapto-1-propanesulfonic acid (sodium salt) [74-61-3]	 (6)	2-mercaptoethyl sulfide [3570-55-6]
 (7)	2,3-dimercapto-1-propanol [59-52-9]	 (8)	3-mercapto-1,2-propanediol [96-27-5]
 (9)	2-mercaptoethanol [60-24-2]		
 (10)	mercaptosuccinic acid [70-49-5]	 (11)	1,2,6-hexanetriol trithioglycolate [19759-80-9]
 (12)	2-aminothiophenol [137-07-5]	 (13)	2,5-dimercapto-1,3,4-thiadiazole [1072-71-5]
 (14)	4-amino-2-mercaptopyrimidine [333-49-3]	 (15)	3-amino-5-mercapto-1,2,4-triazole [16691-43-3]
 (16)	8-quinolinethiol hydrochloride [34006-16-1]	 (17)	trithiocyanuric acid [638-16-4]

4.2.4 Characterization

4.2.4.1 Elemental analysis

Some samples were analyzed in-house for sulfur content [29]. The majority of samples were sent to the University of British Columbia or Robertson Microlit Laboratories (Madison, NJ) to be analyzed for sulfur and nitrogen, where applicable.

4.2.4.2 Infrared spectroscopy

The unmodified resins were characterized using infrared spectroscopic analysis to measure the vinyl group content [2, 30]. Modified resins were characterized to determine consumption of vinyl peaks and appearance of new peaks due to the modifying groups. Samples were ground into powder with FTIR-grade potassium bromide (KBr) and pressed into disks. Fourier transform infrared absorbance spectra were taken with a Bruker IFS 66 spectrometer, using a DTGS detector, at 2 cm^{-1} resolution, with 120 to 200 scans.

4.2.4.3 Raman spectroscopy

Fourier transform Raman spectra were taken using a Bruker IFS 88 spectrometer with FRA-105 Raman module using a Nd^{+3}:YAG laser (1064.1 nm). Samples were ground into powder and packed lightly into an aluminum sample cup. The number of scans ranged from 250 to 5000, with a 4 cm^{-1} resolution. It should be noted that spectra taken with samples held in glass melting point tubes had fluorescence due to the glass, obscuring most peaks, so this method was not used.

4.2.4.4 ^{13}C NMR spectroscopy

Solid-phase ^{13}C CP-MAS (cross-polarization magic angle spinning) NMR spectra were obtained with a Chemagnetics Inc. M-100 instrument, at 25.1 MHz, contact time of 2 ms, pulse delay of 2 s, spinning rate of 3-4 kHz, and high-power proton decoupling during acquisition. The ^{13}C CP-MAS-DD (dipolar dephasing) NMR spectra were obtained with a dephasing time (τ) of 45 μs. Samples were referenced to hexamethylbenzene.

4.2.4.5 Surface area and pore size measurements

As previously reported [2], BET gas adsorption measurements were performed on a Coulter SA-3100 surface area and pore size analyzer (Coulter Scientific Instruments) with nitrogen to determine the surface area and porosity.

4.2.4.6 Electron microprobe analysis of mercaptoethanol-modified XAD-4

Beads of two samples of XAD-4 modified with varying amounts of mercaptoethanol, were embedded in an epoxy resin, Epo-Tek-301, from Epoxy Technology Inc., Billerica, MA. Polishing was done using diamond paste, and the samples were then coated in carbon. Cross sections of the beads were scanned for sulfur (S K_{α}) and oxygen (O K_{α}) using a JEOL 8900 electron microprobe, using 15.0 kV accelerating voltage, 15 nA probe current, 5 μm beam diameter, 20 sec dwell time, and 15 μm distance between points.

4.3. Results and Discussion

4.3.1 Characteristics of starting materials

Previously, we characterized the starting materials with regard to vinyl content, surface area, porosity, and monomer content, and the results are fully presented elsewhere [2]. Table 4.2 summarizes the vinyl content of the starting materials calculated using FTIR spectroscopy [2, 30]. The degree of functionalization (X_{VB}, %) is the percentage of repeat units which are vinylbenzene groups, and the degree of cross-linking (X_{CL}, %) is the percentage of repeat units which cross-link the resin. The commercial resins had higher vinyl contents and cross-linking due to a higher DVB content (80 wt %). Table 4.3 gives the surface areas and porosities for two resins, one lab-made, and one commercial [2]. The pore distribution is based on the percentage of the total pore volume with pores of a given diameter. In contrast to the lab-made (polyDVB-55) resins, the commercial resins were higher in both surface area and porosity. The polyDVB-55 resins had high surface areas, but much smaller pores and total pore volume than the commercial resins.

Table 4.2. Vinyl contents of divinylbenzene copolymers

	Resin	Degree of Functionalization (X_{VB}, %)	Degree of Cross-Linking (X_{CL}, %)	Vinyl Content (mmol/g)
L1	polyDVB-55-d	21 ± 2	34 ± 3	1.6 ± 0.1
X1	XAD-4 lot #1090-7-1473	33 ± 1	47 ± 2	2.5 ± 0.1
X2	XAD-4 lot #03803HF	41 ± 1	39 ± 1	3.1 ± 0.1
X3	XAD-4 lot #00126BZ	29 ± 1	51 ± 2	2.2 ± 0.1

Table 4.3. Surface areas and porosities of divinylbenzene copolymers

Resin	Surface Area (m^2/g)	Total Pore Volume (mL/g)	Pore Size (nm)
polyDVB-55-d (L1)	504	0.502	< 6 (92.39%)
XAD-4 lot #1090-7-1473 (X1)	831	1.181	< 6 (17.3%) 6-10 (20.5%) 10-20 (59.5%)

4.3.2 Modification of XAD-4 by addition of thiols

4.3.2.1 Calculation of the degree of functionalization

The general equation for calculating the degree of functionalization of modified XAD-4 (X_{fg}) is based on the average MW per repeat unit of unmodified resin (130.6 g/mol for 80% DVB content, 130.2 g/mol for polyDVB-55), the mole content of functional group (mol fg/g or functional capacity, C_{fg}, calculated from elemental analysis), and the molecular weight (MW fg) of the modifying group (equation 4.1). For thiol-modified XAD-4, the calculation of degree of functionalization ($X_{2\text{-}SR}$) is shown as equation 4.2. The value "n" is the number of sulfur atoms per modifying group (i.e. 2,3-dimercapto-1-propanol (7) has 2 sulfur atoms, so n = 2). The percent conversion (Φ) of vinyl groups (double bonds) to modified groups is given in equation 4.3.

Equation 4.1
$$X_{fg} = \frac{130.6 \times (\text{mol fg/g})}{1 - (\text{mol fg/g} \times \text{MW fg})} \times 100\%$$

Equation 4.2
$$X_{2\text{-SR}} = \frac{130.6 \times (\text{mol S/g} \div \text{n})}{1 - ((\text{mol S/g} \div \text{n}) \times \text{MW HSR})} \times 100\%$$

Equation 4.3 $$\Phi = \frac{X_{2\text{-SR}}}{X_{VB}} \times 100\%$$

4.3.2.2 Comparison of modification of resins using various organic solvents

During the optimization of reaction conditions, various solvents were tried. A balance between using a solvent which could swell and penetrate the resin, and one that could also dissolve the reagent, was needed to maximize the conversion of vinyl groups to functional groups (Φ, yield of reaction). Table 4.4 lists the solubilities of the thiols studied (listed in table 4.1) in various solvents: NMP (*N*-methyl-2-pyrrolidone), dioxane, THF (tetrahydrofuran), toluene (or benzene (bz) as indicated), DMF (*N,N*-dimethylformamide), DMSO (dimethyl sulfoxide), CH_3CN (acetonitrile), H_2O (water), EtOH (ethanol) and MeOH (methanol). Some data is from the literature, as noted [31-33].

Table 4.5 gives results of thiol additions to polyDVB-55 and XAD-4 in a range of solvents. The modified resins are listed with bold numbers which indicates the thiols used in the functionalizations. The amount of functional group ($C_{2\text{-SR}}$, in mmol/g resin, found by elemental analysis), degree of functionalization ($X_{2\text{-SR}}$) and percent conversion (Φ) of starting vinyl groups to modified groups are given along with the reaction conditions and starting resin used. The reaction conditions that were varied included the resin, thiol, solvent, and presence of PEG-600 or other co-solvent. The form of the modified resin is also noted. Generally, rapid stirring with a magnetic stir bar ground the beads into powder. This may have improved conversions due to an increase in accessibility of vinyl groups, but at the expense of structural integrity. More gentle stirring or use of a mechanical stirrer would minimize bead destruction.

Since we originally chose solvents which tend to swell polystyrene matrices, not all of the solvents listed in table 4.4 were used, but further work using a wider range of solvents is recommended with the principle requirement being the ability to dissolve the thiol used. Generally, there was no one best solvent for all thiols; which one gave the best conversions depended on the thiol. In some cases, such as for thiol **17**, no method worked in modification of the resin; whereas in other cases, high conversions were found, such as for thiol **7** using toluene as the solvent (**7a**, 76% conversion using XAD-4). Ethanol was used in some modifications, including in the preparation of **10a** (39% conversion). Since methanol and 2-propanol swell XAD-4 by 20% in comparison to the shipped volume (imbibed with salts and some water) [27], these solvents are also recommended for further studies.

Table 4.4. Solubilities of thiols at room temperature (a)

Thiol	NMP	Dioxane	THF	Toluene	DMF	DMSO	CH_3CN	H_2O	EtOH	MeOH
(1)	S	I	I	I	S	S	I	S	S	S
(2)	S	I	I	I	SS	S	I	S	SS	S
(3)	S	I	I	I	S	S	I	S	I	S
(4)	SS	I	I	SS	S	S	I	S	I	S
(5)	S	SS	-	SS	S	-	-	S	SS	S
(6)	S	S	S	S	S	S	S	I	I	I
(7) (b)	-	-	-	-	-	-	-	-	S	-
(8) (c)	-	-	-	SS (bz)	-	-	-	SS	S	-
(9)	S	S	S	S	S	S	S	S	S	S
(10) (d)	-	-	-	I (bz)	-	-	-	S	S	-
(11)	S	S	S	S	S	S	S	I	I	I
(12)	S	S	S	S	S	S	S	I	S	S
(13)	S	S	S	S	S	S	SS	S (e)	S	S
(14)	S	I	I	I	S	S	I	I	I	SS
(15)	SS	I	I	I	S	S	I	I	I	I
(16)	S	I	S	I	S	S	S	S	S	S
(17)	S	I (f)	S	I	S	S	I	I	I (f)	I

(a) S is soluble, SS is slightly soluble and I is insoluble.
(b) [31, volume 5, page 4450]. Note: also soluble in "oils".
(c) [31, volume 5, page 4332].
(d) [31], volume 2, page 1807].
(e) [32, volume 6, page 6003].
(f) [33, page 107]. Note: soluble in hot pyridine, slightly soluble in hot ethanol and hot dioxane.

Likewise, the use of additives, including PEG-600, may or may not affect results based on which thiol is used. For thiol **1**, the conversions were 35% (**1a**) and 39% (**1b**) for the reactions using DMF alone and with PEG-600, respectively (for polyDVB-55, L1). When DMF with PEG-600 was used in the modification of XAD-4 with thiol **1**, the conversion increased to 63% (**1c**). The trend in increased conversions when the commercial resins were used (instead of the lab-made resins) was seen for most modifications, and will be further explored in section 4.3.2.3.

With thiol **2**, a hydrochloride salt of an amine, other additives were tried, triethylamine (NEt_3) or sodium bicarbonate ($NaHCO_3$). In general, the modification using the free base formed from the presence of either additive reduced the conversion of vinyl groups. For polyDVB-55, the highest conversion with **2** used toluene-PEG-600 (**2b**, 35%), followed by toluene (**2a**, 17%), then with $NaHCO_3$ present (14% for toluene, with (**2e**) or without (**2d**) PEG-600), and lastly with NEt_3 present (**2c**, 12%). This may be explained by the fact that β-aminomercaptans have low chain transfer constants which may be increased by masking the basicity of the amines by formation of a salt [34]. In general, however, these amines tend to be very good transfer agents for styrene [34].

Some of the highest conversions for modification of XAD-4 were attained using toluene and thiols soluble in it, such as for resins **6a** (70%), **7a** (76%), **8a** (59%), and **9a** (66%, with PEG-600). These four thiols are also liquid at room temperature, and may have been more able to penetrate the resin regardless of their solubility.

In other cases, solubility was not the factor contributing to low conversions. Thiol **17** is soluble in hot pyridine and aqueous sodium hydroxide, and slightly soluble in hot ethanol, hot dioxane, and hot acetone [33]. Even though some of these solvents were used, conversions were negligible (< 2%). This thiol exists as a tautomer [35], which may reduce its reactivity towards radicals, and its ability to form radicals. Using an additive such as $NaHCO_3$, may have helped in this case by converting **17** to the mono- or di-sodium salt. Alternatively, the reaction could have been done in an aqueous system, with careful pH adjustment (pH < 8, 1 or 2 equivalents of base per thiol molecule).

Table 4.5. Degree of functionalization ($C_{2\text{-SR}}$ (mmol SR/g), $X_{2\text{-SR}}$) and percent conversion (Φ) of thiol modification of vinylbenzene groups in organic solvents

Product Resin	Thiol	Starting Resin	Solvent	$C_{2\text{-SR}}$ (mmol SR/g)	$X_{2\text{-SR}}$ (%)	Φ
1a (P)	**1**	L1	DMF	0.55	7.5%	35%
1b (P)	**1**	L1	DMF with PEG-600	0.61	8.4%	39%
1c (P)	**1**	X1	DMF with PEG-600	1.3	21%	63%
2a (P)	**2**	L1	toluene	0.27	3.6%	17%
2b (P)	**2**	L1	toluene with PEG-600	0.55	7.6%	35%
2c (P)	**2**	L1	toluene with 1.25 equiv NEt_3 per HSR	0.20	2.7%	12%
2d (P)	**2**	L1	toluene with 1.25 equiv $NaHCO_3$ per HSR	0.23	3.0%	14%
2e (P)	**2**	L1	toluene with PEG-600, 1.25 equiv $NaHCO_3$ per HSR	0.22	2.9%	14%
2f (P)	**2**	X2	toluene with PEG-600	1.1	18%	43%
2g (P)	**2**	L1	NMP	0.37	5.1%	24%
3a (P)	**3**	L1	DMF	0.55	7.8%	36%
3b (P)	**3**	L1	DMF with PEG-600	0.56	8.0%	37%
3c (P)	**3**	L1	dioxane with PEG-600	0.23	3.1%	14%
3d (B)	**3**	X1	DMF with PEG-600	0.75	11%	34%
4a (P)	**4**	L1	dioxane with PEG-600	0.077	1.0%	4.7%
4b (P)	**4**	L1	DMF with PEG-600	0.48	6.9%	32%
4c (B)	**4**	X1	DMF with PEG-600	0.77	12%	36%
4d (P)	**4**	X2	DMF with PEG-600	1.3	22%	53%
5a (P)	**5**	L1	DMF with PEG-600	0.40	5.7%	27%
5b (B)	**5**	X1	DMF with PEG-600	0.44	6.4%	19%
6a (P)	**6**	X1	toluene	1.4	23%	70%
7a (P)	**7**	X1	toluene	1.6	25%	76%
8a (P)	**8**	X1	toluene	1.3	20%	59%
9a (B)	**9**	X1	toluene with PEG-600	1.5	22%	66%

Reaction conditions unless otherwise noted: 1.5-2 equiv HSR, 1-2 wt % AIBN, 70-80 °C, N_2 atmosphere, 0.5-4 days. Modified resins were either in powder (P) or bead (B) form.

(a) PEG-600: 10 wt % MW 600 poly(ethylene glycol) added.
(b) L1 is polyDVB-55-d ($X_{VB} = 21 \pm 2$ %).
(c) X1 is XAD-4 lot #1090-7-1473 ($X_{VB} = 33 \pm 1$ %).
(d) X2 is XAD-4 lot #03803HF ($X_{VB} = 41 \pm 1$ %).
(e) X3 is XAD-4 lot #00126BZ ($X_{VB} = 29 \pm 1$ %).

Table 4.5. (continued)

Product Resin	Thiol	Starting Resin	Solvent	$C_{2\text{-SR}}$ (mmol SR/g)	$X_{2\text{-SR}}$ (%)	Φ
10a (B)	**10**	X1	ethanol	0.85	13%	39%
11a (P)	**11**	L1	dioxane	0.29	4.3%	20%
12a (P)	**12**	X1	toluene	1.0	15%	45%
13a (P)	**13**	L1	dioxane	0.55	7.9%	37%
13b (P)	**13**	L1	dioxane with PEG-600	0.68	10%	47%
13c (P)	**13**	X3	dioxane with PEG-600	0.72	11%	51%
13d (P)	**13**	X2	dioxane with PEG-600	1.6	27%	66%
14a (P)	**14**	L1	DMF	0.15	2.0%	9.3%
14b (P)	**14**	L1	dioxane with PEG-600	0.03	< 1%	< 2%
15a (P)	**15**	L1	toluene	0.009	< 1%	< 1%
15b (P)	**15**	L1	DMF	0.02	< 1%	< 2%
15c (P)	**15**	L1	DMF with PEG-600	0.02	< 1%	< 2%
15d (P)	**15**	L1	toluene with PEG-600	0.007	< 1%	< 1%
15e (P)	**15**	X2	toluene with PEG-600	1.1	16%	39%
16a (P)	**16**	L1	DMF	0.007	< 1%	< 1%
17a (P)	**17**	X1	toluene with PEG-600	0.04	< 1%	< 2%
17b (P)	**17**	X1	DMF with PEG-600	0.04	< 1%	< 2%
17c (B)	**17**	X1	dioxane, 95 °C	0.05	< 1%	< 2%
17d (P)	**17**	X1	ethanol	0.03	< 1%	< 2%
17e (B)	**17**	X1	pyridine	0.05	< 1%	< 2%

Reaction conditions unless otherwise noted: 1.5-2 equiv HSR, 1-2 wt % AIBN, 70-80 °C, N_2 atmosphere, 0.5-4 days. Modified resins were either in powder (P) or bead (B) form.

(a) PEG-600: 10 wt % MW 600 poly(ethylene glycol) added.
(b) L1 is polyDVB-55-d ($X_{VB} = 21 \pm 2$ %).
(c) X1 is XAD-4 lot #1090-7-1473 ($X_{VB} = 33 \pm 1$ %).
(d) X2 is XAD-4 lot #03803HF ($X_{VB} = 41 \pm 1$ %).
(e) X3 is XAD-4 lot #00126BZ ($X_{VB} = 29 \pm 1$ %).

4.3.2.3 Comparison of modification of XAD-4 and polyDVB-55

Table 4.5 also compares the results of thiol addition to lab-made polyDVB-55 and to commercial XAD-4. Generally, two equivalents of thiol and one weight percent AIBN were used with a temperature of 70-80 °C and a time of 2-4 days. Since the comparison is based on the use of matrix, consistent reaction conditions were used for each thiol. Reactions were first optimized with polyDVB-55, by variation of conditions such as solvent and the presence of other additives. The method which gave the highest conversion of vinyl to functional groups was then used with XAD-4. Most of the modified resins were in powder form.

Since different resins with varying vinyl contents were used, the best basis of comparison is the percent conversion (Φ) of vinyl groups to functional groups. For most resins, the percent conversion was higher when XAD-4 was used as the matrix. This is attributed to the higher porosities and surface areas of XAD-4 (table 4.3), allowing the penetration of reagent into the resin leading to higher degrees of modification. In some cases, large increases in conversion occurred when the resin used was changed from the lab-made polyDVB-55 to XAD-4. For thiol **1**, yields increased from 39% (**1b**) to 63% (**1c**) when XAD-4 was used in place of polyDVB-55. Likewise for thiol **2**, conversions improved (from 35% (**2b**) to 43% (**2f**)) with the use of XAD-4.

Increasing amounts of vinyl groups also tended to increase the conversion; for example, resins **13c** and **13d** were prepared using two different lots of XAD-4 (X3, X_{VB} = 29%, and X2, X_{VB} = 41%, respectively) and a higher conversion was seen for the resin with the higher initial vinyl content (**13d**, 66%, compared to 51% for **13c**). This increase in vinyl group conversion can also be seen with resins **4c** (36%) and **4d** (53%) which were prepared from X1 (X_{VB} = 33%) and X2 (X_{VB} = 41%), respectively. Resins with higher vinyl contents have less cross-linking (table 4.3) which may allow easier penetration of reagents into the beads. Beads with high amounts of vinyl groups may have a higher concentration of them situated at the outer edges, where they are more accessible for modification. We previously found that the vinyl group concentration is higher by as much as 2-fold towards the outside of XAD-4 beads compared to the bead core [2].

4.3.2.4 Comparison of modification of resins using organic solvents and water

Water was used as the solvent with a water-soluble azo initiator (V-50) for some modifications with a few of the water-soluble thiols. Table 4.6 summarizes the results of these reactions and compares them to reactions using organic solvents and similar reaction conditions. The use of water as the solvent eliminates the need for organic solvents, lowering cost and environmental impact. The one-step modification can add functional groups such as sulfonates, attached through spacers to the resin.

Three types of thiol were used: β-aminoethylmercaptans (**1** and **2**), sulfonates (**3**, **4**, and **5**) and a dicarboxylic acid (**10**). The same lot of XAD-4 was used for all experiments. In some cases, XAD-4 that was not pretreated by Soxhlet extraction with acetone, but only dried in vacuo, was used to see if the presence of the imbibed salts (NaCl and Na_2CO_3) affected the results. Since the resins were dried, wetting with pure water was difficult, so small amounts of alcohol were added.

In the case of the amines (**1** and **2**), a significant reduction in yield was seen when water was used as the solvent. For resins modified with sulfonates **3** and **4**, the yields were approximately the same when either an organic solvent or water was used. An almost two-fold increase in yield was seen for sulfonate **5**. A slight increase in yield occurred for the dicarboxylic acid (**10**). The presence of salts did not affect results, as can be seen for the reactions using water and thiols **3** and **4**. The presence of additives such as PEG-600 may aid in solubilizing the reagents, or wetting the resin, but no improvement in yield was seen on comparison of results using water for thiols **3** (no PEG-600) and **4** (PEG-600). Overall, if water is a good solvent for a thiol, it will be an acceptable solvent for its addition to poly(divinylbenzene-*co*-ethylvinylbenzene). We encourage further studies with a larger variety of thiols and reaction conditions than presented here. Further work could include the variation of pH, which may aid in dissolving thiols like **17**.

Although XAD-4 does not swell in water, functionalization was successful. The high degree of cross-linking (39 to 51%) maintained the structural integrity enough to allow penetration of reagents. The most important factors for high conversions of vinylbenzene groups appear to be the solubility of the reagent and the ease of radical formation (chain transfer constant).

Table 4.6. Comparison of modification of XAD-4 using organic solvents or water

Thiol Used	Organic Solvent Reaction Conditions	$C_{2\text{-SR}}$ (mmol/g) $X_{2\text{-SR}}$ (%) (Φ)	Aqueous Reaction Conditions	$C_{2\text{-SR}}$ (mmol/g) $X_{2\text{-SR}}$ (%) (Φ)
1	DMF 10 wt % PEG-600 1.7 wt % AIBN 3 days	1.3 ± 0.2 21% (63%) **1c** (P)	4 parts H_2O, 1 part MeOH 10 wt % PEG-600 1 wt % V-50 3 days (XAD-4 not pretreated)	0.64 ± 0.03 9.0% (27%) **1d** (B)
2	toluene 10 wt % PEG-600 1 wt % AIBN after 1 day: 1 wt % AIBN 2 days (XAD-4 not pretreated)	0.69 ± 0.04 10% (30%) **2h** (B)	4 parts H_2O, 1 part MeOH 10 wt % PEG-600 1.4 wt % V-50 after 1 day: 1 wt % V-50 2 days (XAD-4 not pretreated)	0.34 ± 0.05 4.8% (14%) **2i** (B)
3	DMF 10 wt % PEG-600 1 wt % AIBN 3 days	0.745 ± 0.001 11% (34%) **3d** (B)	4 parts H_2O, 1 part MeOH 1 wt % V-50 3 days	0.78 ± 0.01 12% (36%) **3e** (B)
4	DMF 10 wt % PEG-600 1 wt % AIBN 2 days (XAD-4 not pretreated)	0.773 ± 0.001 12% (36%) **4c** (B)	4 parts H_2O, 1 part MeOH 10 wt % PEG-600 1.3 wt % V-50 after 1 day: 6 parts H_2O and 1 wt % V-50 2 days (XAD-4 not pretreated)	0.773 ± 0.002 12% (36%) **4e** (P)
5	DMF 1.75 eq HSR 10 wt % PEG-600 1 wt % AIBN after 2 days: 1 wt % AIBN 4 days (XAD-4 not pretreated)	0.38 ± 0.01 5.4% (16%) **5c** (P)	5 parts H_2O, 1 part MeOH 1.75 eq HSR 10 wt % PEG-600 1 wt % V-50 after 2 days: 1 wt % V-50 4 days (XAD-4 not pretreated)	0.599 ± 0.001 9.1% (28%) **5d** (B)
10	EtOH 1.5 wt % AIBN 3 days	0.85 ± 0.02 13% (39%) **10a** (B)	4 parts H_2O, 1 part EtOH 1 wt % V-50 3 days	0.930 ± 0.005 14% (43%) **10b** (B)

Reaction conditions unless otherwise noted: 2 equivalents thiol (HSR), N_2 atmosphere, 70-80 °C, XAD-4 lot #1090-7-1473 used (X1, X_{VB} = 33 ± 1%), pretreated by Soxhlet extraction with acetone to remove NaCl and Na_2CO_3. Initiators used were AIBN (2,2'-azobis(isobutyronitrile)), and Wako V-50 ((2,2'-azobis(2-amidinopropane) dihydrochloride). Modifications in water used a solution of 4 to 5 parts (by volume) water to 1 part alcohol (methanol (MeOH) or ethanol (EtOH)). Modified resins were either in powder (P) or bead (B) form.

4.3.3 X-Ray microprobe analysis to measure sulfur and oxygen distribution

Previously, we brominated XAD-4 to determine the vinyl group distribution in the bead by using X-ray microprobe analysis to map the bromine distribution [2]. Here, we have modified XAD-4 with less than an equivalent, and with an excess, of mercaptoethanol, and studied the sulfur and oxygen distribution in each. The results of these modifications are given in table 4.7. Although an excess of **9** was used for **9a**, only 66% of the vinyl groups were modified. The modifications were carried out as all of the thiol additions were done: addition of all reagents followed by flushing with nitrogen and then heating to 70°C. This gave the reagents time to penetrate the beads before the reaction started. Figure 4.2 shows the elemental distributions found by X-ray microprobe analysis for **9a**. The results were similar for **9b**.

Table 4.7. Results of modification of XAD-4 with varying amounts of mercaptoethanol

Modified Resin	Reaction Conditions	$C_{2\text{-SR}}$ (mmol/g)	$X_{2\text{-SR}}$ (%)	Φ
9a	toluene 1 wt % AIBN 2 equiv HSR 10 wt % PEG-600 3 days	1.473 ± 0.008	22%	66%
9b	toluene 1 wt % AIBN ~0.5 equiv HSR 10 wt % PEG-600 3 days	1.34 ± 0.03	20%	59%

Reaction conditions: N_2 atmosphere, 70-80 °C, XAD-4 (X1, X_{VB} = 33 ± 1 %), pretreated by Soxhlet extraction with acetone.

The oxygen distribution is not uniform which is due to the fact that the beads were embedded in an oxygen-containing epoxy during sample preparation. Even at the bead edges, the oxygen count was not zero; whereas the sulfur distribution is uniform across the bead, dropping to zero at the edge. The uniform distribution of functional groups in the resin is contrary to our findings for the brominated XAD-4 (same lot XAD-4 modified by bromination and thiol addition) [2]. We found that the outer edge of the beads were more concentrated in bromine, and since the conversion was 100%, that the bromine distribution reflected the vinyl group distribution [2]. If the vinyl groups had completely reacted with thiol **9** (instead of 66%), then we would have seen the same sulfur distribution as for bromine. It is interesting to note that even the interior of the bead was modified with thiol to the same extent as the rest of the bead, meaning that under optimum conditions reagents are able to fully penetrate the bead. Steric hindrance may have prevented further modification of the vinyl groups situated in the vinyl-rich outer regions.

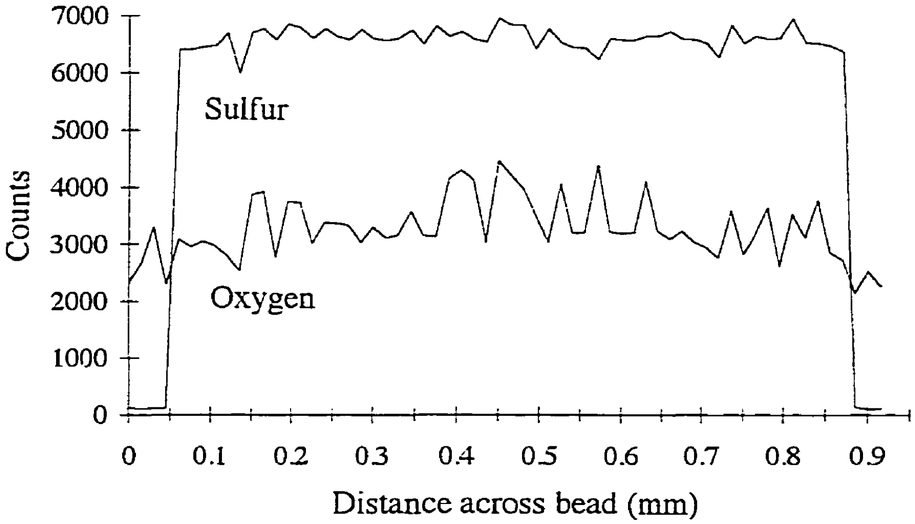


Fig. 4.2. Sulfur and oxygen distribution profiles of **9a**, mercaptoethanol-modified XAD-4.

4.3.4 Spectroscopic characterization

The modified resins were spectroscopically characterized and compared to the starting material using infrared, Raman and ^{13}C NMR spectroscopy. In general, spectra of the resins with the highest percent conversions (Φ) are shown.

4.3.4.1 Infrared spectroscopy

Figures 4.3a to 4.3e compare the FTIR absorbance spectra of XAD-4 and the thiol-modified resins, indicated with a bold number corresponding to the resin characterized. The thiols used (**1-15**) are listed in table 4.1. In most cases, the resin used for each modification was XAD-4.

Peak assignments were done by comparison to the starting thiols and analogous model compounds [36], and with the help of two references on spectroscopy [37,38]. The peak assignments for unmodified poly(divinylbenzene-*co*-ethylvinylbenzene) (XAD-4 and polyDVB-55) have been published elsewhere

[2, 30]. Table 4.8 lists the peak assignments for thiol-modified poly(divinylbenzene-*co*-ethylvinylbenzene). On comparison of the spectra for XAD-4 and the modified resins, the five peaks due to the vinyl groups decrease in relation to the degree of functionalization. The peak at 905 cm^{-1} is due to both vinyl groups and disubstituted phenyls, so it is never completely eliminated.

Table 4.8. Infrared peak assignments for thiol-modified resins

Resin	Band (cm^{-1})	Assignment	Reference	Notes
1c	1700	C=O stretch of residual DMF	[38], p. 195	DMF used as solvent
2h	2770	N-H str. of hydrochloride salt	[37], p. 125	
	1117, 1097, 1056, 1043	C-N stretches	[37], p. 124	
3e, **4e**, **5d**	1360- 1120, 1123, 1049	S=O stretches of sulfonate group	[37], p. 129-130	modifications done in water for these examples
	590, 530	SO_2 rocking, scissoring, deformation	[38], p. 177	
5d	613	C-S stretch	[38], p. 217	
6a	2550	S-H stretch	[38] p. 217	
	1271, 1200	wagging and twisting of methylenes in functional group	[38] p. 202	
7a	3571	O-H stretch	[38], p. 209	thiol peak was not visible for resin **7a**
	1273, 1220, 1065, 1046	various C-O stretches	[38], p. 169, 207	
8a	3571	O-H stretch	[38], p. 209	similar to spectrum of resin modified with **7a**
	1276,1169, 1066, 1019	various C-O stretches	[38], p. 169, 207	peaks listed were more prominent due to the diol (compared to **7a**)
			[36], Volume 1, p. 263	peaks similar to model 3-ethylthio-1,2-propanediol
9a	3460	O-H stretch	[38], p. 209	
	1277, 1221, 1061, 1019, 930	1061 cm^{-1} (strong) C-O stretch	[36], Volume 1, p. 265	peaks similar to model 2-(methylthio)ethanol and to resin **8a**
10b	1740, 1717	carboxylic acid, C=O stretch	[38], p. 195	not dimeric
	1373-1172	broad peak		(dimer peaks occur at 1720-1680 cm^{-1})

The spectra for the aminoethylmercaptan-modified resins (**1c** and **2h**, figure 4.3a) show reductions in the vinyl peaks with the greatest reduction for **1c** (63% conversion, compared to 30% for **2h**). Resin **1c** also had a peak at 1700 cm^{-1}, attributed to residual DMF, the solvent used in this case. The spectrum of another resin modified with **1** (**1d**) in water did not have this peak, but was otherwise identical. Besides a reduction in vinyl peaks, the spectrum of resin **2h** had new peaks due to the functional group (table 4.8).

Table 4.8. Infrared peak assignments for thiol-modified resins (continued)

Resin	Band (cm^{-1})	Assignment	Reference	Notes
11a	1739	C=O stretch	[37], p. 118-120	peaks due to 3 esters per functional group
	1373, 1275, 1147, 1122, 1063, 966	ester C-O stretches		
12a	3468, 3362	N-H stretches of primary amine	[37], p. 123	peaks similar to model 2-(methylmercapto)aniline [36], Volume 1, p. 1196
	1606	aromatic stretch	[37], 158	
	1309	C-N stretch	[37], p. 124	aromatic stretch larger than unmodified XAD-4
	747	ortho-disubstituted phenyl	[38], p. 197	
13d	1420, 1370 1245, 1116, 1055		[36], Volume 2, p. 650	peaks similar to thiol **13** no thiol peaks visible
	652	C-S stretch	[38], p. 217	
14a	3500, 3397	N-H stretches of primary amine	[37] p. 123	
	1587, 1550, 1361, 1342	peaks due to the pyrimidine ring stretching	[38] p. 221	
15e	3380, 1644		[36], Volume 2, p. 628	may have had some **15** physically embedded, since peaks due to the starting material were prominent
	1539, 1349, 1275, 1094, 1065	triazole and amine functionalities	[38], p. 221	

Figure 4.3b shows the spectra of XAD-4 and resins modified with the sulfonate-thiols **3**, **4**, and **5**. The conversion for each resin (all prepared in water) was 36%, 36%, and 28%, respectively. All three spectra have peaks due to the sulfonate groups (table 4.8).

Figure 4.3c shows the spectra of XAD-4 and resins modified with thiols **6**, **7**, and **8**. The conversion for each resin (all prepared in toluene) was 70%, 76%, and 59%, respectively. The spectra have peaks due to the functional groups (table 4.8). A thiol peak was not visible for resin **7a**. The spectrum for resin **8a**, modified with the diol, is similar to that of resin **7a**, with more prominent peaks due to the diol. The peaks are similar to that of the analogous model compound 3-ethylthio-1,2-propanediol [36].

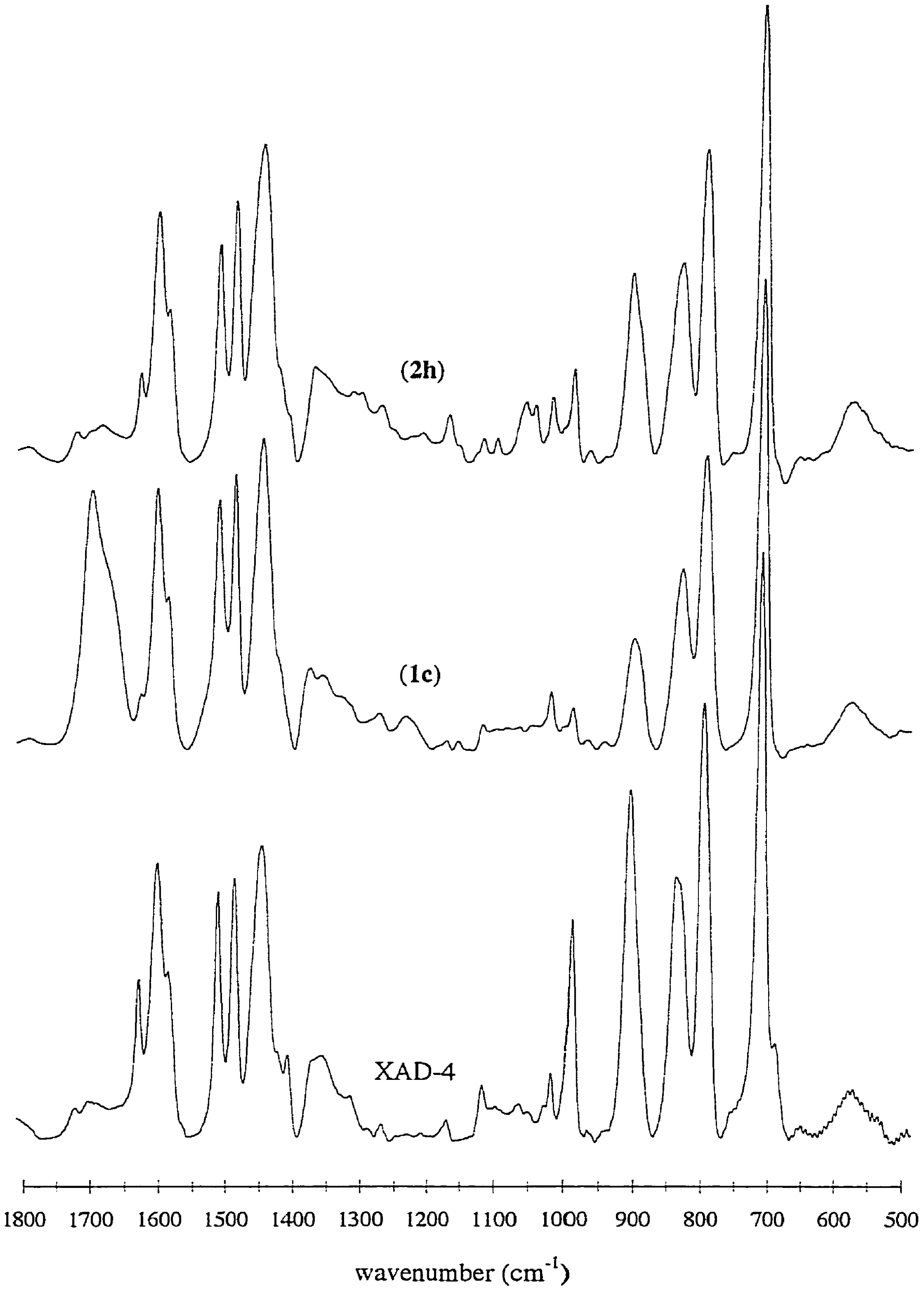


Fig. 4.3a. FTIR absorbance spectra of XAD-4 and thiol-modified resins (**1**-**2**).

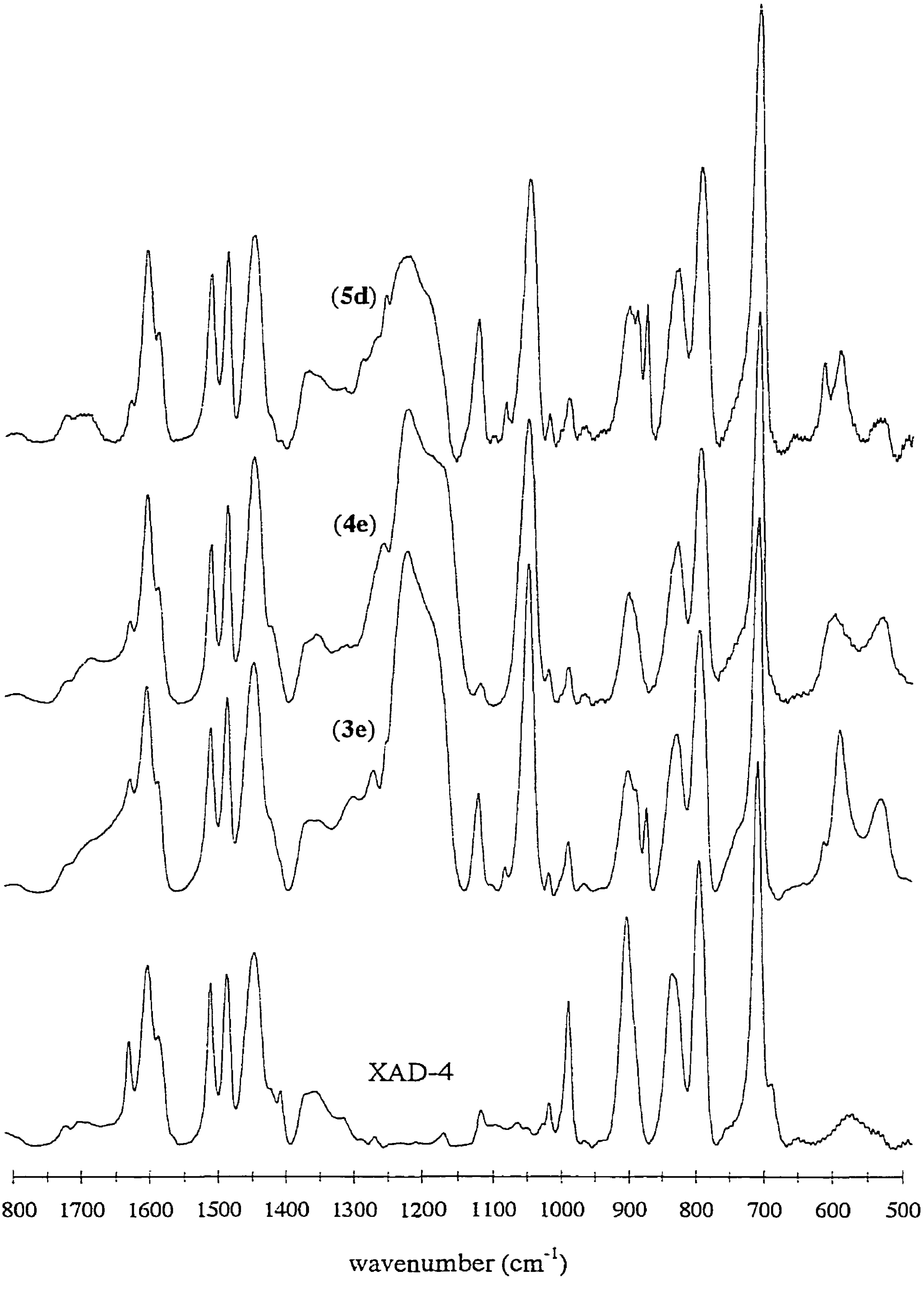


Fig. 4.3b. FTIR absorbance spectra of XAD-4 and thiol-modified resins (**3**-**5**).

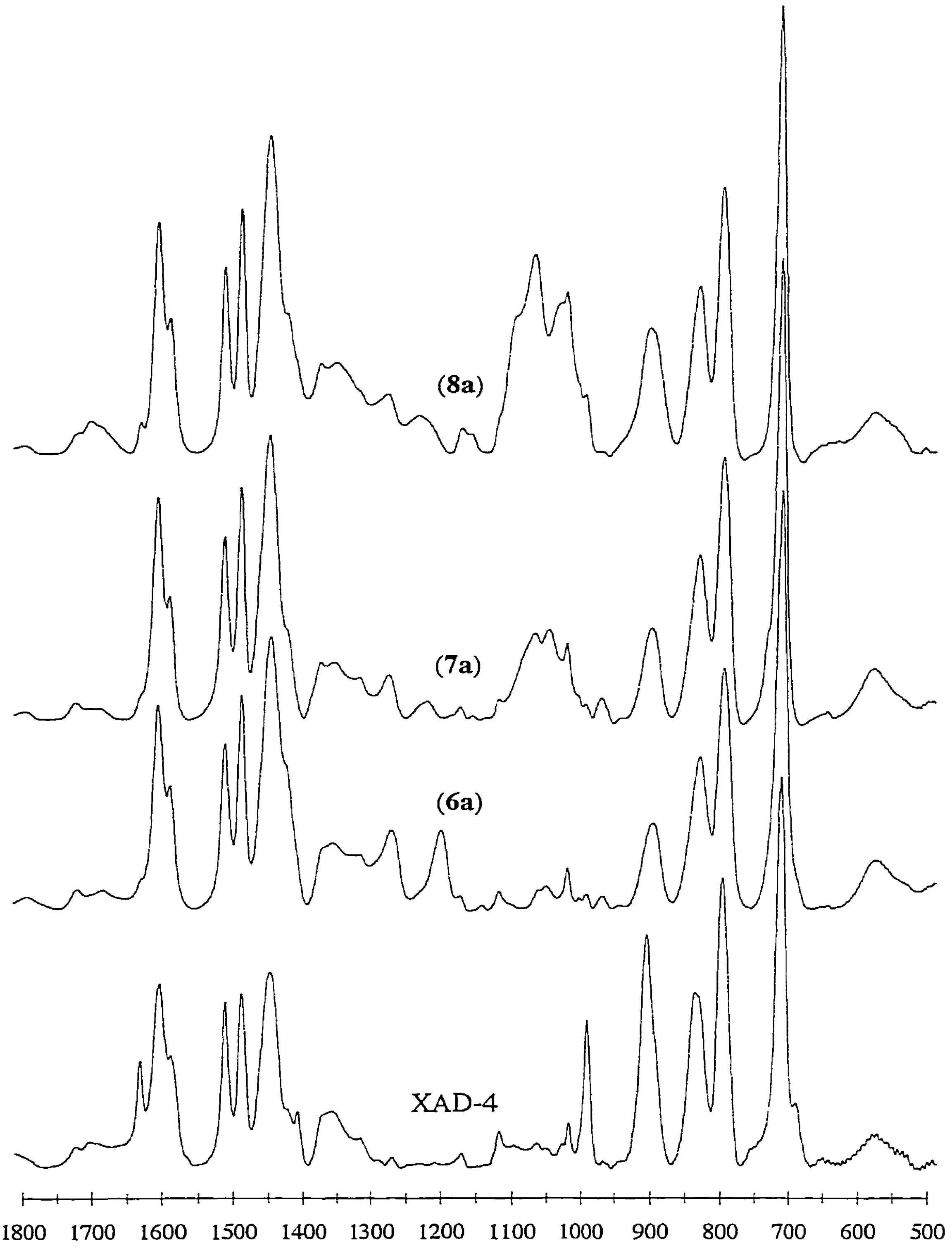


Fig. 4.3c. FTIR absorbance spectra of XAD-4 and thiol-modified resins (**6-8**).

Figure 4.3d shows the spectra of XAD-4 and resins modified with thiols **9**, **10**, and **11**. The conversion for each resin was 66%, 43%, and 20%, respectively. The spectrum for resin **9a** has peaks which are similar to that of the model compound 2-(methylthio)ethanol [36] and of resin **8a**. Resin **10b** has very strong peaks due to the two carboxylic acids per functional group and resin **11a** has peaks due to its three esters per functional group (table 4.8).

Figure 4.3e shows the spectra of XAD-4 and resins modified with thiols **12**, **13**, **14** and **15**. The conversion for each resin was 45%, 66%, 9.3% and 39%, respectively. The spectrum for resin **12a** has peaks which are similar to that of the model compound 2-(methylmercapto)aniline [36]. Resin **13d** had no thiol peaks visible in its spectrum, but has other peaks that are similar to some of those of the starting thiol **13** [36]. The spectrum of resin **14a** has peaks due to the pyrimidine ring stretching [38]. Resin **15e** may have had some thiol physically embedded, since peaks due to thiol **15** were prominent at 3380 and 1644 cm^{-1} (in comparison to the spectrum of thiol **15**, [36]). Other peaks which are present can be attributed to the triazole and amine functionalities [38].

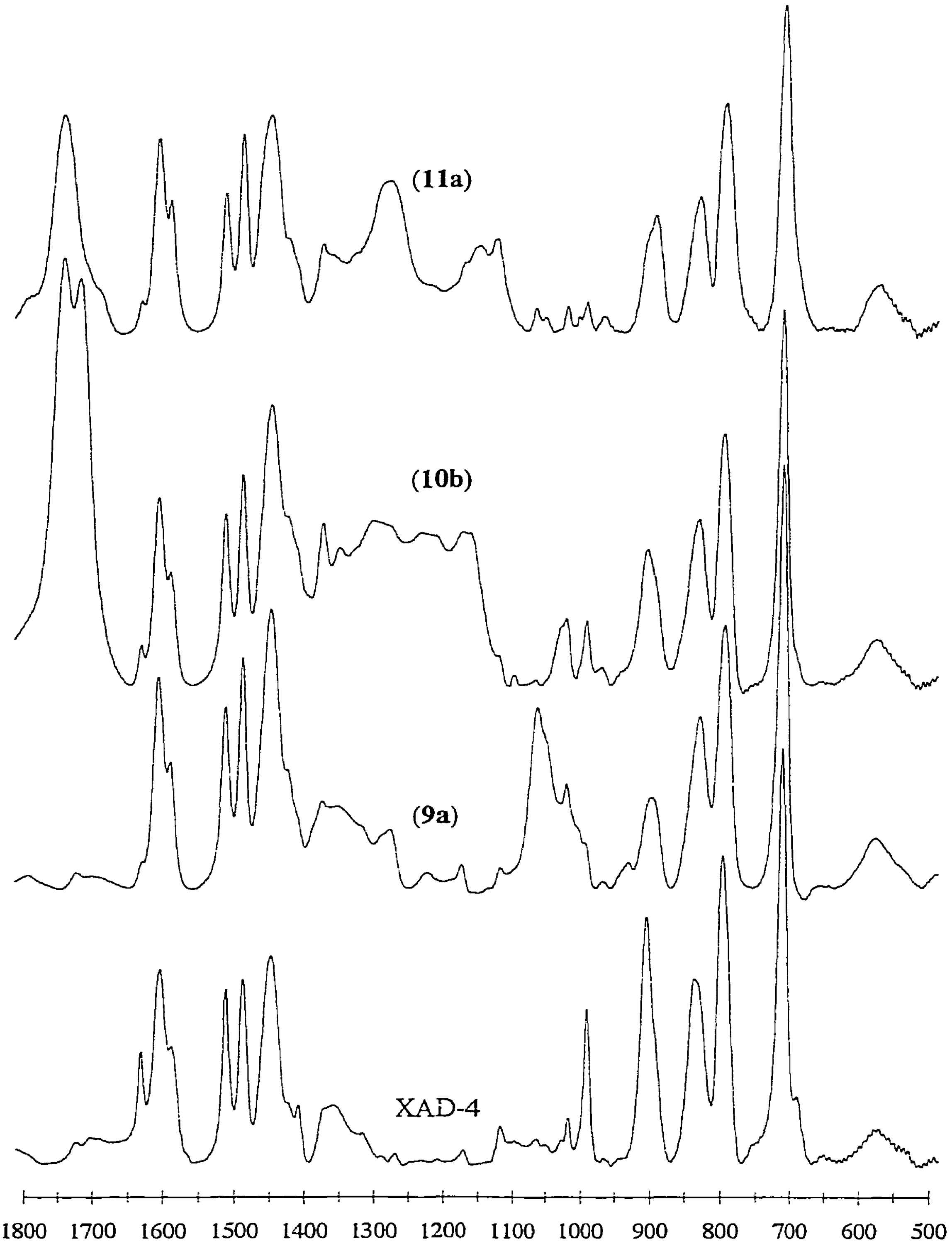


Fig. 4.3d. FTIR absorbance spectra of XAD-4 and thiol-modified resins (**9-11**).

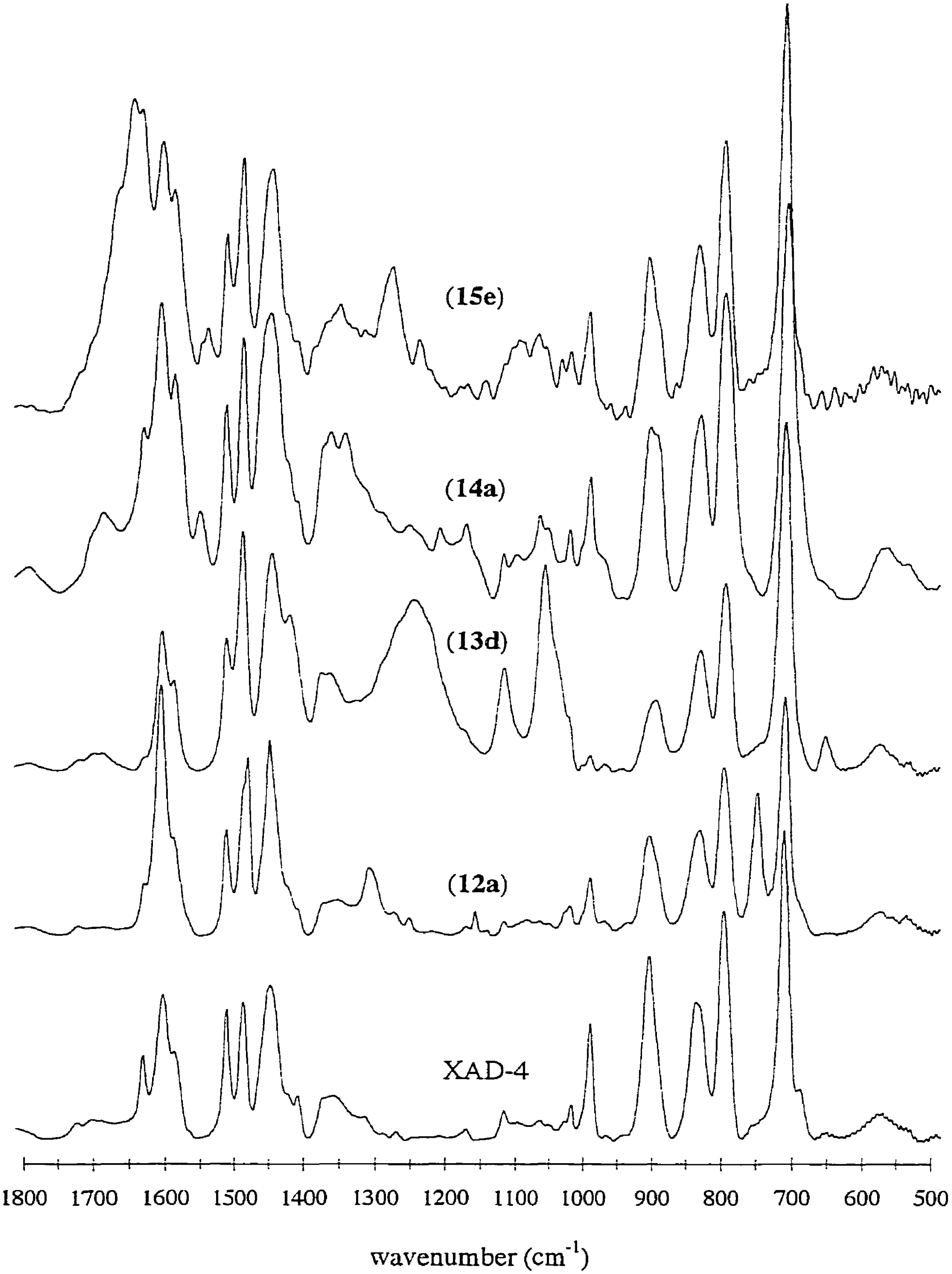


Fig. 4.3e. FTIR absorbance spectra of XAD-4 and thiol-modified resins (**12-15**).

4.3.4.2 Raman spectroscopy

Figures 4.4a to 4.4e compare the Raman spectra of XAD-4 and the thiol-modified resins. The resins used were the same as for the previous section. In most cases, the resin used in the modification was XAD-4. The Raman spectral peaks have previously been assigned for unmodified XAD-4 [2].

As for the infrared spectra, the decrease of vinyl peaks was notable for all spectra. These peaks included 3008, 1632, 1409, and 1209 cm^{-1} [2]. An increase of peak 2910 cm^{-1} was seen for resins modified with aliphatic groups. Raman spectroscopy was most useful in determination of the presence of thiols, and to verify infrared spectral data.

Figure 4.4a compares the spectra of XAD-4 and resins modified with thiols **1** and **2**. A weak peak which may be due to the C-S stretch is visible at 531 cm^{-1} [38, p. 181] for resins **1c** and **2h**. Resin **2h** also has a peak at 2778 cm^{-1} due to the $-NMe_2H^+Cl^-$ [38].

Figure 4.4b compares the spectra of XAD-4 with those of the resins modified with the sulfonate-thiols, **3**, **4**, and **5**. Weak peaks around 530 cm^{-1} may be due to C-S stretches. Resin **5d** has a very weak peak at 2577 cm^{-1}, indicating the presence of a thiol [38].

Figure 4.4c shows the spectra of XAD-4 and resins modified with dithiols **6** and **7**, and thio-diol **8**. The spectrum for resin **6a** has a peak due to the thiol at 2569 cm^{-1} and a C-S stretch at 750 cm^{-1}. These are comparable to some of the Raman peak assignments for the starting thiol: 2560 and 750 cm^{-1} [31]. Resin **7a** also had peaks due to the thiol (S-H) and C-S at 2570 and 735 cm^{-1}, respectively. No thiol peaks were evident for resin **8a**, which would be expected since the starting thiol was not a dithiol, but a diol.

No thiol peaks could be seen in the spectra of resins **9a**, **10b** or **11a** (figure 4.4d). A small peak due to the C=O stretch of the carboxylic acid groups in resin **10b** is seen at 1704 cm^{-1} and the C-S stretch is seen at 545 cm^{-1} [38]. A small peak due to the C=O stretch of the ester groups in resin **11a** is seen at 1790 cm^{-1}, C-S stretches are seen at 591 and 536 cm^{-1} and a peak at 407 cm^{-1} may be due to an S-S stretch [38]. The formation of disulfides of the thiol groups in the 1- and 2-positions of thiol **11** may have occurred.

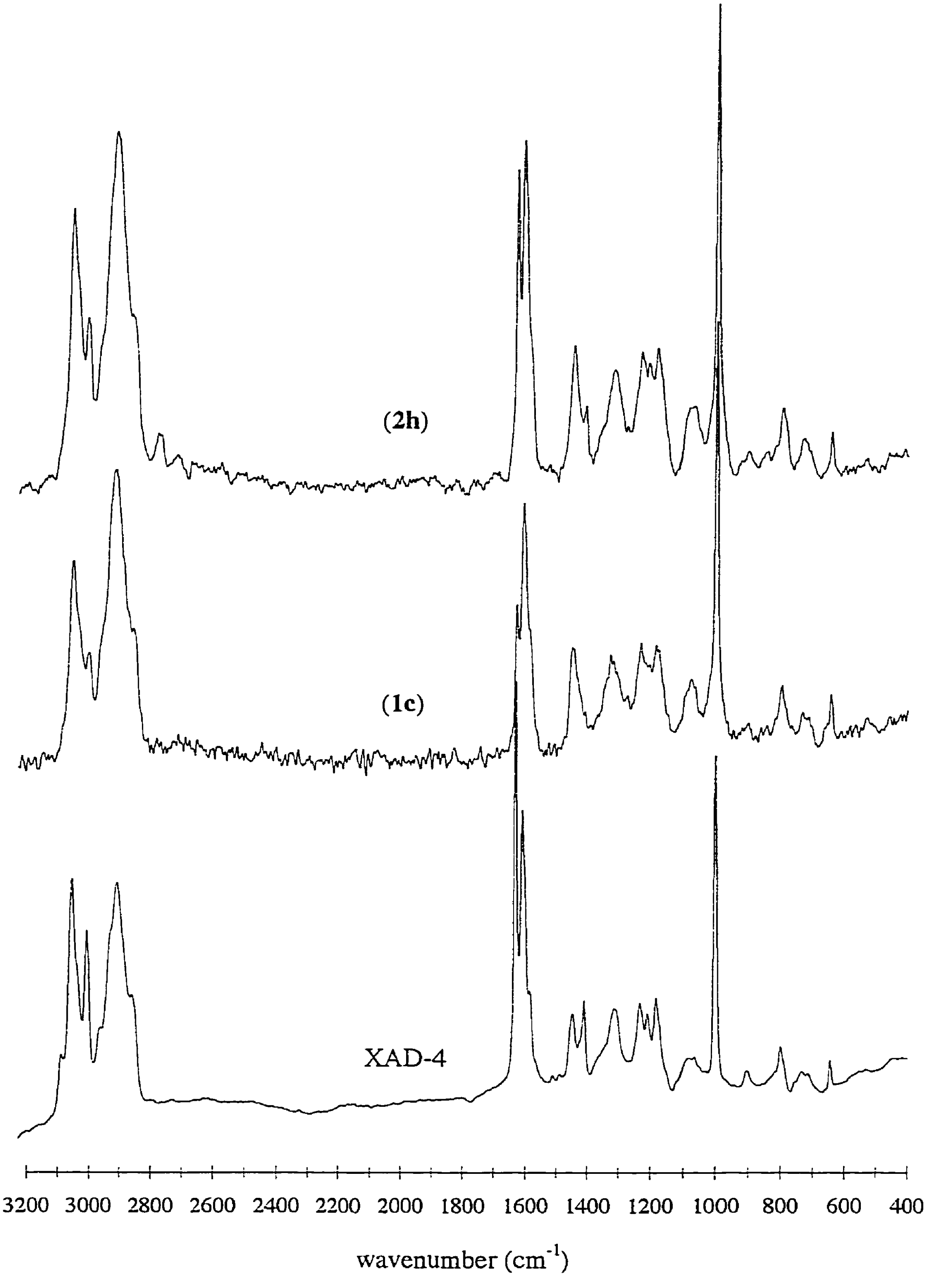


Fig. 4.4a. Raman spectra of XAD-4 and thiol-modified resins (**1**-**2**).

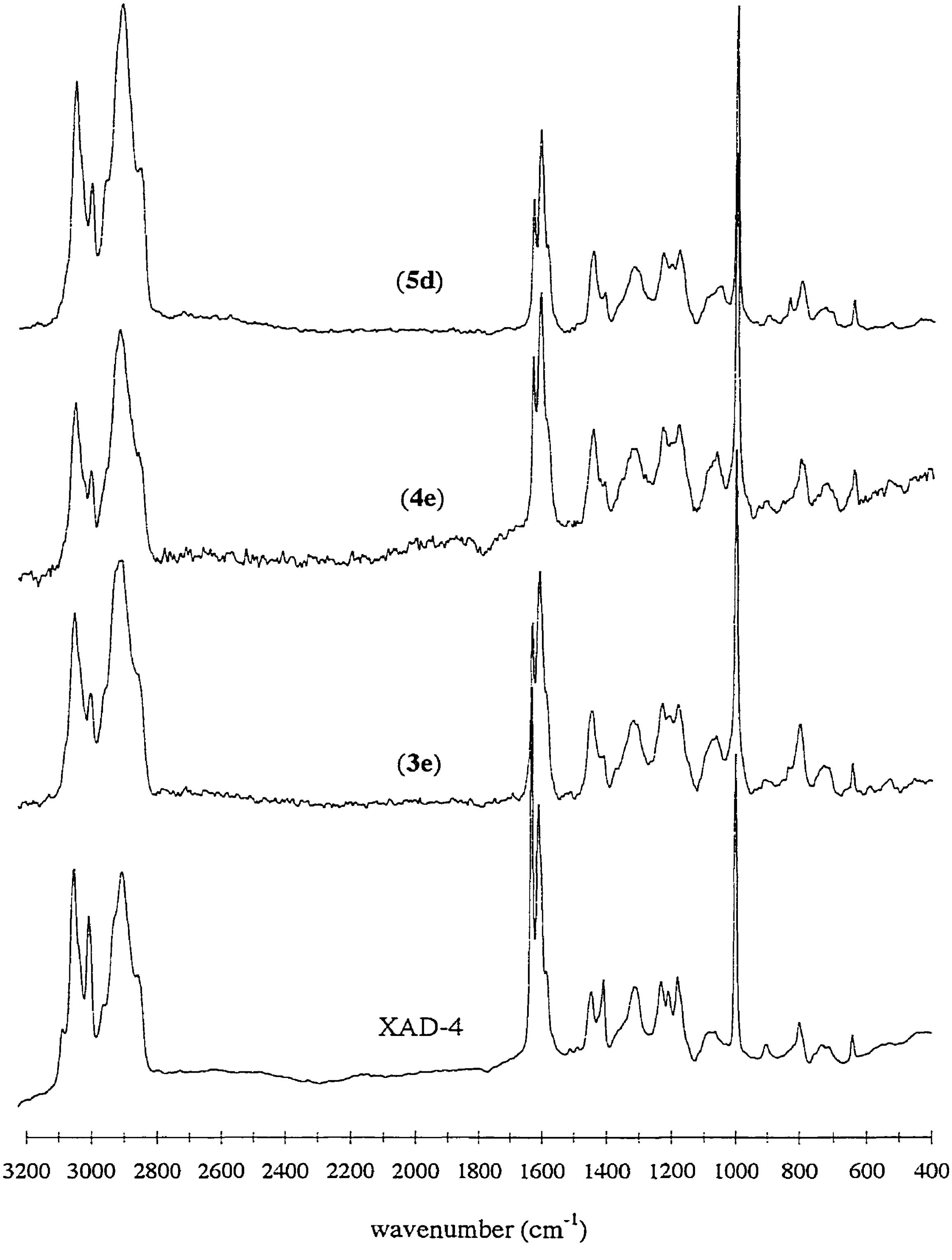


Fig. 4.4b. Raman spectra of XAD-4 and thiol-modified resins (**3**-**5**).

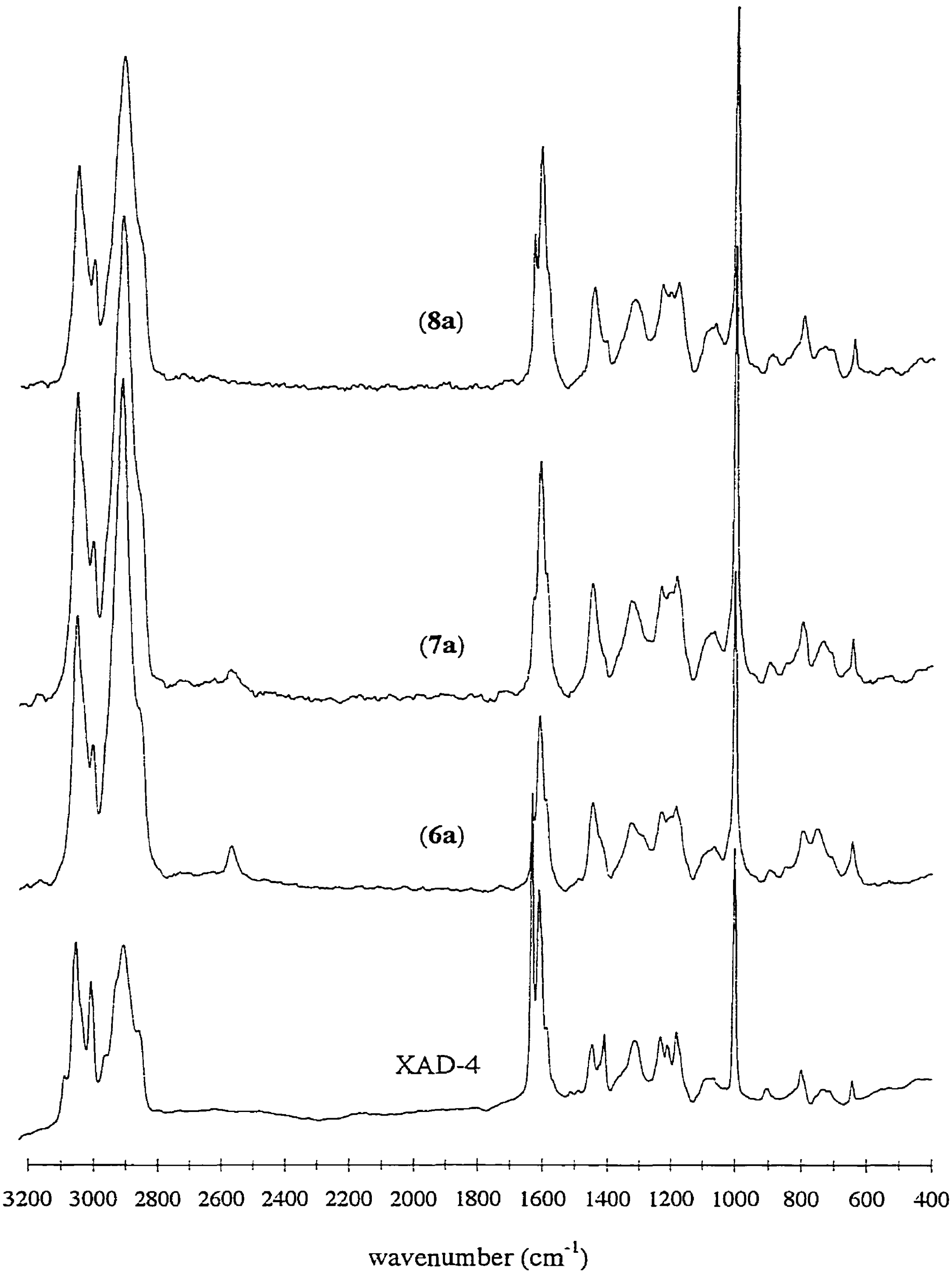


Fig. 4.4c. Raman spectra of XAD-4 and thiol-modified resins (**6**-**8**).

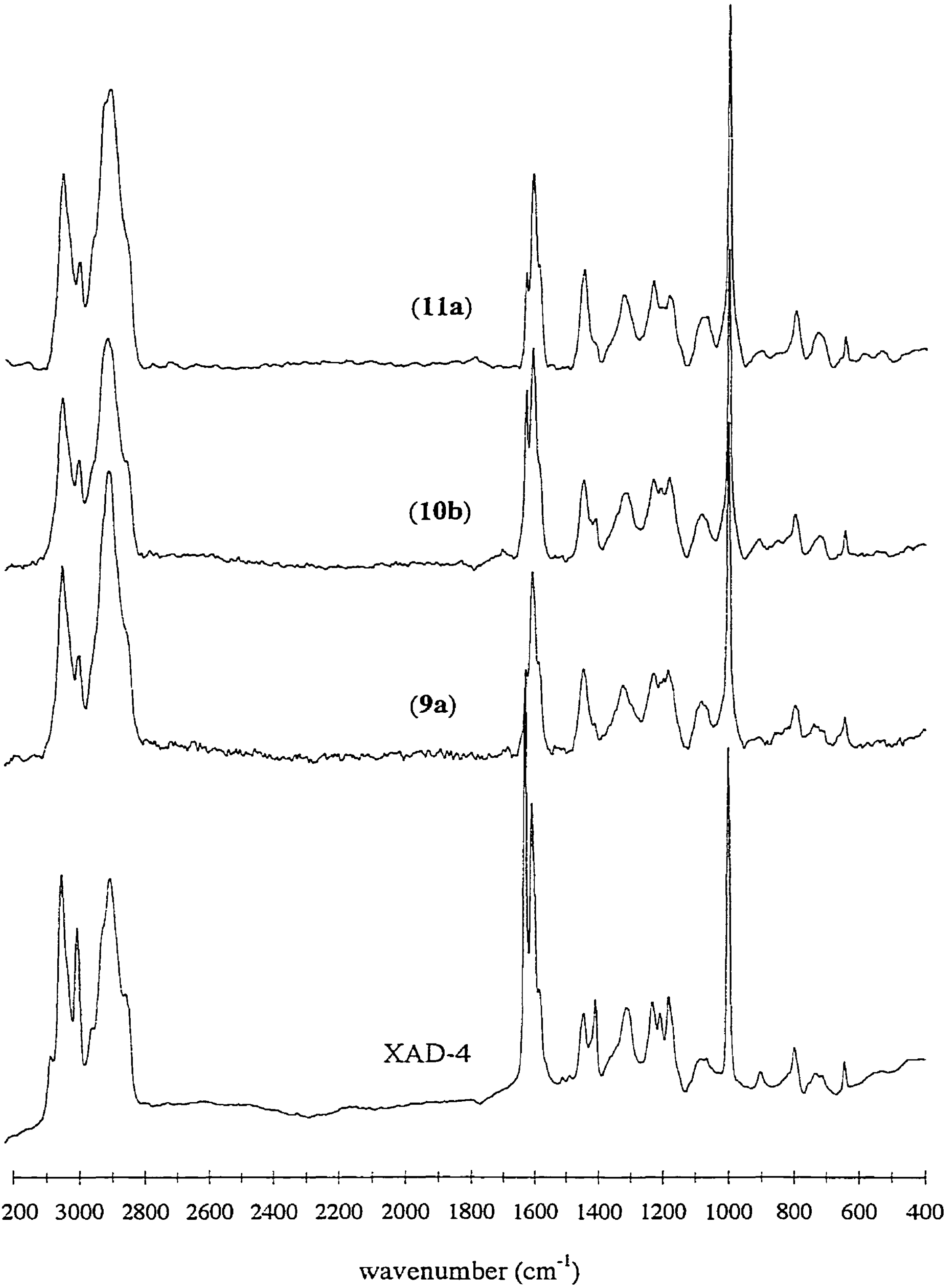


Fig. 4.4d. Raman spectra of XAD-4 and thiol-modified resins (**9-11**).

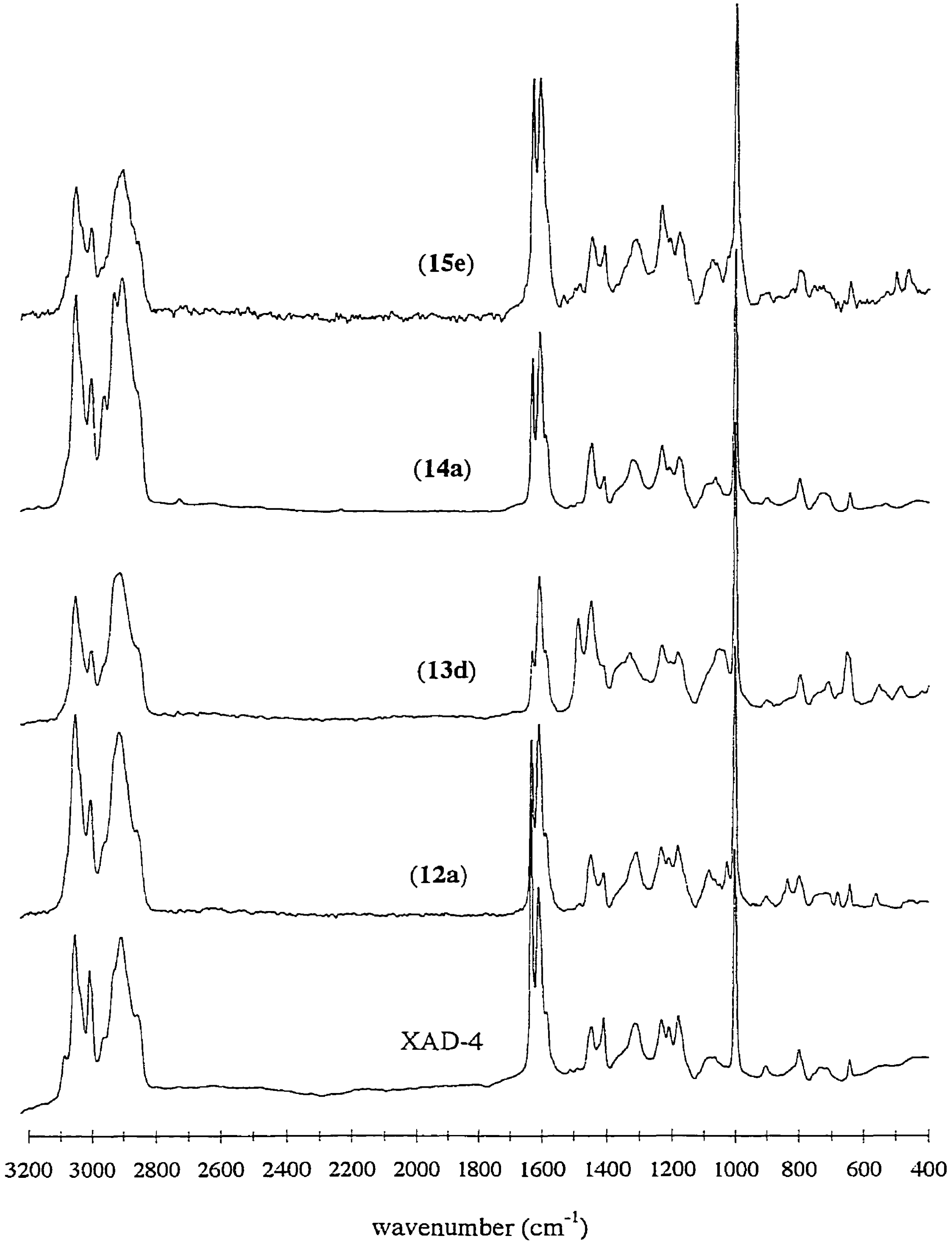


Fig. 4.4e. Raman spectra of XAD-4 and thiol-modified resins (**12**-**15**).

Figure 4.4e gives the spectra of XAD-4 and resins **12a**, **13d**, **14a** and **15e**. The spectrum of resin **12a** has a slightly larger peak (due to C-H stretches of the benzene rings) at 3055 cm^{-1} than for XAD-4. Peaks attributed to the functional group include 1085, 1027, 836, and 681 cm^{-1} [31]. A C-S stretch is seen at 562 cm^{-1} [38]. No thiol peaks are evident for resin **13d**, the functional group may be in the thione-form. New peaks due to the functional group in **13d** are seen at 1487, 712, 653, 553, 486, 393, and 317 cm^{-1} [31]. The spectrum for **14a** has a new peak at 2933 cm^{-1} likely due to the amine (N-H stretch) or pyrimidine. The spectrum for **15e** has two C-S stretches at 501 and 466 cm^{-1}.

4.3.4.3 ^{13}C NMR spectroscopy

Figure 4.5a shows the solid-phase ^{13}C CP-MAS NMR spectra and figure 4.5b shows the solid-phase ^{13}C CP-MAS-DD NMR spectra for XAD-4 and the resins modified with thiols **5**, **6**, **7**, **8**, and **10**. For all cases, XAD-4 was used in the modification.

The ^{13}C NMR spectral peaks have previously been assigned for unmodified XAD-4 [2]. Table 4.9 gives the ^{13}C CP-MAS-DD NMR spectral peak assignments for modified XAD-4 and for the starting thiols or analogous model compounds [22, 39]. Dipolar dephasing eliminates the peaks due to the vinyl carbons, the dimethylene spacer linking the thioether to the resin, and the polymer backbone (CH_2, CH, phenyl CH) [26]. The peak at 144 ppm corresponds to the (non-hydrogen) substituted phenyl carbons and the peak at 15-16 ppm corresponds to the methyl carbon of the pendant ethylbenzene groups [26].

The NMR spectra of the modified resins are similar to those of modified polyDVB-55 [26]. As for the infrared and Raman spectra, the intensities of the peaks due to the vinyl group are less in the modified resins (137 and 114 ppm, figure 4.5a). The dipolar-dephased spectra (figure 4.5b) show some of the functional group carbon peaks clearly. For resin **5d**, the peak at 68 ppm is due to the methylene carbon next to the sulfonate group, and the peak at 30 ppm is due to the methylene carbon next to the thioether.

For resin **6a**, the peaks correspond to the carbons in the order of the following structure, XAD-4–S-CH_2CH_2-S-CH_2CH_2-SH, at 32, 25, 25, and 36 ppm.

Table 4.9. ^{13}C CP-MAS-DD NMR peak assignments for thiol-modified XAD-4

Thiol Used	Thiol ^{13}C NMR peak assignments (a)	C (ppm)	CH_3 (ppm)	CH_2 (ppm)
5	–	144	15	68, 30
6	36.26, 34.31, 31.71, 24.75, 15.56* (b)	144	15	36, 32, 25
7	65.34, 45.00*, 29.46 (c)	144	15	66, 30
8	70.54*, 65.37, 35.09, 26.38, 14.79* (d)	144	15	72, 66, 36, 30
10	173.32, 171.60, 39.52, 35.48* (e)	178, 172, 144	15	29

(a) Data from [39], unless otherwise noted, * means odd parity (i.e. CH, CH_3).
(b) $CH_3SCH_2CH_2SCH_2CH_2SH$, [22].
(c) 2,3-Dimercapto-1-propanol, [39, Vol. 1, p. 423].
(d) 3-Ethylthio-1,2-propanediol, [39, Vol. 1, p. 445].
(e) Mercaptosuccinic acid, [39, Vol. 1, p. 819].

The peaks of resin **7a** correspond to the C-OH group (65 ppm), and a broad peak between 25 ppm and 50 ppm may be due to the two other carbons in the group. As with thiol **5**, there were two thiol groups in **7**, and either could have acted as a point of attachment to the resin. Unfortunately, we were unable to determine which linked the functional group to the resin, and a mixture of functionalities is possible. ^1H NMR spectroscopy could help to determine this, but we were not able to perform this experiment since the resins are insoluble. Comparison of the spectra to that of resin **8a** did not aid in solving this question.

The resin modified with the thio-diol, **8a**, had peaks corresponding to the carbons in the structure, XAD-4–S-$CH_2CH(OH)CH_2OH$, at 36, 72, and 66 ppm. The peak at 30 ppm may have been due to the methylene (of the former vinylbenzene) attached to the thioether or to the pendant ethylbenzene units.

For the resin modified with the thio-dicarboxylic acid, **10b**, the peaks at 178 ppm and 172 ppm are due to the carboxylic acid carbons, and the peak at 29 ppm is likely due to the methylene carbon in the functional group.

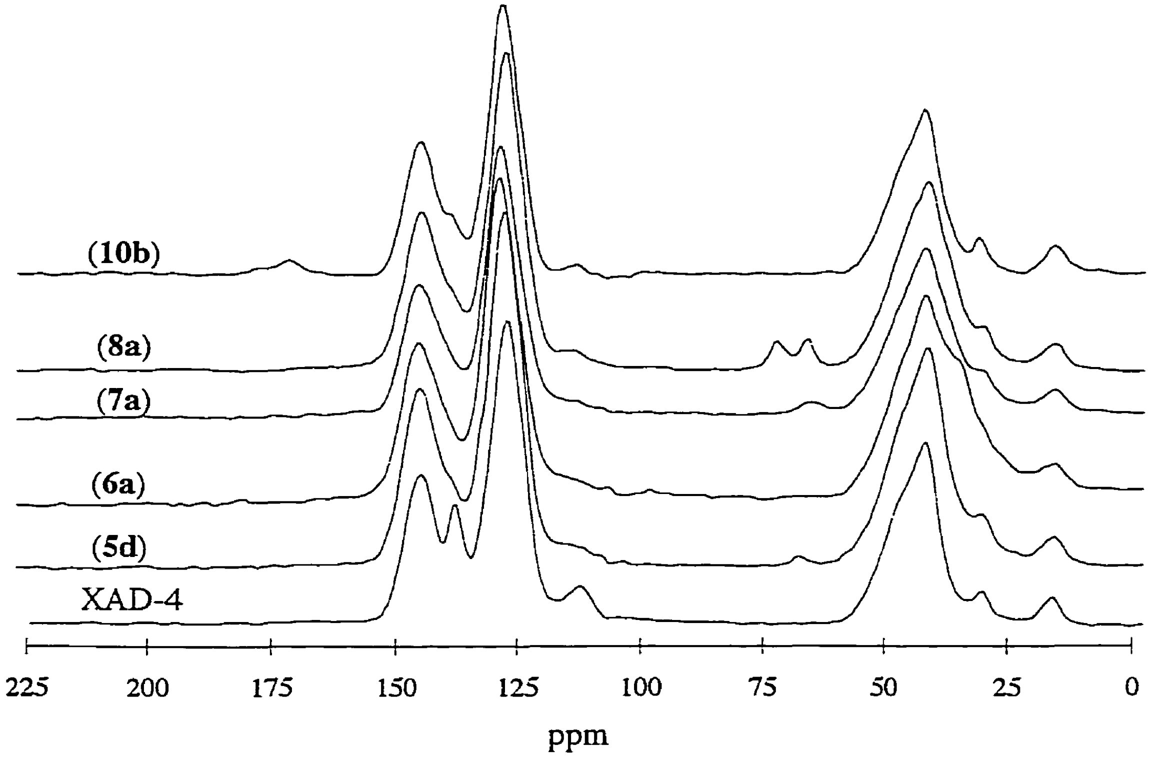


Fig. 4.5a. ^{13}C CP-MAS NMR spectra of XAD-4 and thiol-modified XAD-4.

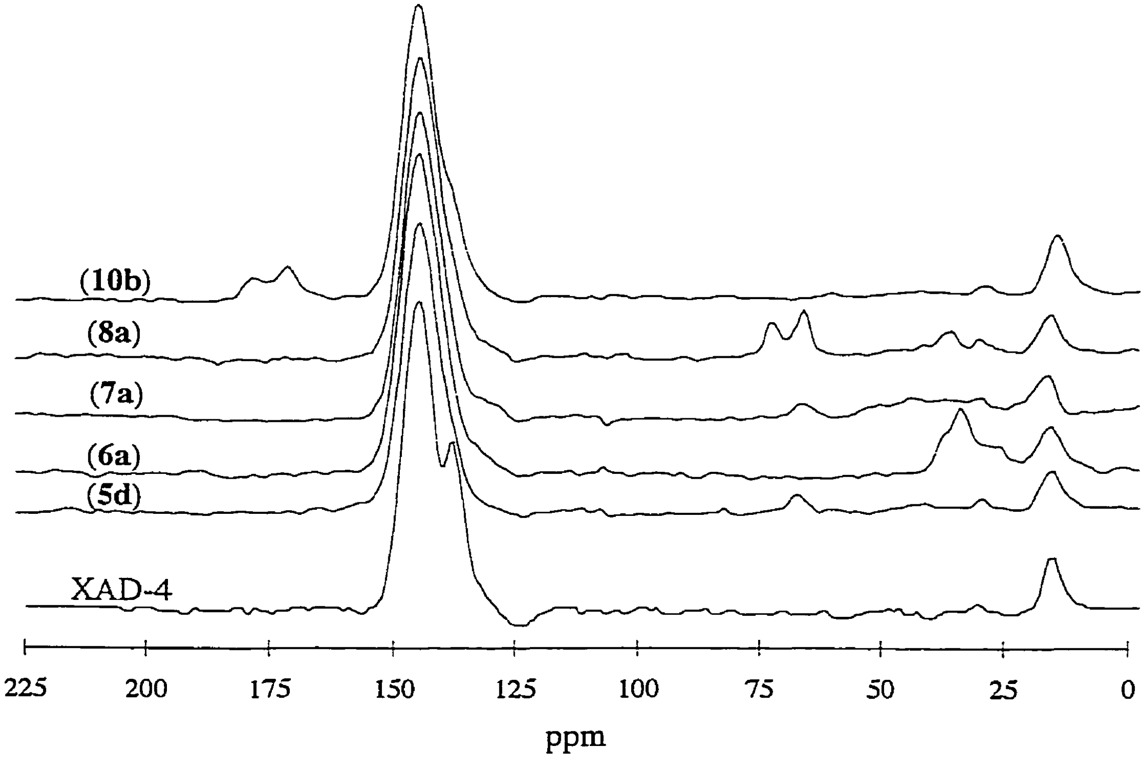


Fig. 4.5b. ^{13}C CP-MAS-DD NMR spectra of XAD-4 and thiol-modified XAD-4.

4.3.5 Potential applications of thiol-modified resins

We have prepared resins which may have potential applications as ion-exchangers, coordinating resins, solid-phase protecting groups and adsorbents. Modification can change properties of the resins, such as hydrophilicity, which may change behaviour in separation applications such as chromatography [1]. XAD-4 was previously modified for these applications using traditional methodologies, such as chloromethylation with subsequent reactions [40]. No one has previously modified the vinylbenzene groups of XAD-4 to change its sorption properties.

We modified XAD-4 with some thiols used by other researchers in the modification of different types of polymers. Like thiol **17**, thiol **13** exists as a tautomer, having four forms [24, 41]. However, unlike thiol **17**, modification was successful when **13** was used (**13d**, 66% conversion using XAD-4 and dioxane, PEG-600, table 4.5). Three of the tautomers have at least one thiol present. It is known that **13** adds to a variety of alkenes, including styrene [42]. As mentioned in the introduction, this thiol has been used in the modification of PVC [24]. The yield for the functional polymer was 3.6 mmol SR/g; compared to 1.6 mmol SR/g for our resin. Since PVC has one chlorine atom per repeat unit, a higher quantity of functional groups would be possible. However, only one-third of the chlorine atoms were substituted by the thiol, giving a conversion (and degree of functionalization) of 33%. Side-reactions also occurred, such as cross-linking and dehydrochlorination. XAD-4 initially had 41% of the repeat units having a vinyl group (X_{VB}), $X_{2\text{-}SR}$ was 27%, and the conversion was 66%. Overall, the degrees of functionalization (33% for theirs and 27% for ours) are similar, with a higher conversion in our case. The advantages of using XAD-4 over PVC are that the reaction does not leave any reactive precursor functional group (such as alkyl chloride), and XAD-4, being a cross-linked styrenic resin, has a more appropriate morphology for engineering applications.

A similar thiol, 1,3,4-thiadiazole-2-amino-5-thiol, was used by others to modify chloromethylated polystyrene with a 77% degree of functionalization (83% conversion) and 16% of the chloromethyl groups remaining unreacted [25, 43]. Although we did not use this thiol, it would be possible to modify XAD-4 with it using our methodology. Resins modified with **13** and 1,3,4-thiadiazole-2-amino-5-thiol have been used as coordinating resins for selective metal uptake, including for precious metals (gold, silver and platinum-group) [24, 25, 43].

Some of the resins may be used for solid-phase protecting groups, such as those modified with thiols **7** (thiol-alcohol group) and **8** (1,2-diol group). Since the introduction is one-step, the presence of other functionalities is prevented in general. However, since **7** has two thiol groups, modification may have occurred through either thiol. We were unable to determine spectroscopically which thiol was converted to the thio-ether linkage.

Resins modified with some of the thiols can be used as ion-exchangers. Weak acid exchangers with carboxylate groups (i.e. XAD-4 modified with **10**) may be advantageous over the traditional acrylic acid polymers in their structural features and integrity. Stronger-acid functionalities, such as sulfonates (**3**, **4**, **5**), can also be added to XAD-4 using our methodology. These resins may have different behaviors than the traditional sulfonated polystyrenes. Many of the resins prepared can act as weak-base resins due to the presence of amines, and with further modification as strong-base resins. Thiols used which introduced amine groups include **1**, **2**, **12**, **14**, and **15**.

The preparation of resins with free thiol groups is also desired. They can act as redox polymers and are excellent for mercury removal [44-46]. Preparations of thiol-containing resins have been multi-step, involving laborious conditions. We were able to prepare thiol-containing resins by the use of the one-step addition of compounds having more than one thiol group to the vinyl groups of resins. These thiols included **5**, **6**, **7**, **11**, and **13**. Some of these were multi-functional and were attached through spacers to the resin. Resins modified with thiol **11** have two thioglycolate functionalities per functional group added, the third being used in attachment to the resin. Resin **11a** had 0.29 mmol SR/g, with a maximum of 0.58 mmol thioglycolate groups per gram, with $X_{2\text{-SR}}$ 4.3% and a conversion of 20% (prepared using polyDVB-55). This one-step modification to introduce thioglycolate functionalities is advantageous over the tedious three-step modification of XAD-4 to introduce the same type of functionality done by other researchers [47]. Their resin was able to extract various metal ions (silver, gold, mercury, bismuth, tin, antimony, lead and uranium) from acidic solutions. Our preparative method eliminated the risk of introduction of other functionalities, and also introduced a larger spacer group. Modification of XAD-4 with our procedure will most likely lead to higher conversions than for the resins prepared with lab-made polyDVB-55 (L1).

The choice of thiols to attach to the resin depends on the intended application. For the development of coordinating or ion exchange resins, potential ligands could be pre-screened using titration techniques [48]. In order to properly gauge a ligand's behaviour, models which emulate how the ligand is attached to the resin should be studied. For example, thioethers of the thiols should also be studied since the coordinating ability of a thioether is much less than a thiol. We have studied the interactions with various base metals of some of the ligands used in this paper [48]. Two model compounds studied were 2-(ethylthio)ethylamine hydrochloride and 2-(methylmercapto)-aniline which were equivalent to thiols **1** and **12**. The models showed little metal-complexing ability compared to the thiols.

4.4. Conclusions

Amberlite XAD-4, a commercially-available styrenic copolymer, is the best choice of resin for the preparation of functional resins by modification to the accessible pendant vinylbenzene groups based on its high surface area, porosity, and vinyl group content. We have demonstrated that the anti-Markovnikov addition of a wide-range of thiols can lead to a great number of functionalized resins, using a simple one-step reaction. Conversions were as high as 76%, and degrees of functionalization were as high as 27%. The most important variables for high conversions of the vinyl groups are the solubility of the thiol in an appropriate solvent, the thiol's chain transfer constant, and the use of commercial resin. Further work with regard to expanding the choice of solvents and thiols is encouraged. We have shown that water can be used for many reactions. As we have shown for one thiol, ethanol can also be used successfully. Ethanol, 2-propanol, and methanol, should also be tried with more thiols.

4.5. Acknowledgements

We wish to thank Rohm and Haas Company for donation of 5 kg of Amberlite XAD-4, and for providing some literature cited in this paper. ^{13}C NMR spectra were taken by Dr. F.G. Morin of the Department of Chemistry, McGill University. Samples for X-ray microprobe analysis were prepared by G. Panagiotidis and analysis was done by G. Poirier, both of the Department of Earth and Planetary Sciences, McGill University. Surface areas and pore sizes were measured by the lab group of Dr. J. Zhu, University of Montreal. Elemental analyses were performed in part by M. Soon, Department of Oceanography, University of British Columbia. Some repeats of preparations and sulfur analyses were done by J. Dracopoulos. Some of the infrared spectra were taken by M. Ruzicka, K. Schantz and N. Walicki. Thanks also go to Dr. R.B. Lennox, Dr. D.N. Harpp, and Dr. D.S. Argyropoulos for helpful discussion. Funding for this project was provided by a Natural Sciences and Engineering Research Council of Canada Strategic Grant and MEND (Mine Environment Neutral Drainage) grant (Government of Canada).

4.6. References

[1] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted April 1997. Chapter 2 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[2] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted April 1997. Chapter 3 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[3] R. Kunin, Amberhilites (produced by Rohm and Haas Co.), Number 161 (spring 1979).

[4] R. Kunin, Amberhilites (produced by Rohm and Haas Co.), Number 163 (winter 1980).

[5] E.F. Meitzner and J.A. Oline, U.S. Patent 4,382,124, issued May 3, 1983.

[6] Food and Drug Administration, U.S. Government, 173.65, page 100 in "Code of Federal Regulations", 21, Food and Drugs. Parts 170 to 199, revised April 1, 1994.

[7] R.L. Albright, React. Polym., 4 (1986), 155.

[8] Supelco Product Catalogue, 1995, page 264.

[9] N.A. de Munck, M.W. Verbruggen and J.J.F. Scholten, J. Mol. Catal., 10 (1981), 313.

[10] J.P.C. Bootsma, B. Eling and G. Challa, React. Polym., 3 (1984), 17.

[11] M Periyasamy, W.T. Ford and F.J. McEnroe, J. Polym. Sci., Polym. Chem. Ed., 27 (1989), 2357.

[12] M.C. Faber, H.J. van den Berg, G. Challa and U.K. Pandit, React. Polym., 11 (1989), 117.

[13] Z. Zhengpu, P. Hodge and P.W. Stratford, React. Polym., 15 (1991), 71.

[14] K.H. Eppinger and M.B. Jackson, J. Macromol. Sci., Chem., A14 (1980), 121.

[15] T. Nishikubo, T. Shimokawa and H. Arita, Makromol. Chem., 188 (1987), 2105.

[16] T. Nishikubo, A. Kameyama, M. Sasano and M.A. Sawada, J. Polym. Sci., Polym. Chem. Ed., 31 (1993), 91.

[17] E. Klemm and U. Gorski, Angew. Makromol. Chem., 207 (1993), 187 (in German).

[18] U. Gorski and E. Klemm , Angew. Makromol. Chem., 224 (1995), 125 (in German).

[19] B. Boutevin, E. Fleury, J.P. Parisi and Y. Pietrasana, Makromol. Chem., 190 (1989), 2363 (in French).

[20] B. Boutevin, Y. Hervaud and M. Nouri, Eur. Polym. J., 26 (1990), 877 (in French).

[21] H. Nakamura, T. Takata and T. Endo, Macromolecules, 23 (1990), 3032.

[22] M. Lauth, Y. Frere, B. Meurer and P.H. Gramain, React. Polym., 13 (1990), 63.

[23] J. Chen and R. Xiao, Gaofenzi Tongxun, 6 (1986), 467 (in chinese); Chem. Abstr. 106 (1987), 214796v.

[24] M.J. Hudson and M.J. Shepherd, Hydrometallurgy, 9, (1983), 223.

[25] M.J. Hudson and B. Kar-On Leung, in M.J. Slater (Editor), Ion Exchange Advances. Proceedings of IEX '92. (Papers presented at the SCI Conference IEX '92-Ion Exchange Advances, held at Churchill College, Cambridge, UK, 12-17 July 1992), Elsevier Applied Science, London, 1992, page 398.

[26] J.P. Gao, F.G. Morin and G.D. Darling, Macromolecules, 26 (1993), 1196.

[27] Rohm and Haas Company, "Amberlite XAD-4. Polymeric Adsorbent." product literature, June 1993.

[28] Wako Pure Chemical Industries, Ltd. product information pamphlets: "V-50. 2,2'-azobis(2-amidinopropane) dihydrochloride" and "Azo Polymerizaton Initiators."

[29] B. Budesinsky, Anal. Chem., 37 (1965), 1159.

[30] M. Bartholin, G. Boissier and J. Dubois, Makromol. Chem., 182 (1981), 2075.

[31] D.R. Lide and G.W.A. Milne (Editors), Handbook of Data on Organic Compounds. 3rd Ed. CRC Press, Inc., Boca Raton, 1994. Volume 2, pages 1239, 1807; volume 3, page 2663; and volume 5, pages 4332, 4450, 5023.

[32] J.I.G. Cadogan, S.V. Ley, G. Pattenden, R.A. Raphael and C.W. Rees (Editorial Board), Dictionary of Organic Compounds. 6th Ed. Chapman and Hall, London, 1996. Volume 6, page 6003.

[33] E.M. Smolin and L. Rapoport, The Chemistry of Heterocyclic Compounds. *s*-Triazines and Derivatives. Interscience Publishers Inc., New York, 1959, page 107.

[34] C.P. Reghunadhan Nair, M.C. Richou, P. Chaumont and G. Clouet, Eur. Polym. J., 26 (1990), 811.

[35] J.C. Chudy and J.A.W. Dalziel, J. Inorg. Nucl. Chem., 37 (1975), 2459.

[36] C.J. Pouchert (Editor), The Aldrich Library of FT-IR Spectra, Edition 1. Aldrich Chemical Company, Inc., Milwaukee, 1985. Volume 1, pages 261, 262, 263, 265, 350, 351, 528, 891, 1196; and Volume 2, pages 628, 650, 825.

[37] R.M. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric Identification of Organic Compounds, 5th Edition, John Wiley and Sons, Inc., New York, 1991. pages 110-120, 123-125, 128-130, 158.

[38] J.B. Lambert, H.F. Shurvell, D.A. Lightner and R.G. Cooks, Introduction to Organic Spectroscopy, MacMillan Publishing Co., New York, 1987. pages 169-181, 186-221.

[39] C.J. Pouchert and J. Behnke (Editors), The Aldrich Library of ^{13}C and ^{1}H FT-NMR Spectra, Edition 1. Aldrich Chemical Company, Inc., Milwaukee, 1993. Volume 1, pages 423, 445, 819.

[40] T.A. Armer, Ph.D. Thesis, Tulane University, Diss. Abstr. Int. B 43 (6) (1982), 1910; Chem. Abstr. 98 (1983), 35435w.

[41] M.V. Castano, M.M. Plasencia, A. Macias, J.S. Casas, J. Sordo and E.E. Castellano, J. Chem. Soc., Dalton Trans., (1989), 1409.

[42] E.K. Fields, J. Org. Chem., 21 (1956), 497.

[43] B. Kar-On Leung and M.J. Hudson, Solvent Extr. Ion Exch., 10 (1992), 173.

[44] H.P. Gregor, D. Dolar and G.K. Hoeschele, J. Am. Chem. Soc., 77 (1955), 3675.

[45] C.G. Overberger and A. Lebovits, J. Am. Chem. Soc., 77 (1955), 3675.

[46] R. Bogoczek and E. Kociolek-Balawejder, Przem. Chem., 65 (1986), 368 (in Polish); Chem. Abstr. 106 (1987), 34148b.

[47] R.J. Phillips and J.S. Fritz, Anal. Chem., 50 (1978), 1504.

[48] K.L. Hubbard, G.D. Darling and J.A. Finch, Minerals Eng., 10 (1997), 41.

Chapter 5

Disulfide Addition to the Pendant Vinylbenzene Groups of Commercial poly(Divinylbenzene-*co*-Ethylvinylbenzene). Modification with Alkyl and Aryl Disulfides.

Forward to Chapter 5

The content of the following section is comprised of a paper with the same title which was submitted to the journal Reactive and Functional Polymers (K.L. Hubbard, G.D. Darling and J.A. Finch, submitted May 1997).

Since the previous chapter concluded that the commercial resin has superior qualities over the laboratory-prepared resin, commercial Amberlite XAD-4 was used for the remainder of the work presented in this thesis. Since it was also found that the degree of functionalization depends on the vinylbenzene group content, even with different lots of XAD-4, one lot was used for the remainder of the work performed. Use of a consistent starting polymer matrix allowed comparison of modifications without matrix effects.

The previous chapter focused on the radical addition of thiols to poly(divinylbenzene-*co*-ethylvinylbenzene) to prepare monosubstituted resins in which the functional groups were attached to the resin via a thioether-dimethylene spacer linkage. For the long-term goal of preparing resins which could have applications in separation science, the introduction of vicinal groups which could possibly interact cooperatively with a molecule or ion is desirable. The first group studied was 1,2-dithioether groups, formed by the addition of disulfides to the vinylbenzene groups of the resin. Since this type of reaction has been relatively obscure in the past, simple disulfides were used in this study. A novel polymer modification technique has now been developed, utilizing simple chemistry and reaction conditions. The work presented here is by far the most extensive to date utilizing this chemistry.

Abstract

Poly(divinylbenzene-*co*-ethylvinylbenzene), commercially-available as Amberlite XAD-4, was modified by the iodine-catalyzed addition of disulfides to its pendant vinylbenzene groups. Depending on the disulfide, different solvents were used in order to optimize functionalization. The most important factors for maximum yield were the solubility of the disulfide and the ability to form the sulfuryl-iodide intermediate. The degree of functionalization of modified XAD-4 was as much as 18%, representing a conversion of vinylbenzene groups to (1,2-dithioether-ethyl)benzene functional groups by as much as 55%. Other methods attempted with limited success for disulfide addition included the use of an azo initiator, a photochemical reactor, or boron trifluoride etherate as catalyst.

Keywords: Amberlite XAD-4, pendant vinyl groups, poly(divinylbenzene-*co*-ethylvinylbenzene), disulfide

5.1. Introduction

This paper discusses the modification of vinyl groups in a cross-linked polystyrene-like matrix. Commercial poly(divinylbenzene-*co*-ethylvinylbenzene) was modified by the addition of disulfides to the pendant vinylbenzene groups. Variations of reaction conditions and disulfides used were studied. We also compare these modifications to those done by the radical addition of analogous thiols.

Previously, our group modified laboratory-made poly(divinylbenzene-*co*-ethylvinylbenzene) by the anti-Markovnikov radical addition of a few simple thiols to the pendant vinyl groups [1]. We have recently expanded upon this work to include the use of a commercial resin, Amberlite XAD-4, as well as a greater range of thiols and conditions [2].

5.1.1 Review of poly(divinylbenzene-*co*-ethylvinylbenzene), including XAD-4

Copolymers of divinylbenzene and ethylvinylbenzene have a cross-linked structure with pendant vinylbenzene and ethylbenzene groups (figure 5.1). The degrees of functionalization are indicated by the symbols X_{CL}, X_{VB}, and X_{EB}, (CL for cross-linked, VB for vinylbenzene, and EB for ethylbenzene). The randomly-occurring repeat units are meta- and para-disubstituted.

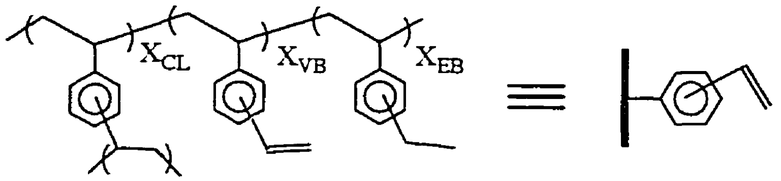


Fig. 5.1. Structure of poly(divinylbenzene-*co*-ethylvinylbenzene).

Amberlite XAD-4 (Rohm and Haas Company) is a macroporous resin prepared from 80 to 85 wt % divinylbenzene and 15 to 20 wt % ethylvinylbenzene [3-9]. Since XAD-4 has a high surface area (725 to 1040 m^2/g) and porosity (0.98 to 1.55 mL/g), vinyl groups should be accessible to modifying reagents, which would tend to promote high conversions to functional groups [3, 4, 9-11]. The vinyl content ranges from 29 to 41% (2.2 to 3.1 mmol/g) depending on lot [4]. Besides ourselves, only five research groups have mentioned the presence of vinyl groups in XAD-4 [11-15], and of these, only two actually modified the resin by reaction with the vinyl functionality [14, 15].

5.1.2 Review of disulfide chemistry, including thermal and radical reactions with alkenes

To our knowledge, no researcher has previously modified polymers by the addition of disulfides to form polymer-bound 1,2-dithioether groups. We will review some chemistry of disulfides and their use in polymer chemistry.

The dihedral angle between the two substituents of the disulfide is normally 90° to minimize electron repulsions of the lone pairs on each sulfur [16]. Cyclic 5-membered ring disulfides have a torsional strain, increasing the reactivity of the disulfide. Since lipoic acid (1,2-dithiolane-3-pentanoic acid) has a dihedral angle of 27°, cleavage of the S-S bond occurs more readily [16]. Disulfides can dissociate homo- and heterolytically, depending on conditions. They react readily with free radicals with homolytic cleavage of the S-S bond [16]. The reactivity depends on the steric bulk of the substituents on the disulfide. The greater the substitution on the α-carbon, the lower the disulfide reactivity. Upon comparison of the reactivity of various disulfides (RSSR) in competition with CCl_4 in reaction with phenyl radicals, the ratio of rates (of reaction of phenyl radical with RSSR to that with CCl_4) has been determined (table 5.1) [16].

Table 5.1. Relative reactivities of disulfides compared to CCl_4 in reaction with phenyl radicals (reproduced from [16])

R of RSSR	Ratio of rate constants with RSSR to CCl_4
$-CH_3$ (methyl)	31
$-CH_2CH_3$ (ethyl)	17
$-CH_2CH_2CH_3$ (*n*-propyl)	16
$-CH(CH_3)_2$ (isopropyl)	3.3
$-C(CH_3)_3$ (*tert*-butyl)	0.23

Disulfides can also be homolytically cleaved by photolysis with wavelengths of light above 230 nm. Shorter wavelengths cause C-S bond cleavage [17].

Radical addition of disulfides to double bonds to produce 1,2-bis-monosulfides (1,2-dithioethers) is possible [18]. For example, *n*-butyl disulfide was reacted with vinyl acetate to produce 1,2-bis(*n*-butylthio)ethyl acetate using photoinitiation [19]. Thiocyanogen, $(SCN)_2$, has been reacted with many alkenes, with products resulting from either addition to the double bond or allylic substitution [19]. Trifluoromethyl disulfide was added to many alkenes using photoinitiation [20]. Disubstitution with ethylene and propene predominated, whereas for fluorinated alkenes, telomers were also formed [20].

5.1.3 Review of reactions of styrene with disulfides

Styrene has been polymerized thermally (130-150 °C) in the presence of *n*-butyl disulfide or diethyl ether disulfide (a cyclic disulfide) [21]. With the use of the cyclic disulfide, copolymerization occurred, incorporating larger amounts of the disulfide into the polymer compared to end-capping of polystyrene with the use of *n*-butyl disulfide [21].

Further studies involving the polymerization of styrene in the presence of various disulfides were done using thermal and photochemical initiations [22]. The disulfides studied were phenyl, benzyl, benzoyl, benzothiazoyl, and various tetra-substituted thiuram disulfides. The thiuram disulfides were the most effective thermal initiators, while all, except for benzyl disulfide, were able to act as photoinitiators.

The chain transfer constants were calculated for many disulfides in the polymerization of styrene [23]. Table 5.2 lists some of the disulfides studied and their chain transfer constants. Aryl disulfides tended to have higher transfer constants than alkyl disulfides. Methyl substitution of these was more effective in the ortho position than the para position. Methyl substitution in both ortho positions further increased the transfer constant. 2-aminophenyl disulfide had the highest constant for the phenyl disulfides, followed by the 2-chloromethyl and 2-bromomethyl-substituted phenyl disulfides.

Table 5.2. Chain transfer constants of disulfides (reproduced in part from [23])

Disulfide	Transfer Constant	Disulfide	Transfer Constant
2-ethyl hexyl disulfide	< 0.005		
phenyl disulfide	0.06	benzyl disulfide	0.03
o-tolyl disulfide	0.23	*p*-tolyl disulfide	0.11
2,6-xylyl disulfide	0.69	2,3,5,6-tetramethyl phenyl disulfide	0.73
2-chloromethyl phenyl disulfide	1.3	2-bromomethyl phenyl disulfide	1.0
2-aminophenyl disulfide	3.0	2-benzothiazyl disulfide	2.1
4-carboxyphenyl disulfide	0.11	4-carboethoxyphenyl disulfide	0.11
4-hydroxymethyl phenyl disulfide	0.09	isopropyl-xanthogen disulfide	5.3

Lipoamide (4-(1,2-dithiolan-3-yl)valeramide), a cyclic disulfide, was successfully copolymerized with styrene [24]. Thermal copolymerization was initiated by the formation of styryl radicals; whereas photopolymerization was initiated by the homolytic ring-opening of the disulfide to form a diradical. The random copolymer had sulfide and disulfide linkages.

Styrene was thermally polymerized in the presence of tetramethylene disulfide, a six-membered cyclic disulfide [25]. A living radical polymerization mechanism was suggested: a styryl radical attacks the disulfide, causing ring-opening and one thiyl radical which can further react with either another disulfide, styrene, styryl radical or polymer chain. The C-S bonds of the polymer could then dissociate, forming more radicals, continuing the process.

Styrene, methyl methacrylate, or ethyl methacrylate were photochemically polymerized in the presence of various disulfides to synthesize macroinitiators for use in the preparation of block copolymers [26]. Some of the disulfides used were phenyl disulfide, 2,4,5-trichlorophenyl disulfide, 2-aminophenyl disulfide, 4-aminophenyl disulfide, 2-nitrophenyl disulfide, and benzyl disulfide. Styrene was the least reactive of the three monomers. The highest yields for the polymerization of styrene with the phenyl disulfides occurred with those having chloro or amino substituents, due to their resonance stabilization of the phenylthiyl radical. Yields were negligible when 2-nitrophenyl disulfide or benzyl disulfide were used with styrene.

Modifications to a cross-linked polystyrene matrix using disulfides has so far been limited to conversion of the 4-bromobenzene functionality to a thioether group [27]. Polystyrene resin was brominated in the para position, lithiated, and then reacted with methyl disulfide to produce 4-(methylmercapto)benzene groups. The resin had 3.56 mmol S/g and was used as a solid-phase reagent in the oxidation of primary and secondary alcohols.

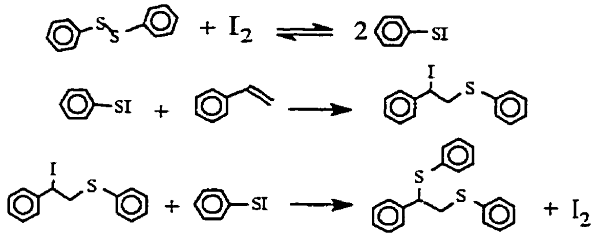
5.1.4 Iodine-catalyzed addition of disulfides to alkenes

Various synthetic methods have been used to convert alkenes to 1,2-disubstituted thioethers using disulfides. Iodine has been used to catalyze the addition of disulfides to styrene since 1938 [28, 29]. Holmberg studied the addition of dithioglycolic acid to styrene using iodine in anhydrous ether [28]. Other disulfides were then used: ethyl dithioglycolate, methyl disulfide, ethyl disulfide, and phenyl disulfide [29]. Solvents used (optional, in order of preference) included absolute (dry) ether, benzene, ordinary ether (trace water present), carbon disulfide, acetone, and acetic acid. Yields for the reaction of styrene with methyl disulfide, ethyl disulfide, and phenyl disulfide were 75%, 90%, and 75%, respectively. Reactions were run at room temperature between 2 and 10 days.

Holmberg's method was also used to modify *n*-butyl vinyl sulfide with *n*-butyl disulfide in 21% yield, and methyl vinyl sulfide with methyl disulfide in 54% yield [30]. No solvents were used and reactions ran for 4 to 5 days at room temperature.

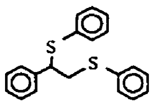
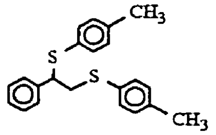
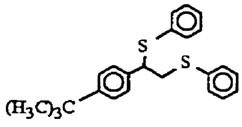
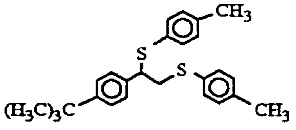
The iodine-catalyzed addition of methyl disulfide to linear alkenes has been used for derivatization purposes [31]. The reaction involved mixing 1 equivalent alkene, 6 equivalents disulfide and 0.05 equivalents iodine for one day at room temperature in a nitrogen atmosphere. When the reaction was run at 80 °C, it was complete after 2 hours, but side-products containing only one methylthio group were also produced.

Styrene and *p-tert*-butylstyrene were reacted with phenyl disulfide and *p*-tolyl disulfide using iodine as the catalyst [32, 33]. The syntheses were done using 1.0 equivalent each of disulfide and styrene, 0.76 equivalents of iodine, anhydrous ether and run for 2 days at room temperature [33]. Mass spectrometry and NMR spectroscopy aided in characterization of products. The proposed reaction pathway is shown in scheme 5.1 [32]. Table 5.3 lists the adducts prepared, their yields, melting points and spectral information [32, 33].



Scheme 5.1. Proposed steps of iodine-catalyzed addition of disulfides to styrene [32].

Table 5.3. Results of iodine-catalyzed addition of aryl disulfides to styrene derivatives (Data taken from [32, 33], published with permission of the authors)

Product	Yield	^{1}H NMR shifts (ppm)	^{13}C NMR shifts (ppm)
 mp 57-58 °C	89%	7.2, 4.3, 3.5	—
 mp 73 °C	99%	7.3-6.9, 4.2, 3.4, 2.31	139.91-127.59, 52.68, 40.14, 21.09, 21.00
 (oil)	99%	7.6-7.1, 4.32, 3.4, 1.28	150.09, 136.28-125.12, 51.91, 39.60, 34.16, 31.16
 (oil)	95%	7.5-6.9, 4.2, 3.35, 2.28, 2.26, 1.28	150.13, 137.25-125.14, 52.38, 40.17, 34.30, 31.25, 20.9

5.1.5 Other catalyzed additions of disulfides to alkenes

Disulfides have also been added to alkenes using boron trifluoride etherate [34]. Methyl disulfide, ethyl disulfide, isopropyl disulfide, *tert*-butyl disulfide and phenyl disulfide were used with a variety of alkenes. With cis- and trans-2-butene, yields were high using methyl disulfide (91-96%), ethyl disulfide (90-92%) and phenyl disulfide (98% with cis-2-butene). Yields were lower with the use of isopropyl disulfide (20% with trans-, 76% with cis-) and no reaction occurred with *tert*-butyl disulfide. The reaction involved mixing 1 equivalent disulfide with 2 equivalents alkene in a dichloromethane-nitromethane solvent mixture (1:1 v/v), cooling to 0 °C, adding 0.08 equivalents (per RSSR) boron trifluoride etherate and after 30 minutes, warming to room temperature and stopping the reaction by addition of sodium bicarbonate solution. When methyl disulfide was reacted with phenylacetylene, the yield was less than 10%.

Hydrogen fluoride has also been used to catalyze the addition of disulfides to alkenes [35]. Ethylene was reacted with ethyl disulfide in the presence of anhydrous HF at 31 °C for 1 hour, yielding 70% product.

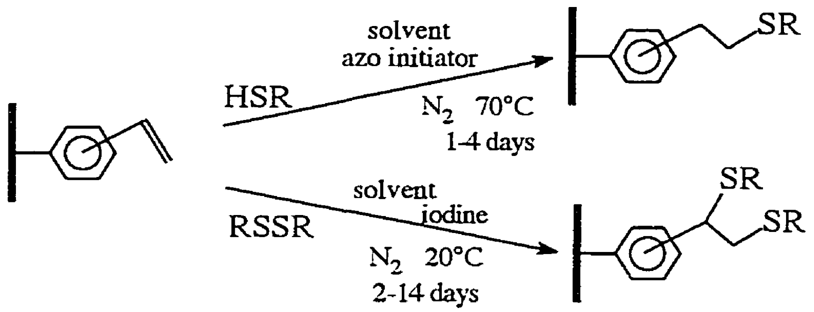
5.1.5 Addition of disulfides to poly(divinylbenzene-*co*-ethylvinylbenzene)

We have used some of these techniques in order to modify the pendant vinylbenzene groups of XAD-4 by disulfide addition. We will also compare the addition of analogous thiols in terms of yield and spectroscopic information.

Scheme 5.2 illustrates the reaction scheme for modification of XAD-4 with thiols to produce a monosubstituted pendant group, and with disulfides, catalyzed by iodine, to produce a 1,2-disubstituted pendant group. The thiols and disulfides used are listed in table 5.4 in the experimental section. The IUPAC names and CAS registry numbers are included.

We are the first to take advantage of the ideal characteristics of XAD-4 to prepare functional resins by modification of the vinyl groups through the addition of thiols and disulfides and present our results on modifying XAD-4 with a variety of disulfides and reaction conditions.

One advantage of using this method to prepare functional resins is that only a one-step modification of a commercially-available preformed matrix is needed. The reaction conditions are straightforward and no side-products are formed. Purification of the modified resin is also simple.



Scheme 5.2. Thiol and disulfide addition to vinylbenzene groups of poly(divinylbenzene-*co*-ethylvinylbenzene).

5.2. Experimental

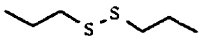
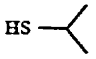
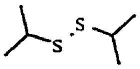
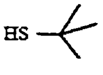
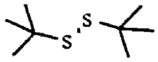
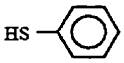
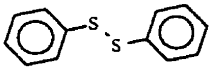
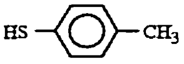
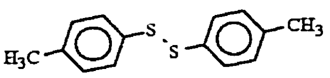
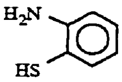
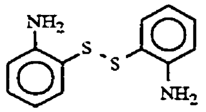
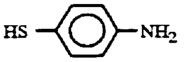
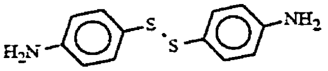
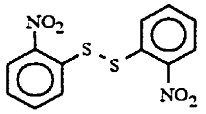
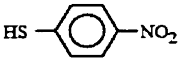
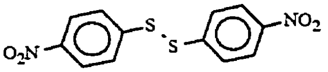
5.2.1 Materials

Unless otherwise noted, all materials were purchased from Aldrich Chemical Company and used as received. The same lot (#1090-7-1473) of Amberlite XAD-4 was used throughout this study, obtained from Rohm and Haas Co. XAD-4 comes imbibed with sodium chloride and sodium carbonate to retard bacterial growth [36]. All resins were pretreated by Soxhlet extraction with acetone for several days, followed by drying under vacuum overnight at 60 °C. Reactions used either iodine, boron trifluoride-diethyl etherate, UV light (365 nm) or AIBN (2,2'-azobis(isobutyronitrile)). Unless otherwise noted, solvents were used as received. For some experiments (as noted), solvents were pre-dried with appropriate reagents and methods. Table 5.4 lists the thiols and disulfides used and table 5.5 gives a list of some of the solvents that these reagents are soluble in [37].

5.2.2 Addition of disulfides to pendant vinylbenzene groups

Work-up for all reactions involved filtering the resin, washing with solvent and then Soxhlet extraction for several days with a variety of solvents (choice depended on solubilities, table 5.5). The solvents used for Soxhlet extraction of modified resins included dioxane, methanol (MeOH), ethanol (EtOH), tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), water, ethanol-dioxane azeotrope (90.7:9.3 w/w, bp 78.1 °C), water-dioxane azeotrope (18.4:81.6 w/w, bp 87.8 °C), or acetone. The purified resins were dried under vacuum (70 °C) for one day.

Table 5.4. Thiols and disulfides used in modification of vinylbenzene groups

Thiol Structure	IUPAC Name [CAS number]	Disulfide Structure	IUPAC Name [CAS number]
 **(1a)**	1-propanethiol [107-03-9]	 **(1b)**	*n*-propyl disulfide [629-19-6]
 **(2a)**	2-propanethiol [75-33-2]	 **(2b)**	isopropyl disulfide [4253-89-8]
 **(3a)**	2-methyl-2-propanethiol [75-66-1]	 **(3b)**	*tert*-butyl disulfide [110-06-5]
 **(4a)**	thiophenol [108-98-5]	 **(4b)**	phenyl disulfide [882-33-7]
 **(5a)**	*p*-toluenethiol [106-45-6]	 **(5b)**	*p*-tolyl disulfide [103-19-5]
 **(6a)**	2-aminothiophenol [137-07-5]	 **(6b)**	2-aminophenyl disulfide [1141-88-4]
 **(7a)**	4-aminothiophenol [1193-02-8]	 **(7b)**	4-aminophenyl disulfide [722-27-0]
		 **(8b)**	2-nitrophenyl disulfide [1155-00-6]
 **(9a)**	4-nitrothiophenol [1849-36-1]	 **(9b)**	4-nitrophenyl disulfide [100-32-3]

5.2.2.1 Iodine-catalyzed addition

In a 50 mL 2-neck round bottom flask with magnetic stirring bar, 1 g of resin, 5 equivalents disulfide (per vinyl group), 25 mL of solvent and 0.1 equivalent iodine (per vinyl group) were added. The stirring mixture was flushed with nitrogen, and the reaction was allowed to run at room temperature under nitrogen between 1 and 14 days. The solvents used (both pre-dried and as received) for the reaction included toluene, *N,N*-dimethylformamide (DMF), dichloromethane, diethyl ether, dimethyl sulfoxide (DMSO), acetone, tetrahydrofuran, nitromethane ($MeNO_2$), and nitromethane-dichloromethane (50:50 v/v). A control experiment was done using *n*-propyl disulfide and no catalyst to determine if any disulfide was physically adsorbed.

Table 5.5. Solubilities of reagents (Data from [37])

Thiol	Solvents	Disulfide	Solvents
(1a)	H_2O, EtOH, ether, acetone, benzene	**(1b)**	—
(2a)	H_2O, EtOH, ether, acetone, chloroform	**(2b)**	—
(3a)	heptane, carbon tetrachloride	**(3b)**	—
(4a)	EtOH, ether, acetone, chloroform, carbon tetrachloride	**(4b)**	EtOH, ether, benzene, CS_2
(5a)	EtOH, ether, chloroform	**(5b)**	EtOH, ether, acetone
(6a)	EtOH, ether	**(6b)**	EtOH, ether
(7a)	H_2O, EtOH	**(7b)**	H_2O, EtOH, ether, acetone, chloroform, ligroin
		(8b)	EtOH, acetone, benzene, acetic acid
(9a)	H_2O, EtOH, ether, acetone, acetic acid, ligroin	**(9b)**	EtOH, acetic acid

5.2.2.2 Boron trifluoride-diethyl etherate-catalyzed addition

Using a similar set-up as above, 1 g dried resin was mixed with disulfide (5 equiv), and 40 mL nitromethane-dichloromethane (dried, 50:50 v/v) solvent mixture, flushed with nitrogen, and cooled to 0 °C. Boron trifluoride-diethyl etherate (0.1 equiv per vinyl group) was slowly added to the stirring mixture. The reaction proceeded at room temperature and was either stopped after one day, or continued with the addition of more catalyst (0.1 equiv) for an additional day. The reaction was quenched with water, followed by purification in the usual manner.

5.2.2.3 AIBN initiated radical addition

In a 100 mL 2-neck round bottom flask equipped with condenser and magnetic stirring bar, 1 g of resin, 2 to 5 equivalents disulfide (per vinyl group), 50 mL of toluene (or DMF, both as received), and 0.1 equivalent AIBN (per vinyl group) were added. The stirring mixture was flushed with nitrogen, and the reaction was allowed to run at 70 °C under nitrogen for 2 days.

5.2.2.4 Ultraviolet-light initiated radical addition

In a 30 mL glass vial with screw cap lid, 0.5 g resin, 20 mL solvent (cyclohexane or ethanol), and disulfide (5 equiv per vinyl group) were mixed, and the vial flushed with nitrogen then sealed with electrical tape. The vial was placed in a Rayonet Photochemical Reactor (The Southern New England Ultraviolet Co.) and exposed to UV-light (365 nm) for 2 to 6 days at room temperature.

5.2.3 Addition of analogous thiols to pendant vinylbenzene groups

Using methods previously established [1, 2], we modified XAD-4 with thiols analogous to the disulfides studied (table 5.4). In a 250 mL 2-neck round bottom flask equipped with condenser and magnetic stirring bar, 2 g of resin, 5 equivalents (per vinyl group) thiol, 100 mL of toluene, and 0.1 equiv (per vinyl group) AIBN were added. The stirring mixture was flushed with nitrogen, heated to 70 °C, and the reaction was allowed to run for 2 to 5 days.

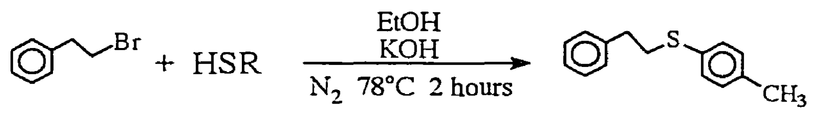
5.2.4 Addition of analogous thiols to pendant (1,2-dibromoethyl)benzene groups

XAD-4 was brominated in carbon tetrachloride at room temperature for 12 hours as reported elsewhere [4]. The resin was then reacted with thiols (table 5.4) in basic media to convert the (1,2-dibromoethyl)benzene groups to thioether groups. The procedure involved adding 5 equiv thiol (per Br), 5-6 equiv base, and 100 mL solvent to 1 g resin, and heating at 78-90 °C under nitrogen for 3-5 days. Either DMF with triethylamine or absolute ethanol with potassium hydroxide were used.

5.2.5 Preparation of model compounds

5.2.5.1 Preparation of 2-(4-methylphenylthio)ethylbenzene

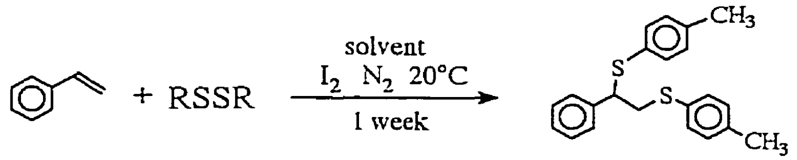
In a 100 mL 2-neck round bottom flask equipped with condenser and magnetic stirring bar, *p*-toluenethiol (**5a**, 2.51 g, 20.2 mmol), potassium hydroxide (1.13 g, 20.2 mmol) and 50 mL of anhydrous ethanol were mixed. The stirring mixture was flushed with nitrogen, and (2-bromoethyl)benzene (2.73 mL, 20 mmol) was added dropwise. The mixture was refluxed (78 °C) under nitrogen for 2 hours. Work-up involved filtration of KBr salt, evaporation of solvent, extraction with diethyl ether and water (pH 10 first then pH 7 until washings were neutral). The ether layer was dried with magnesium sulfate and evaporated. The crude product was distilled under vacuum (115-118 °C/0.1 mm Hg) to yield a pale yellow oil, 70% yield. Characterization was done by NMR.



Scheme 5.3. Preparation of monosubstituted model compound.

5.2.5.2 Di-1,2-(4-methylphenylthio)ethylbenzene prepared by iodine-catalyzed addition of *p*-tolyl disulfide to styrene

In a 50 mL 2-neck round bottom flask, styrene (1.2 mL, 10 mmol), *p*-tolyl disulfide (**5b**, 2.46 g, 10 mmol) and iodine (0.25 g, 1 mmol) were dissolved with anhydrous dichloromethane (20 mL). The flask was left under nitrogen at room temperature for one week. Work-up of the reaction involved washing with sodium thiosulfate solution, then water, and drying the dichloromethane layer with magnesium sulfate followed by evaporation. The product was recrystallized with ice-cold ethanol to produce white crystals, mp 61-62 °C, in 54% yield. Characterization was done by NMR.



Scheme 5.4. Preparation of disubstituted model compound.

5.2.6 Characterization

5.2.6.1 Elemental analysis

Samples were sent to the University of British Columbia or Robertson Microlit Laboratories (Madison, NJ) to be analyzed for sulfur, nitrogen, bromine and/or iodine, where applicable.

5.2.6.2 Infrared spectroscopy

The unmodified resin was characterized using infrared spectroscopic analysis to measure the vinyl group content [4, 38]. Modified resins were characterized to determine reduction of vinyl peaks and introduction of peaks due to the modifying groups. Samples were ground into powder with FTIR-grade potassium bromide (KBr) and disks were prepared. Fourier transform infrared absorbance spectra were taken with a Bruker IFS 66 spectrometer, using a DTGS detector and 2 cm^{-1} resolution, with 120 to 200 scans. Model compounds were characterized neat between NaCl plates.

5.2.6.3 Raman spectroscopy

Fourier transform Raman spectra were taken using a Bruker IFS 88 spectrometer with FRA-105 Raman module using a Nd^{+3}:YAG laser (1064.1 nm). Samples were ground into powder and packed lightly into an aluminum sample cup. The number of scans ranged from 250 to 5000, with a 4 cm^{-1} resolution. It should be noted that spectra taken with samples held in glass melting point tubes had fluorescence due to the glass, obscuring most peaks, so this method was not used. The liquid model compound was characterized with the sample in an NMR tube.

5.2.6.4 ^1H and ^{13}C NMR spectroscopy

Solid-phase ^{13}C NMR spectra were obtained with a Chemagnetics Inc. M-100 instrument. ^{13}C CP-MAS (cross-polarization magic angle spinning) NMR spectra were obtained at 25.1 MHz with contact time of 2 ms, pulse delay of 2 s, spinning rate of 3-4 kHz, and high-power proton decoupling during acquisition.

The ^{13}C CP-MAS-DD (DD is dipolar dephasing) NMR spectra were obtained similarly, with dephasing time (τ) of 45 μs. Samples were referenced to hexamethylbenzene. ^{1}H NMR spectra were not taken for solid samples.

Model compounds were dissolved in either deuterated chloroform or deuterated benzene, with tetramethylsilane as internal standard. ^{1}H and ^{13}C NMR spectra were measured on either a Gemini 200 MHz or a Jeol 270 MHz spectrometer.

5.3. Results and Discussion

5.3.1 Characteristics of starting materials

Previously, we characterized the starting material with regard to vinyl content, surface area, porosity, and monomer content, and the results are presented elsewhere [4]. Table 5.6 summarizes these characteristics. The vinyl content was calculated using FTIR spectroscopy [4, 38]. The degree of functionalization (X_{VB}, in %) is the percentage of repeat units which have vinylbenzene groups, and the degree of cross-linking (X_{CL}, in %) is the percentage of repeat units which cross-link the resin. The pore size distribution is based on the percent of the total pore volume with pores of a given diameter.

Table 5.6. Characteristics of XAD-4 (data from [4])

Surface Area (m^2/g)	Total Pore Volume (mL/g)	Pore Size (nm)	Degree of Functionalization (X_{VB}, %)	Degree of Cross-Linking (X_{CL}, %)	Vinyl Content (mmol/g)
831	1.181	< 6 (17.3%) 6-10 (20.5%) 10-20 (59.5%)	33 ± 1	47 ± 2	2.5 ± 0.1

5.3.2 Modification of XAD-4 by addition of thiols and disulfides

5.3.2.1 Calculation of the degree of functionalization

The general equation for calculating the degree of functionalization of modified XAD-4 (X_{fg}) is based on: the average MW per repeat unit of unmodified resin (130.6 for 80% DVB content), the mole content of functional group (mol fg/g, also called functional capacity, $C_{2\text{-}SR}$ for thiol-modified resins and $C_{1,2\text{-}SR}$ for disulfide-modified resins, calculated from elemental analysis), and the molecular weight (MW fg) of the modifying group (equation 5.1). For thiol-modified XAD-4, the calculation of degree of functionalization ($X_{2\text{-SR}}$) is shown as equation 5.2. The value "n" is the number of sulfur atoms per modified repeat unit (i.e. 2,3-dimercapto-1-propanol has 2 sulfur atoms, so n = 2). For disulfide-modified XAD-4, the calculation of degree of functionalization ($X_{1,2\text{-SR}}$) is shown as equation 5.3, the value for "n" will be a multiple of 2, since each repeat unit will have two thioether functionalities. The percent conversion (Φ) of vinyl groups (double bonds) to modified groups is given in equation 5.4.

Equation 5.1
$$X_{fg} = \frac{130.6 \times (\text{mol fg/g})}{1 - (\text{mol fg/g} \times \text{MW fg})} \times 100\%$$

Equation 5.2
$$X_{2\text{-SR}} = \frac{130.6 \times (\text{mol S/g} \div n)}{1 - ((\text{mol S/g} \div n) \times \text{MW HSR})} \times 100\%$$

Equation 5.3
$$X_{1,2\text{-SR}} = \frac{130.6 \times (\text{mol S/g} \div n)}{1 - ((\text{mol S/g} \div n) \times \text{MW RSSR})} \times 100\%$$

Equation 5.4
$$\Phi = \frac{X_{fg}}{X_{VB}} \times 100\%$$

5.3.2.2 Results of disulfide addition using various solvents with iodine

The results of all disulfide additions to the pendant vinylbenzene groups of XAD-4 are listed in table 5.7. The bold number indicates the disulfide used, as shown in table 5.4. Most reactions were done using iodine as the catalyst, and these results will be discussed first. In general, yields (Φ, degree of conversion of vinyl to functional groups) increased with the use of anhydrous solvents. The presence of water may destroy the sulfenyl iodide intermediate (shown in scheme 5.1). We did not attempt any reactions using the liquid disulfides without solvent due to the hazards involved in handling these reagents, since larger volumes would have been needed.

An increase in the amount of iodine used (from 0.1 equiv per vinyl group to as much as 1 equiv) may increase the conversions, and this variable could be examined in future.

The resin with the highest yield was analyzed for iodine content with a nil result. To determine if disulfide was being physically adsorbed, we ran a control with no catalyst using *n*-propyl disulfide (**1b**) with dichloromethane for two weeks, followed by Soxhlet extraction for a few days with dichloromethane. There was no sulfur present, and infrared and Raman spectra were identical to those of unmodified XAD-4.

The best results were found using dichoromethane and/or nitromethane. Reactions run for 2 weeks compared to 3 days (using dichoromethane as the solvent in both cases) improved results by as much as two-fold. These results were comparable to those when nitromethane was used for only 3 days. The disulfides giving the highest yields were *n*-propyl disulfide (**1b**, 55%), phenyl disulfide (**4b**, 48%), isopropyl disulfide (**2b**, 41%), and *p*-tolyl disulfide (**5b**, 36%). In comparison, the results with the other disulfides were lower (2-aminophenyl disulfide (**6b**, 14%), *tert*-butyl disulfide (**3b**, 13%), 4-aminophenyl disulfide (**7b**, 9.4%), 4-nitrophenol disulfide (**9b**, 7.5%), and 2-nitrophenol disulfide (**8b**, 5.3%)). As seen in table 5.8 for the results of addition of *n*-propyl disulfide, there seems to be no correlation between solvent polarity and conversion of vinylbenzene groups.

The yields with the use of the alkyl disulfides decreased with increasing bulk of the R group on the disulfide. The relative reactivities, as found in radical reactions, were 70, 14 and 1 for *n*-propyl, isopropyl and *tert*-butyl disulfides [16]. This trend was seen for the yields: 55%, 41% and 13%, respectively. While the relative reactivity (in radical reactions) for *n*-propyl disulfide to that of *tert*-butyl disulfide was 70-fold, the yield of disulfide addition was 4-fold. In general, the bulk of the functional groups will decrease the yield to some extent.

In a previous study of the photochemical polymerization of styrene with some of the same aryl disulfides as we have studied, yields also depended on the substituents of the aryl groups [26]. The disulfides which gave the highest yields in the polymerization of styrene were: phenyl disulfide (**4b**, 2.0% yield), 4-aminophenyl disulfide (**7b**, 2.2% yield), and 2-aminophenyl disulfide (**6b**, 2.0% yield). With 2-nitrophenol disulfide (**8b**), no polymer resulted (1000 equivalents styrene to 1 equivalent disulfide) [26]. This trend was also seen with our results to some degree: phenyl disulfide (**4b**, 48% conversion), 2-aminophenyl disulfide (**6b**, 14% conversion), 4-aminophenyl disulfide (**7b**, 9.4% conversion) and 2-nitrophenol disulfide (**8b**, 5.3% conversion).

5.3.2.3 Comparison of catalysts or initiators used

The highest conversions for disulfide addition were found with the use of iodine as the catalyst, with the exception of the radical addition of 2-aminophenyl disulfide (17% with AIBN, 14% with iodine).

The results with iodine as the catalyst do not correlate to the chain transfer constants found for some of these disulfides (table 5.2). The disulfide with the highest constant (of those studied in [23]) was 2-aminophenyl disulfide (3.0, [23]), while *p*-tolyl disulfide and phenyl disulfide had lower constants (0.11 and 0.06, respectively [23]). However, when a radical initiator (AIBN) was used, disulfide addition was highest with 2-aminophenyl disulfide (17%) followed by phenyl disulfide (6.4%) (*p*-tolyl disulfide was not used). Little or no addition occurred using the alkyl disulfides. The chain transfer constant for one alkyl disulfide (2-ethyl hexyl disulfide) was low (< 0.005) in comparison with the aryl disulfides [23].

The use of boron trifluoride-diethyl etherate as the catalyst yielded products only with *n*-propyl disulfide (14-17%).

Attempts using ultraviolet light (365 nm) also had limited results. The best result used phenyl disulfide (22%), followed by *tert*-butyl disulfide (4.6%), isopropyl disulfide (3.6%) and *n*-propyl disulfide (< 3%).

Table 5.7. Degree of functionalization ($C_{1,2\text{-SR}}$ (mmol fg/g), $X_{1,2\text{-SR}}$) and percent conversion (Φ) by disulfide addition (a)

Solvent	Disulfide used $C_{1,2\text{-SR}}$ (mmol fg/g), $X_{1,2\text{-SR}}$, (Φ)			
	1b	**2b**	**3b**	**4b**
CH_2Cl_2	0.71, 10.5% (32%)	0.31, 4.3% (13%)	0.02, < 1% (< 1%)	0.62, 9.4% (28%)
CH_2Cl_2 (dry)	0.85, 13% (39%)	0.37, 5.1% (16%)	0.12, 1.6% (4.8%)	0.65, 10% (29%)
CH_2Cl_2 (dry) 2 weeks	1.0, 16% (49%)	0.59, 8.0% (26%)	0.30, 4.1% (13%)	0.96, 16% (48%)
ether	0.29, 4.0% (12%)	0.05, < 1% (< 2%)	0	0.51, 7.5% (23%)
ether (dry)	0.51, 7.2% (22%)	0.90, 14% (41%)	0.07, < 1% (< 3%)	0.37, 5.3% (16%)
acetone	0.08, 1.1% (3.2%)	0.05, < 1% (< 2%)	0	0.10, 1.3% (4.0%)
acetone (dry)	0.26, 3.5% (11%)	0.09, 1.1% (3.4%)	0.05, < 1% (< 3%)	0.10, 1.4% (4.2%)
toluene	0.29, 4.0%, (12%)	0.03, < 1% (< 1%)	0	0.31, 4.4% (13%)
toluene (dry)	0.57, 8.1% (25%)	0.12, 1.6% (5.0%)	0	0.61, 9.0% (28%)
toluene (AIBN, 75-80 °C)	0.06, < 1% (< 3%)	0	0	0.15, 2.1% (6.4%)
THF (dry)	0.53, 7.4% (23%)	0.09, 1.2% (3.6%)	0	0.27, 3.8% (11%)
DMF	0.10, 1.3% (4.0%)	0.03, < 1% (< 2%)	0.02, < 1% (< 2%)	0.04, < 1% (< 2%)
DMF (AIBN, 75-80 °C)	-	0	0	0.04, < 1% (< 2%)
DMSO	0.18, 2.4% (7.1%)	0.06, < 1% (< 3%)	0	0.11, 1.5% (4.5%)
DMSO (dry)	0.19, 2.5% (7.7%)	0.09, 0.12% (3.5%)	0.06, < 1% (< 3%)	0.12, 1.5% (4.7%)
$MeNO_2$ (dry)	1.2, 18% (55%)	0.62, 8.9% (27%)	0.11, 1.5%, (4.4%)	0.95, 16%, (48%)
$MeNO_2$-CH_2Cl_2 (dry)	1.0, 16% (49%)	0.52, 7.0% (23%)	0.11, 1.5%, (4.4%)	0.90, 15% (44%)
$MeNO_2$-CH_2Cl_2 (dry) (BF_3-OEt_2)	0.34, 4.6% (14%)	0	0	0.03, < 1% (< 1%)
$MeNO_2$-CH_2Cl_2 (dry) (2X BF_3-OEt_2)	0.41, 5.7% (17%)	0	0	0
cyclohexane (UV initiation, 2-6 days)	0.07, < 1% (< 3%)	0.090, 1.2% (3.6%)	0.11, 1.5% (4.6%)	0.50, 7.4% (22%)

(a) Reaction conditions unless otherwise noted: 5 equiv RSSR, 0.1 equiv catalyst (I_2) or other initiator, room temperature, nitrogen atmosphere, 2-3 days.

Table 5.7. (continued) (a)

Solvent	Disulfide used $C_{1,2\text{-SR}}$ (mmol fg/g), $X_{1,2\text{-SR}}$, (Φ)				
	5b	**6b**	**7b**	**8b**	**9b**
CH_2Cl_2	-	0.05, < 1% (< 2%)	-	0	-
CH_2Cl_2 (dry)	-	0.18, 2.5% (7.0%)	-	0.07, 1.0% (2.9%)	-
CH_2Cl_2 (dry) 2 weeks	0.74, 12% (36%)	0.28, 3.9% (12%)	-	0.13, 1.7% (5.3%)	-
ether	-	0.09, 1.2% (3.6%)	-	0	-
ether (dry)	-	0.13, 1.7% (5.0%)	-	0.08, 1.1% (3.4%)	-
acetone	-	0.06, < 1% (< 3%)	-	0	-
acetone (dry)	-	0.05, < 1% (< 3%)	-	0.04, < 1% (< 2%)	-
toluene	-	0.03, < 1% (< 1%)	-	0	-
toluene (dry)	-	0.06, < 1% (< 3%)	-	0.05, < 1% (< 2%)	-
toluene (AIBN, 75-80 °C)	-	0.38, 5.5% (17%)	-	-	-
THF (dry)	-	0	-	0.06, < 1% (< 3%)	-
DMF	-	0	-	-	-
DMF (AIBN, 75-80 °C)	-	0	-	-	-
DMSO	-	0.09, < 2% (< 4%)	-	0	-
DMSO (dry)	-	0.07, < 1% (< 3%)	-	0	-
$MeNO_2$ (dry)	-	0.31, 4.0% (14%)	-	0.05, < 1% (< 3%)	-
$MeNO_2$-CH_2Cl_2 (dry)	-	0.27, 3.9% (12%)	0.22, 3.1% (9.4%) (2 weeks)	0.06, < 1% (< 3%)	0.18, 2.5% (7.5%) (2 weeks)
$MeNO_2$-CH_2Cl_2 (dry) (BF_3-OEt_2)	-	-	-	0	-
$MeNO_2$-CH_2Cl_2 (dry) (2X BF_3-OEt_2)	-	-	-	0	-
ethanol (UV initiation, 5 days)	-	0.05, < 1% (< 3%)	-	0.02, < 1% (< 1%)	-

(a) Reaction conditions unless otherwise noted: 5 equiv RSSR, 0.1 equiv catalyst (I_2) or other initiator, room temperature, nitrogen atmosphere, 2-3 days.

Table 5.8. Comparison of percent conversion (Φ) to solvent polarity for various solvents used in the iodine-catalyzed addition of *n*-propyl disulfide to the pendant vinylbenzene groups of XAD-4 (a)

Solvent	Dielectric Constant [39]	Φ
DMSO (dry)	46.68	7.7%
DMF	36.71	4.0%
$MeNO_2$ (dry)	35.87	55%
acetone (dry)	20.7	11%
CH_2Cl_2 (dry)	9.08	39%
THF (dry)	7.58	23%
ether (dry)	4.34	22%
toluene (dry)	2.28 (benzene)	25%
$MeNO_2$-CH_2Cl_2 (dry) (50:50 v/v)		49%

(a) Reaction conditions: 5 equiv *n*-propyl disulfide, 0.1 equiv catalyst (I_2), room temperature, nitrogen atmosphere, 2-3 days.

5.3.2.4 Comparison of thiol and disulfide addition to XAD-4

Table 5.9 compares the results of thiol addition to the vinylbenzene groups to form monosubstituted functional units and those with analogous disulfides to form disubstituted functional units (as seen in scheme 5.2). The thiols were added using free radical conditions (AIBN-initiated), while the disulfides were added using iodine as the catalyst. The degree of functionalization for both is given by the amount of functional pendant groups (C_{fg}, mmol/g). This (C_{fg}) is equal to the quantity of thioether groups for the thiol-addition resins and to half the quantity of thioether groups for the disulfide-addition as each functionalized unit had two thioether groups (mmol SR/g listed below C_{fg} in table 5.8). For example, resin **1a** was modified with 1-propanethiol (**1a**) with 1.1 mmol SR/g, $X_{2\text{-SR}}$ 16% and yield (Φ) of 49%, while resin **1b** was modified with *n*-propyl disulfide (**1b**) with 1.2 mmol fg/g (or 2.4 mmol SR/g), $X_{1,2\text{-SR}}$ 18% and yield (Φ) of 55%. While the conversions of vinylbenzene groups to modified groups were similar, the disulfide-modified resin had twice the quantity of thioether groups. The advantage of disulfide addition is this increase in functional groups and also the possibility of interactions between two functionalities. The general trend was a lower conversion of vinyl groups with disulfide addition, but an overall larger amount of thioether groups in comparison to thiol addition.

Table 5.9. Comparison of the degree of functionalization and conversion (Φ) of modified XAD-4 by thiol addition ($C_{2\text{-SR}}$ (mmol fg/g), $X_{2\text{-SR}}$) to best disulfide results ($C_{1,2\text{-SR}}$ (mmol fg/g and mmol SR/g), $X_{1,2\text{-SR}}$) (a, b)

Thiol or Disulfide used
C_{fg} (mmol fg/g), X_{fg}, (Φ)

1a	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
1.1	1.2	1.2	0.90	0.74	0.30	1.4	0.96
	(2.4) (c)		(1.8) (c)		(0.60) (c)		(1.9) (c)
16%	18%	18%	14%	10%	4.1%	21%	16%
(49%)	(55%)	(53%)	(41%)	(31%)	(13%)	(64%)	(48%)
5a	**5b**	**6a**	**6b**	**7a**	**7b**	**9a**	**9b**
1.11	0.74	1.0	0.31	0.27	0.22	0.11	0.18
	(1.5) (c)		(0.62) (c)		(0.44) (c)		(0.36) (c)
17%	12%	15%	4.0%	3.6%	3.1%	1.5%	2.5%
(51%)	(36%)	(45%)	(14%)	(11%)	(9.4%)	(4.6%)	(7.5%)
				(EtOH)		(EtOH)	

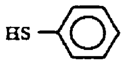
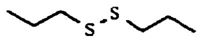
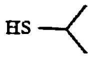
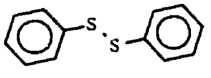
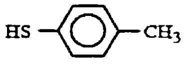
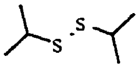
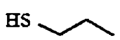
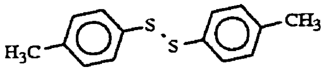
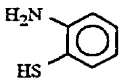
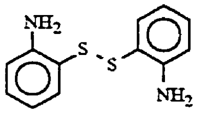
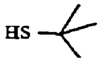
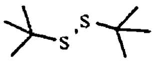
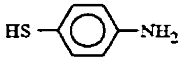
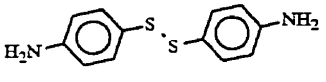
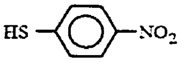
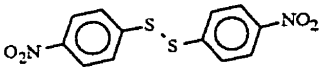
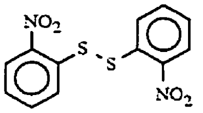
(a) Reaction conditions for thiol addition unless otherwise noted: 5 equiv HSR, 0.1 equiv AIBN, toluene, 70-80 °C, nitrogen atmosphere, 2-3 days.

(b) See table 5.7 for details of disulfide additions, all done using iodine as catalyst.

(c) Quantity of thioether groups in mmol SR/g resin (twice the number of functionalized repeat units, C_{fg}, mmol fg/g).

Table 5.10 summarizes the results of radical addition of thiols and iodine-catalyzed addition of disulfides to the pendant vinylbenzene groups of XAD-4 in order of percent conversion. As previously noted, the conversions tended to be higher for each thiol compared to its disulfide analogue. Steric hindrance may be a factor in disulfide addition, especially with the alkyl disulfides. Yields were significantly lower with substitution on the aryl disulfides. Electronic and steric factors and differences in solubility likely all contributed to variations in percent conversions of vinylbenzene groups to modified groups.

Table 5.10. Comparison of percent conversion (Φ) of thiol and disulfide addition to the pendant vinylbenzene groups of XAD-4, in order of yield (a, b)

	Thiol	Φ		Disulfide	Φ
(4a)		64%	**(1b)**		55%
(2a)		53%	**(4b)**		48%
(5a)		51%	**(2b)**		41%
(1a)		49%	**(5b)**		36%
(6a)		45%	**(6b)**		14%
(3a)		31%	**(3b)**		13%
(7a)		11%	**(7b)**		9.4%
(9a)		4.6%	**(9b)**		7.5%
			(8b)		5.3%

(a) Reaction conditions for thiol addition: 5 equiv HSR, 0.1 equiv AIBN, 70-80 °C, nitrogen atmosphere, 2-3 days (see table 5.9 for details).

(b) Reaction conditions for disulfide addition: 5 equiv RSSR, 0.1 equiv iodine, room temperature, nitrogen atmosphere, 2-3 days or 2 weeks (see table 5.7 for details).

5.3.2.5 Comparison of disulfide addition to XAD-4 with thiol modification of brominated XAD-4

Table 5.11 gives the results of modification of the (1,2-dibromoethyl)benzene groups of brominated XAD-4. The method using ethanol and KOH gave higher quantities of thioether groups than when DMF and triethylamine were used (based on sulfur contents). However, conversion was incomplete in all cases with bromine-containing units present. Elimination also occurred (as will be seen in the spectral characterization section). The quantities of thioether groups were also less than when thiol or disulfide addition was done to XAD-4. Many functional units were possible: 1,2-dibromo, 1,2-dithioether, 1-bromo-2-thioether, 1-thioether-2-bromo, as well as unsaturated groups which may have had functionalities. Because of a less-defined structure and low conversion of functional groups, this method is not recommended for the addition of thiols. However, the brominated XAD-4 is useful in the preparation of other functional resins, as will be seen in some of our other work [40].

Table 5.11. Degree of functionalization (C_{fg} (mmol SR/g) for the modification of (1,2-dibromoethyl)benzene groups with analogous thiols (a)

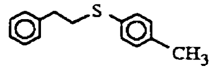
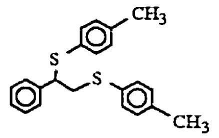
Reaction Conditions	Thiol used (C_{fg1}, mmol SR/g) (C_{fg2}, mmol Br/g) 1a	2a	3a	4a
Ethanol 5 equiv HSR per Br 6 equiv KOH per Br 78°C, N_2, 5 days	0.37 mmol SR/g 1.34 mmol Br/g	0.32 mmol SR/g 1.36 mmol Br/g	0.32 mmol SR/g 1.39 mmol Br/g	0.99 mmol SR/g 1.46 mmol Br/g
DMF 5 equiv HSR per Br 5 equiv NEt_3 per Br 90°C, N_2, 3 days	—	0.14 mmol SR/g 2.89 mmol Br/g	0.096 mmol SR/g 2.83 mmol Br/g	0.92 mmol SR/g 1.75 mmol Br/g

(a) Brominated XAD-4 had 3.99 mmol Br/g (2.0 mmol fg/g), $X_{1,2\text{-}Br} = 35\%$.

5.3.3 Model compounds

Table 5.12 lists the results and NMR spectral information for the model compounds. Both had been prepared previously, and spectral data matches the literature values [33,41].

Table 5.12. Results of preparation of model compounds

Product	^1H NMR shifts (ppm)	^{13}C NMR shifts (ppm)
 bp 115-118 °C/0.1 mm Hg lit. [41] bp 105-106 °C/0.05 mm Hg pale yellow oil, 70% yield	2.43 (s, 3H, CH_3), 3.01-3.24 (m, 4H, CH_2), 7.2-7.43 (m, 9H, aromatic)	20.91, 35.64, 126.26-129.95, 132.45, 135.97, 140.20
 mp 61-61 °C lit. [33] mp 73 °C white crystals, 54% yield	1.96 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 3.25-3.57 (m, 2H, CH_2) 4.34-4.36 (m, 1H, CH) 6.72-6.79 (m, 5H, aromatic) 7.04-7.20 (m, 8H, aromatic)	21.12, 21.17, 40.60, 53.35, 127.70-128.80, 130.05-132.87, 133.92, 136.45, 137.82, 140.71

The monosubstituted adduct was previously prepared by the radical addition of *p*-toluenethiol to styrene using AIBN as the initiator with 91% yield [41]. These model compounds confirm the proposed structures of the pendant groups (in the modified resins) with regard to substitution patterns since they have been prepared using the same methods as the polymer modifications [33, 41]. Samples were also blended with unmodified XAD-4 for infrared spectroscopic examination and compared to the modified resins, as will be discussed in the next section.

5.3.4 Spectroscopic characterization

The modified resins were characterized and compared to the starting material using infrared, Raman and ^{13}C NMR spectroscopy.

5.3.4.1 Infrared spectroscopy

Figures 5.2a to 5.2d compare the FTIR absorbance spectra of XAD-4 and the modified resins, indicated with a bold number corresponding to the thiol or disulfide used. Figure 5.2e compares the FTIR absorbance spectra of brominated XAD-4 and the thiol-modified resins prepared from brominated XAD-4.

Peak assignments were done by comparison to the thiols, disulfides and analogous model compounds [33, 41, 42], and with the help of a reference book on spectroscopy [43]. The FTIR spectral peaks have previously been assigned for unmodified poly(divinylbenzene-*co*-ethylvinylbenzene) (XAD-4) [4, 38]. Table 5.13a lists the peak assignments for thiol and disulfide-modified XAD-4 for the resins with *n*-propyl (**1a**, **1b**), isopropyl (**2a**, **2b**), and *tert*-butyl groups (**3a**, **3b**). Table 5.13b lists the peak assignments for the resins modified with aryl thiols and disulfides (**4a-9b**).

On comparison of the spectra for XAD-4 and the modified resins, the five peaks due to the vinyl groups decrease in relation to the degree of functionalization. The peak at 905 cm^{-1} is due to both vinyl groups and disubstituted phenyls, so it is never completely eliminated.

Figure 5.2a compares the IR spectrum of XAD-4 with those of XAD-4 modified by alkyl thiols (**1a**, **2a**, **3a**) and disulfides (**1b**, **2b**, **3b**). The resins modified with 1-propanethiol (**1a**) and *n*-propyl disulfide (**1b**) were comparable in their degrees of functionalization, 49% and 55% yields, respectively. The disulfide-modified resin had twice as many propyl groups (2.3 mmol SR/g compared to 1.1 mmol SR/g for thiol-modified resin) and consequently had more prominent peaks due to the functional groups. Peaks due to the functional groups were seen and were comparable to those of the starting materials [42].

Table 5.13a. Infrared peak assignments for thiol and disulfide-modified resins

Resin	Band (cm^{-1})	Assignment	Reference	Notes
1a	1375	symmetrical deformation of CH_3	[43], p. 201	peaks similar to starting thiol (**1a**), disulfide (**1b**) and *n*-propyl sulfide
and	1294, 1239	CH_2 wagging and twisting	[43], p. 202	
1b			[42], Volume 1, p. 255, 266 Vol. 3, p. 349	
2a	1381, 1365	symmetrical deformation of CH_3 of isopropyl groups (2 bands)	[42], Volume 1, p. 257, 267-268	peaks due to isopropyl groups
and				
2b	1244, 1156, 1052		[43], p. 201	peaks similar to starting thiol (**2a**), disulfide (**2b**) and isopropyl sulfide
3a	1365	symmetrical deformation of CH_3 of *tert*-butyl groups (2 bands, weak one ~1395 cm^{-1}, not seen)	[43], p. 201	peak due to *tert*-butyl groups
and				
3b	1165		[42], Volume 1, p. 258, 268-269	peaks similar to starting thiol (**3a**), disulfide (**3b**) and *tert*-butyl sulfide

Figure 5.2b shows the spectra of XAD-4 and resins modified with two of the aryl thiols (**4a**, **5a**) and disulfides (**4b**, **5b**). Resins **4a** and **4b** were modified with thiophenol (**4a**) and phenyl disulfide (**4b**) which introduced monosubstituted phenyl groups. In comparison to the spectrum of XAD-4, some peak heights increased (1586, 1482, and 1449 cm^{-1}), and new peaks due to the monosubstituted phenyl groups were introduced [42, 43]. Resins **5a** and **5b** were modified with *p*-toluenethiol (**5a**) and *p*-tolyl disulfide (**5b**) which introduced para-disubstituted phenyl groups. In comparison to the spectra of XAD-4, the model compounds, and XAD-4 with either model compound mixed in, peaks due to the functional groups of the modified resins were elucidated. Since the peaks due to the resin obscure most of the functional group peaks, no differentiation could be made between the resin with the monosubstituted groups (**5a**) or the disubstituted groups (**5b**). In comparison to the spectrum for XAD-4, the peak at 1511 cm^{-1} decreased, the peak at 1492 cm^{-1} increased, and new peaks, which were also seen in the spectra of the model compounds, were seen.

Table 5.13b. Infrared peak assignments for thiol and disulfide-modified resins

Resin	Band (cm^{-1})	Assignment	Reference	Notes
4a and **4b**	737, 690	monosubstituted aromatic	[43], p. 197	peaks similar to starting thiol (**4a**), disulfide (**4b**) and thioanisole
	Also: 1439, 1273, 1156, 1091, 1025		[42], Volume 1, p. 1173, 1182-1183	
5a and **5b**	500	C-S stretch	[43], p. 219	peaks similar to starting thiol (**5a**), disulfide (**5b**) and model compounds
	Also: 1211, 1179, 1092		[42], Volume 1, p. 1177, 1185	
6a and **6b**	1309 or 1251	phenyl-N stretch	[43], p. 211	peaks similar to starting thiol (**6a**), disulfide (**6b**) and 2-(methylmercapto)aniline
	747	ortho-disubstituted aromatic	[43], p. 197	
	458	C-S stretch	[43], p. 219	
	Also: 1158, 967		[42], Volume 1, p. 1196-1197	
7a and **7b**	1352 or 1316	phenyl-N stretch	[43], p. 211	peaks similar to starting thiol (**7a**), disulfide (**7b**)
	515	C-S stretch	[43], p. 219	
	Also: 1290, 1177		[42], Volume 1, p. 1210	
8b	1340	NO_2 symmetric stretch	[43], p. 211	peaks similar to starting disulfide (**8b**)
	733	ortho-disubstituted aromatic	[43], p. 197	
			[42], Volume 1, p. 1210	
9a and **9b**	1340	NO_2 symmetric stretch	[43], p. 211	peaks similar to starting thiol (**9a**), disulfide (**9b**)
	852	para-disubstituted aromatic	[43], p. 197	
	Also: 1182, 1116, 1089, 742		[42], Volume 1, p. 1341, 1386	

Figure 5.2c shows the spectra of XAD-4 and resins modified with the amino-aryl thiols (**6a**, **7a**) and disulfides (**6b**, **7b**). Resins **6a** and **6b** were modified with 2-aminothiophenol (**6a**) and 2-aminophenyl disulfide (**6b**) which introduced ortho-disubstituted phenyl groups. Resins **7a** and **7b** were modified with 4-aminothiophenol (**7a**) and 4-aminophenyl disulfide (**7b**) which introduced para-disubstituted phenyl groups. Resin **6a** had 1.0 mmol SR/g, $X_{2\text{-SR}}$ 15% and yield of 45%, whereas resin **6b** had 0.6 mmol SR/g (0.3 mmol fg/g), $X_{1,2\text{-SR}}$ 4% and yield of 14%. Peaks due to the functional groups could be seen in the spectra of both resins, although more predominately for **6a**. Compared to the spectrum of

XAD-4, the peak at 1606 cm^{-1} increased, and new peaks were seen. Resins **7a** and **7b** also had peaks due to the functional groups, and the peaks at 1599 cm^{-1} and 1494 cm^{-1} increased in comparison to those of the spectrum of XAD-4.

Figure 5.2d shows the spectra of XAD-4 and resins modified with the nitro-aryl thiols (**9a**) and disulfides (**8b**, **9b**). Resin **8b** was modified with 2-nitrophenyl disulfide (**8b**), introducing ortho-disubstituted phenyl groups, while resins **9a** and **9b** were modified with 4-nitrothiophenol (**9a**) and 4-nitrophenyl disulfide (**9b**), introducing para-disubstituted phenyl groups. Although resin **8b** had a low quantity of functional groups (0.26 mmol SR/g, $X_{1,2\text{-SR}}$ 1.7% and yield of 5.3%), the peaks due to the vinyl groups were reduced slightly in comparison to XAD-4, and peaks due to the functional group were seen.

Resins **9a** and **9b** also had low quantities of functional groups (0.11 mmol SR/g, $X_{2\text{-SR}}$ 1.5% and yield of 4.6% for **9a**, and 0.36 mmol SR/g, $X_{1,2\text{-SR}}$ 2.5% and yield of 7.5% for **9b**). Nevertheless, the peaks due to the vinyl groups were reduced slightly in comparison to XAD-4, and peaks due to the functional group were seen.

Figure 5.2e compares the spectra of brominated XAD-4 to the resins prepared by the base-induced thiol addition to brominated XAD-4 (results in table 5.9). For the brominated XAD-4, the vinyl peaks (1630, 1410, 1015, and 990 cm^{-1}) were absent, and peaks due to the (1,2-dibromoethyl)benzene functionality were seen (1236, 1215, 1176, 1130, 602, and 571 cm^{-1}) [42]. The peak at 900 cm^{-1} was also reduced, with a second peak at 892 cm^{-1} visible. As with figures 5.2a and 5.2b, peaks due to the functional groups were also seen in the spectra of the modified resins.

For the resins modified using ethanol (EtOH) and potassium hydroxide, vinyl peaks (1630 and 990 cm^{-1}) appeared in the spectra. Other peaks at 1472 and 1020 cm^{-1} appeared, attributed to the presence of an unsaturated bromine-containing group (e.g. –CR=CBrR', where R or R' is phenyl or H) [43]. Peaks due to CH-Br at 1236 and 1176 cm^{-1} [43] were also present, but to a lesser degree than brominated XAD-4. For the resin modified with thiophenol (**4a**) using ethanol-KOH, peaks due to the thiophenyl groups were seen as well (1439, 1273, 1156, 1091, 1025, 737, and 690 cm^{-1}, as in figure 5.2b).

For the resins modified using DMF and triethylamine, elimination did not occur as extensively. Peaks at 1472 and 1020 cm^{-1} appeared, but little or no peaks were seen at 1630 and 990 cm^{-1}.

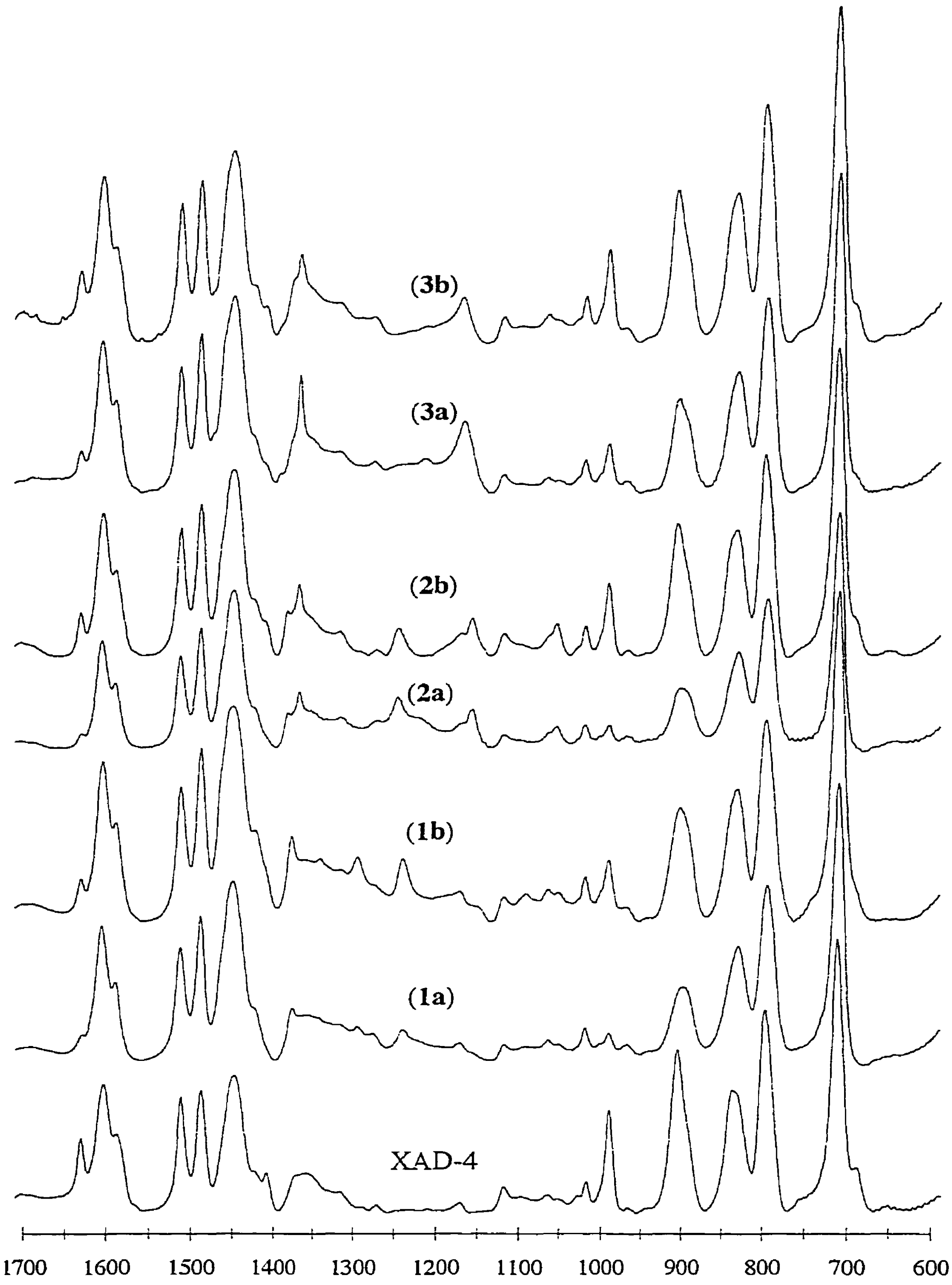


Fig. 5.2a. FTIR absorbance spectra of XAD-4 and modified resins.

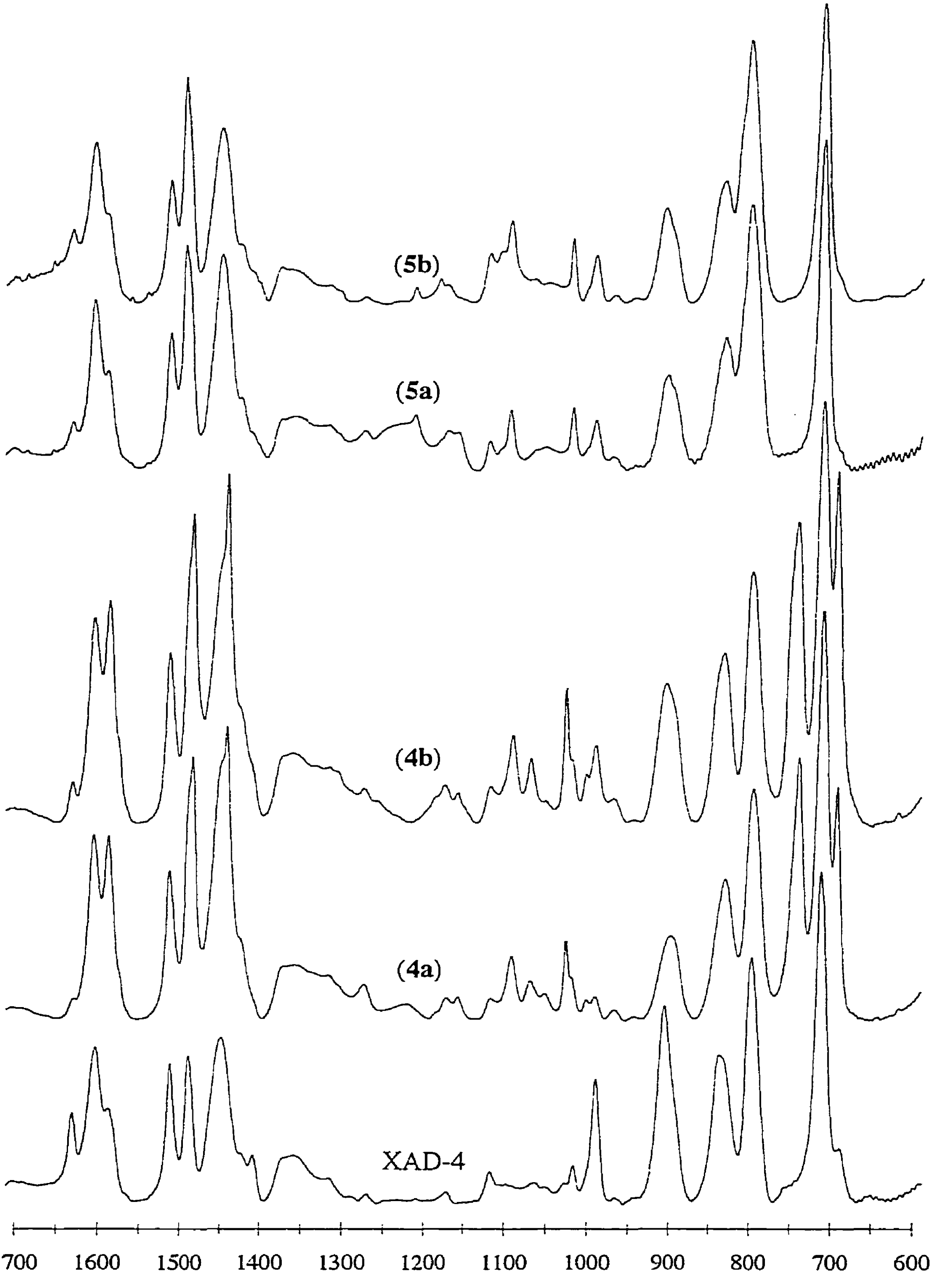


Fig. 5.2b. FTIR absorbance spectra of XAD-4 and modified resins.

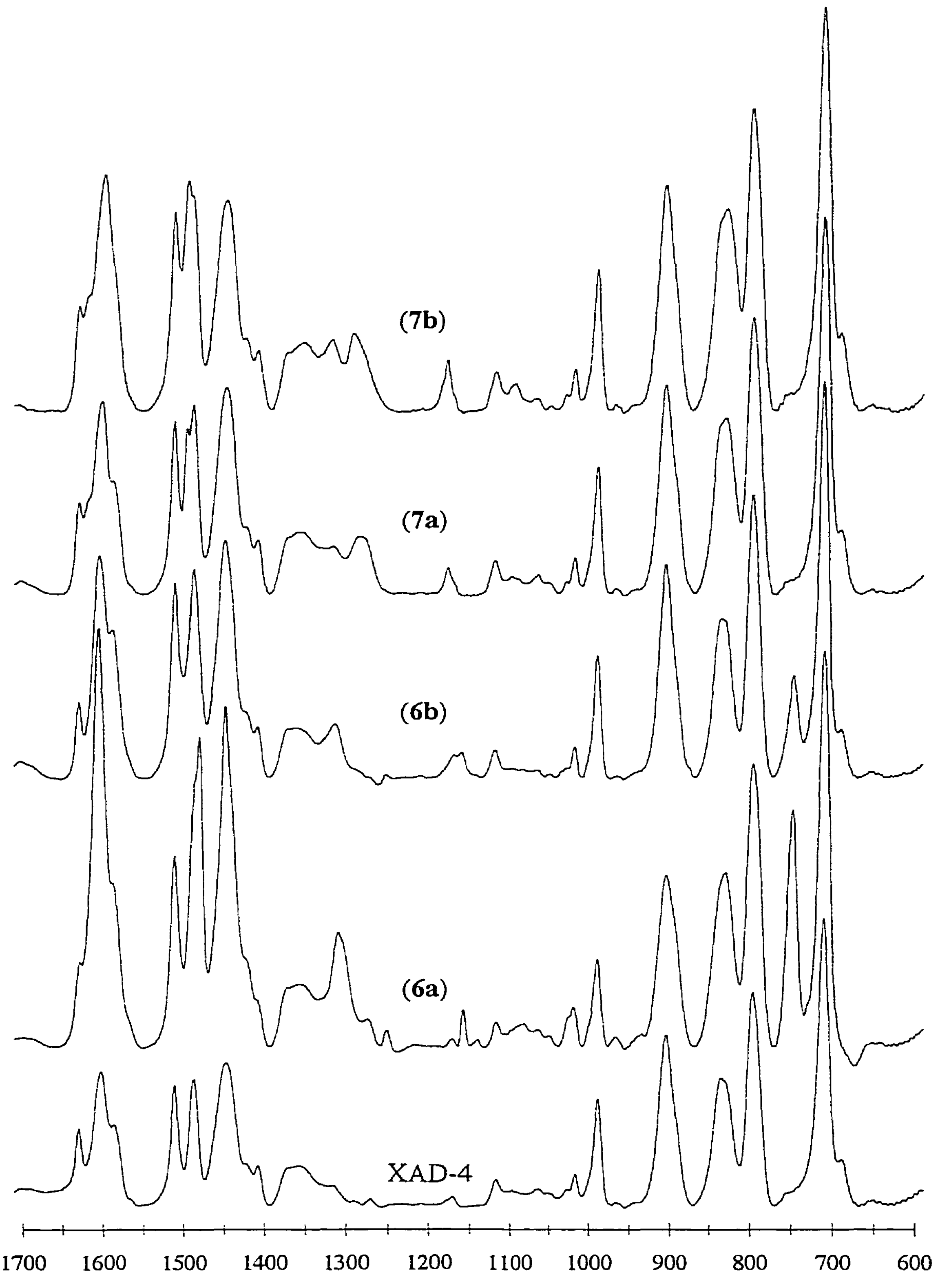


Fig. 5.2c. FTIR absorbance spectra of XAD-4 and modified resins.

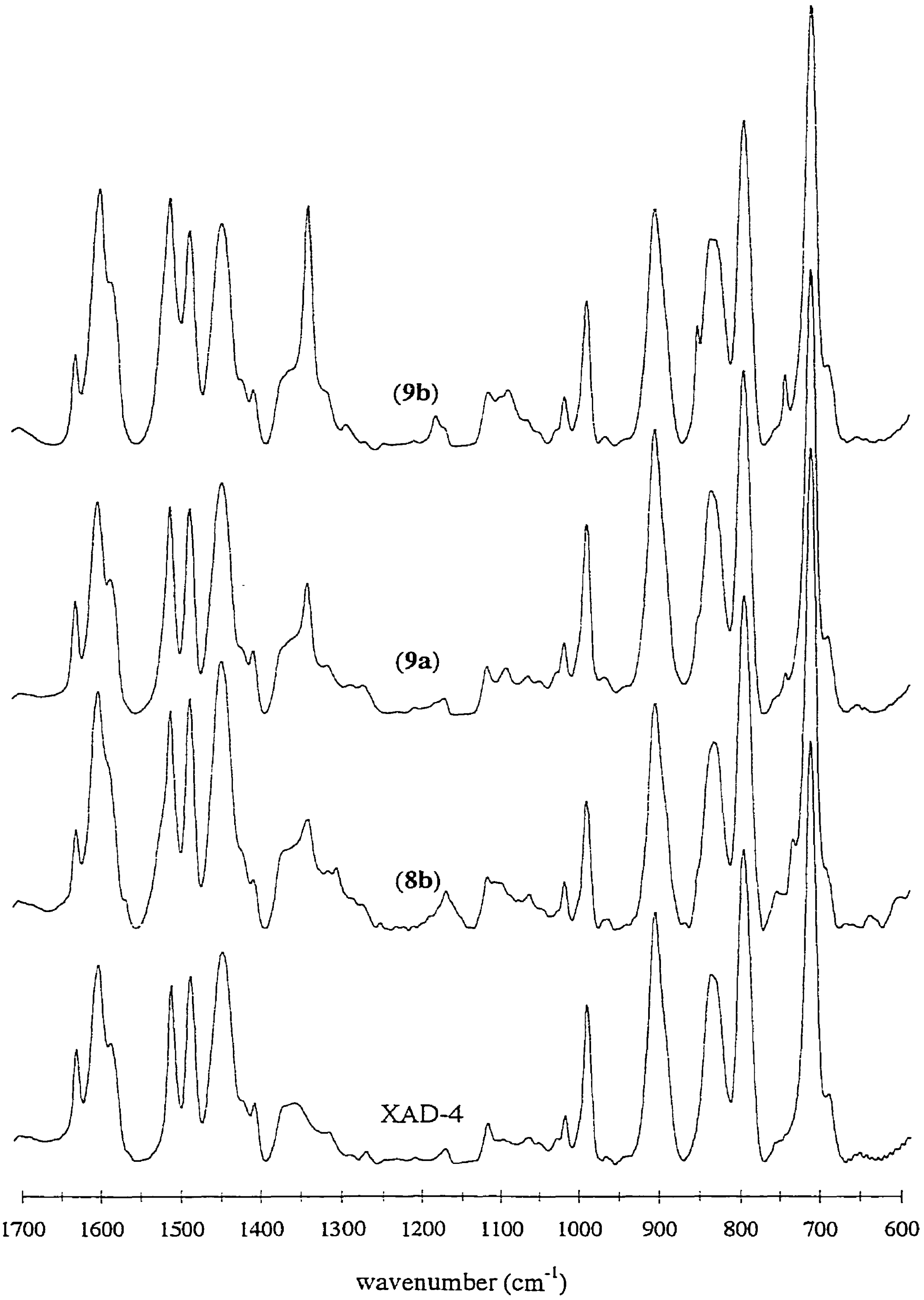


Fig. 5.2d. FTIR absorbance spectra of XAD-4 and modified resins.

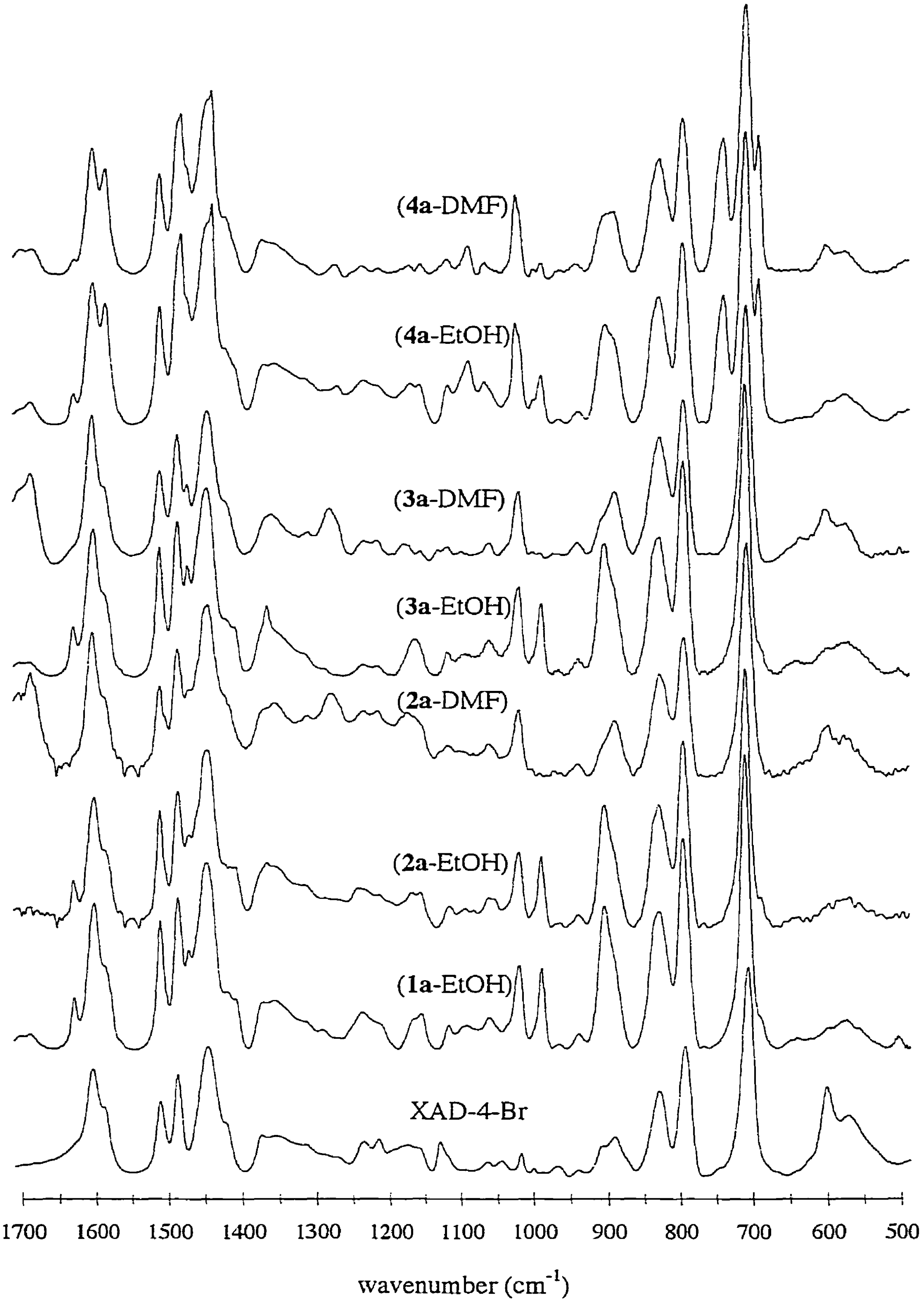


Fig. 5.2e. FTIR absorbance spectra of XAD-4-Br and thiol-modified XAD-4-Br.

5.3.4.2 Raman spectroscopy

Further characterization included Raman spectroscopy. Essentially, a loss of vinyl peaks was seen (1632, 1409, and 1209 cm^{-1}). No thiol (S-H) or disulfide (S-S) peaks were seen in any spectra, confirming that reagents were not physically adsorbed. Spectra did not vary substantially from XAD-4 to modified resins, so none are shown. We have previously shown Raman spectra for XAD-4 [4], and for thiol-modified resins [2].

5.3.4.3 ^{13}C NMR spectroscopy

The ^{13}C NMR spectral peak assignments for unmodified XAD-4 have been presented elsewhere [4]. Table 5.14 gives the ^{13}C CP-MAS-DD NMR peak assignments for modified XAD-4 and for analogous model compounds [44]. The peak at 144 ppm corresponds to the (non-hydrogen) substituted phenyl carbons and the peak at 15-16 ppm corresponds to the methyl carbon of the pendant ethylbenzene groups. The dimethylene spacer was not seen due to limited mobility.

Figure 5.3a shows the solid-phase ^{13}C CP-MAS NMR spectra and figure 5.3b shows the solid-phase ^{13}C CP-MAS-DD NMR spectra for XAD-4 and for the resins modified by alkyl thiols (**1a**, **2a**, **3a**) and disulfides (**1b**, **2b**, **3b**).

Figure 5.4a shows the solid-phase ^{13}C CP-MAS NMR spectra and figure 5.4b shows the solid-phase ^{13}C CP-MAS-DD NMR spectra for XAD-4 and for the resins modified by aryl thiols (**4a**, **5a**, **6a**) and disulfides (**4b**, **5b**, **6b**).

As was seen with the infrared spectra, the intensity of the vinyl peaks were less (137 ppm and 114 ppm) for all modified resins in comparison to XAD-4. The only difference in the spectra of the thiol and disulfide modified resins was the peak intensities, which are dependant on the degree of functionalization as well as the mobility of the functional groups. Dipolar dephasing eliminated the peaks due to the vinyl carbons, the dimethylene spacer linking the thioether(s) to the resin, and the polymer backbone (CH_2, CH, phenyl CH).

The resins modified with 1-propanethiol (**1a**) and *n*-propyl disulfide (**1b**) were comparable in their degrees of functionalization; the disulfide-modified resin had twice as many propyl groups (1.1 mmol SR/g, $X_{2\text{-SR}}$ 16% and yield of 49% for **1a**, and 2.3 mmol SR/g, $X_{1,2\text{-SR}}$ 18% and yield of 55% for **1b**). Unlike the infrared spectra, however, the peaks were more prominent in the NMR spectrum of resin **1a** than that of resin **1b**. This is probably due to the lower mobility of the second propyl group attached to the α carbon in the disubstituted functional group. This trend was seen for the NMR spectra of all resins.

Table 5.14. ^{13}C CP-MAS-DD NMR peak assignments for modified XAD-4

Reagent Used	^{13}C NMR peak assignments for model compounds (a)	C (ppm)	CH_3 (ppm)	CH_2 (ppm)	CH (ppm)
1a, 1b	34.20, 23.07, 13.54* (b)	144	14	35, 23	-
2a, 2b	33.45*, 23.66* (c)	144	22, 14	-	35
3a, 3b	45.50, 33.15* (d)	144, 42	31, 15	-	-
4a, 4b	135.74, 130.95*, 129.08*, 126.93* (e)	144, 138	14	-	129
5a, 5b	140.71, 137.82, 136.45, 133.92, 132.87-132.05, 128.80-127.70, 53.35, 40.60, 21.17*, 21.12* (f)	144, 135-8	20, 15	-	130
6a, 6b	147.82, 134.11*, 129.59*, 120.92, 119.43*, 115.59*, 18.46* (g)	144, 135	15	-	115-120

(a) Data from [44], unless otherwise noted. * means odd parity (i.e. CH, CH_3).
(b) *n*-Propyl sulfide, [44, Vol. 1, p. 428]. Peak at 14 ppm due to CH_3 of *n*-propyl and ethylbenzene groups.
(c) Isopropyl sulfide, [44, Vol. 1, p. 430].
(d) *Tert*-butyl sulfide, [44, Vol. 1, p. 431].
(e) Phenyl sulfide, [44, Vol. 2, p. 440].
(f) Table 5.12. Broad peak at 135-8 ppm due to phenyl carbons (C and CH) of functional group.
(g) 2-(Methylmercapto)aniline, [44, Vol. 1, p. 465]. Broad peak at 115-120 due to many phenyl carbons (C and CH) of functional group.

Figures 5.5a and 5.5b show the solid-phase ^{13}C CP-MAS and ^{13}C CP-MAS-DD NMR spectra for brominated XAD-4 and for the resins modified by base-catalyzed thiol addition to brominated XAD-4 using 1-propanethiol (**1a**) and thiophenol (**4a**) with ethanol and potassium hydroxide (results in table 5.11). The model compound, (1,2-dibromoethyl)benzene, has peaks at 138.53, 129.07*, 128.76*, 127.57*, 50.85*, and 34.99 ppm [44]. These peaks overlap the polymer backbone peaks in the CP-MAS spectrum (figure 5.5a), and the methylene and methine carbons are not mobile enough to be seen in the dipolar-dephased spectrum (figure 5.5b). No peaks due to vinyl groups were seen for the CP-MAS spectrum of brominated XAD-4, whereas the modified resins had vinyl peaks (137 and 114 ppm, figure 5.5a). Small peaks due to the *n*-propyl (**1a**) or phenyl (**4a**) functional groups were seen in the CP-MAS-DD NMR spectra (figure 5.5b) as for the spectra of thiol and disulfide-modified XAD-4 (figures 5.3b, 5.4b, table 5.14).

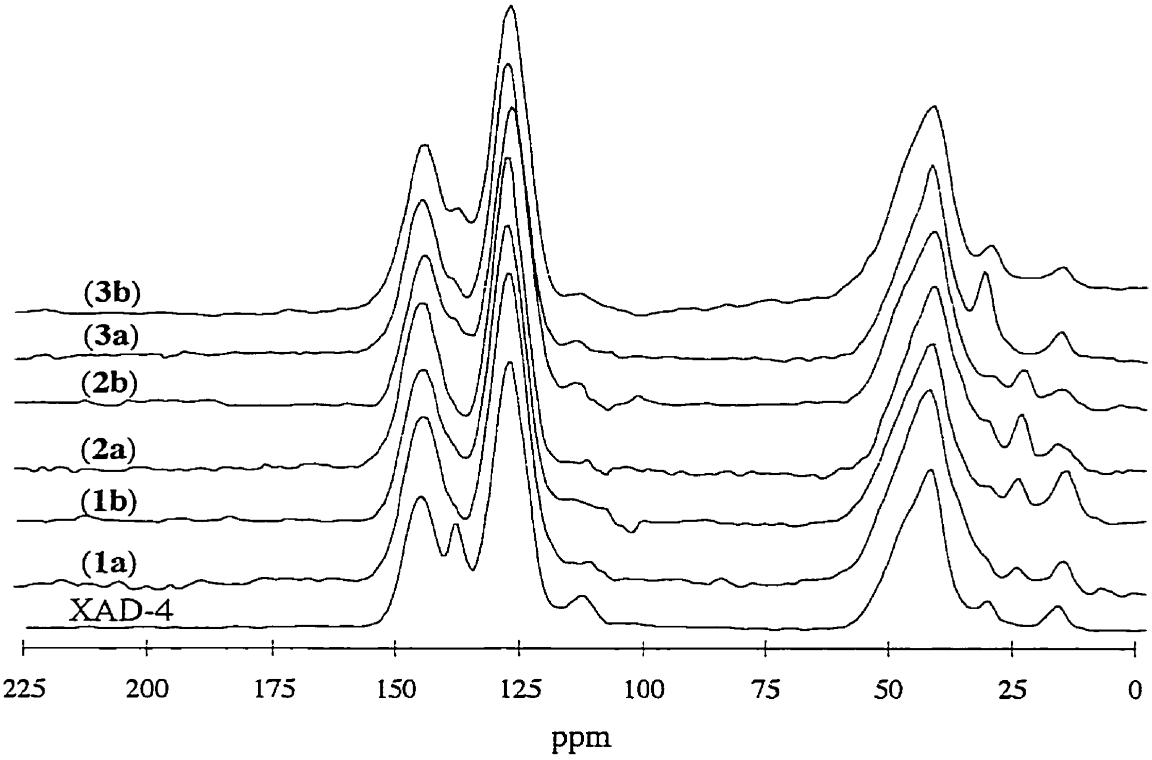


Fig. 5.3a. ^{13}C CP-MAS NMR spectra of XAD-4 and modified XAD-4.

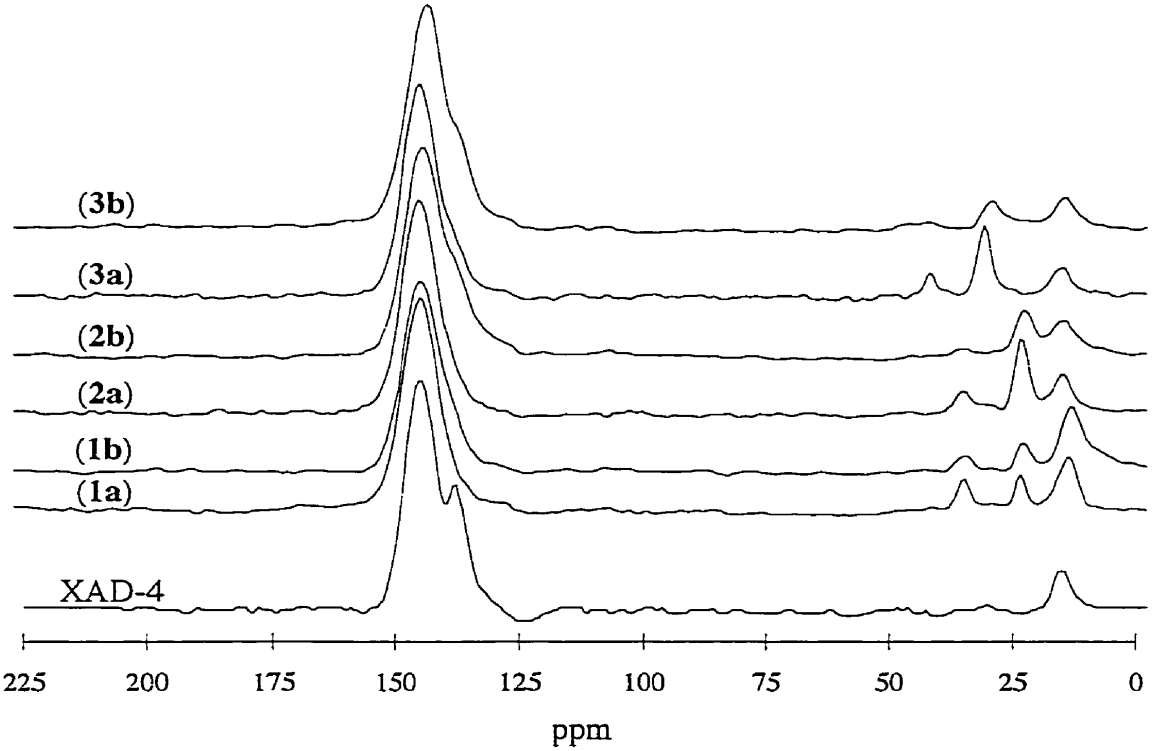


Fig. 5.3b. ^{13}C CP-MAS-DD NMR spectra of XAD-4 and modified XAD-4.

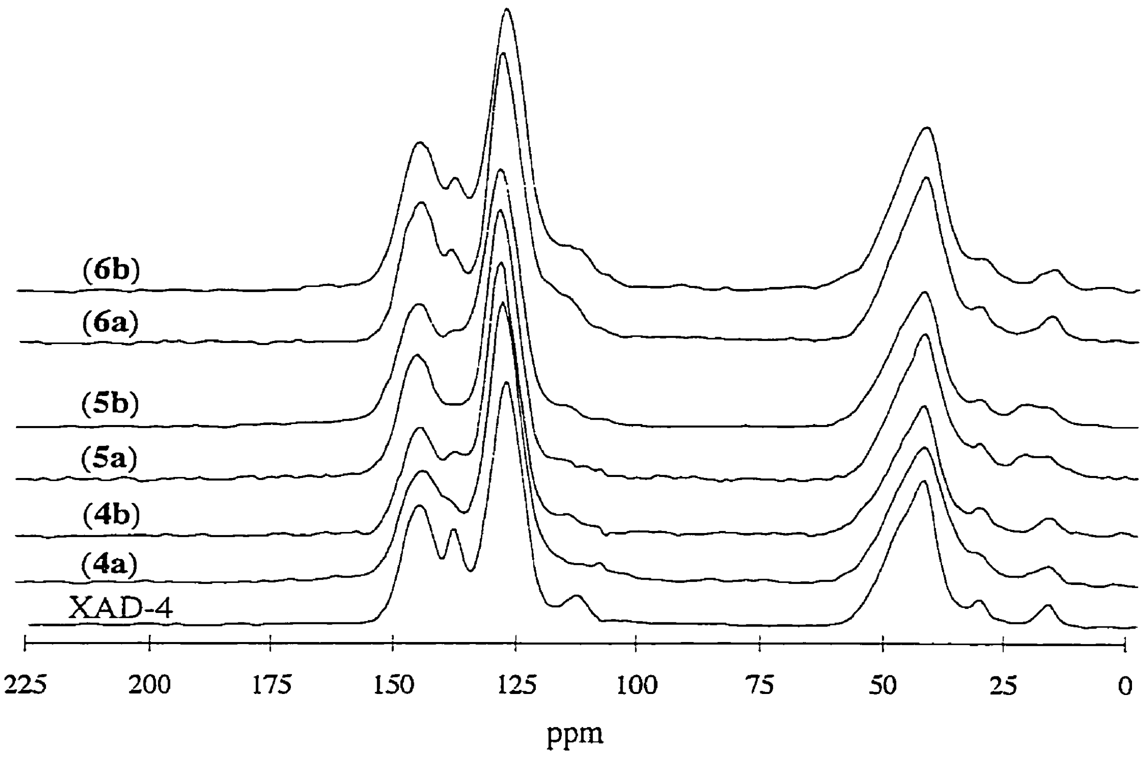


Fig. 5.4a. ^{13}C CP-MAS NMR spectra of XAD-4 and modified XAD-4.

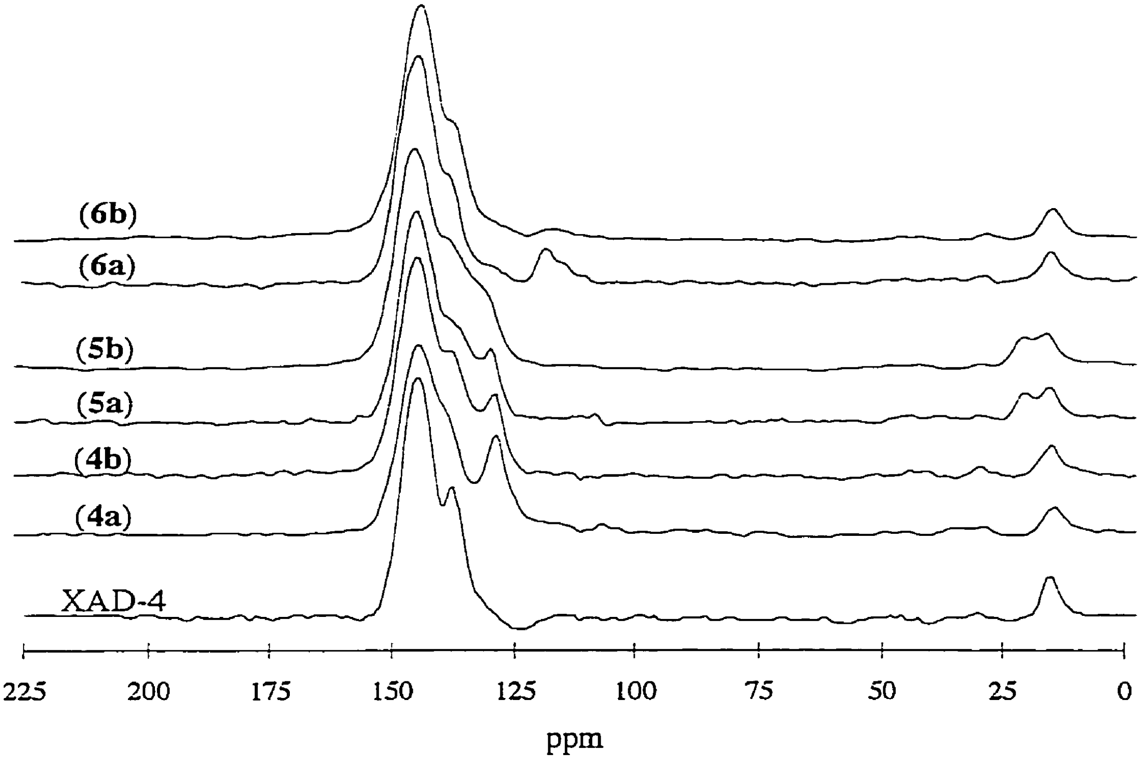


Fig. 5.4b. ^{13}C CP-MAS-DD NMR spectra of XAD-4 and modified XAD-4.

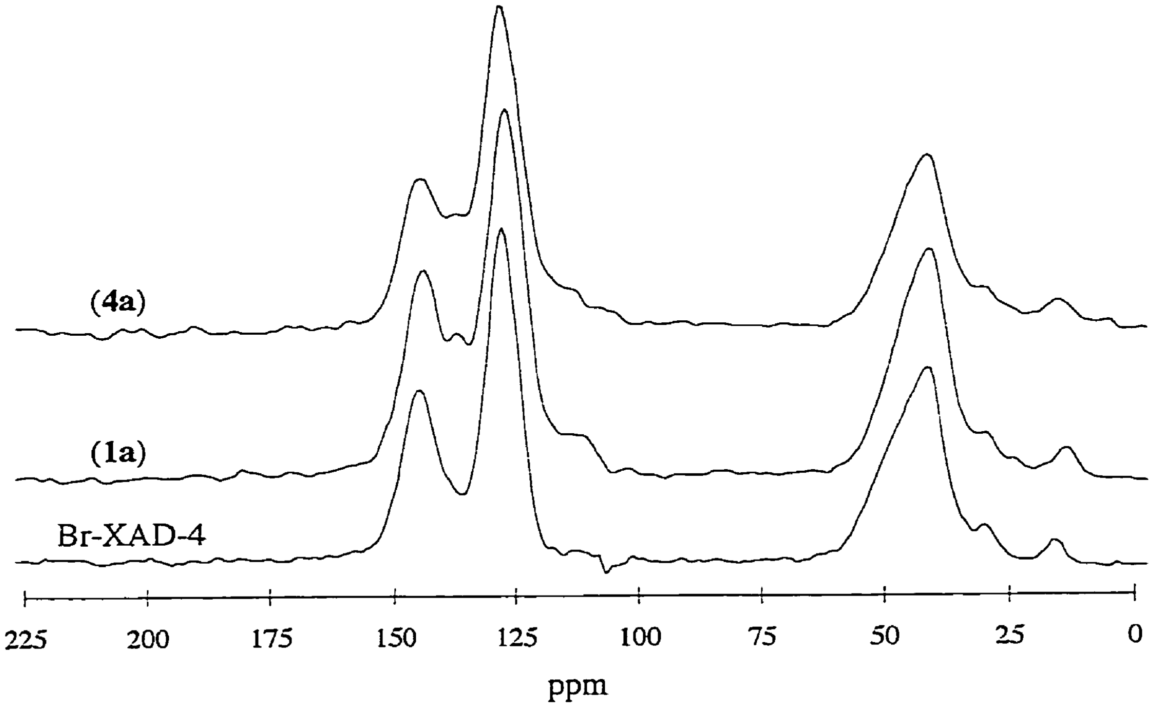


Fig. 5.5a. ^{13}C CP-MAS NMR spectra of brominated XAD-4 and thiol-modified XAD-4-Br.

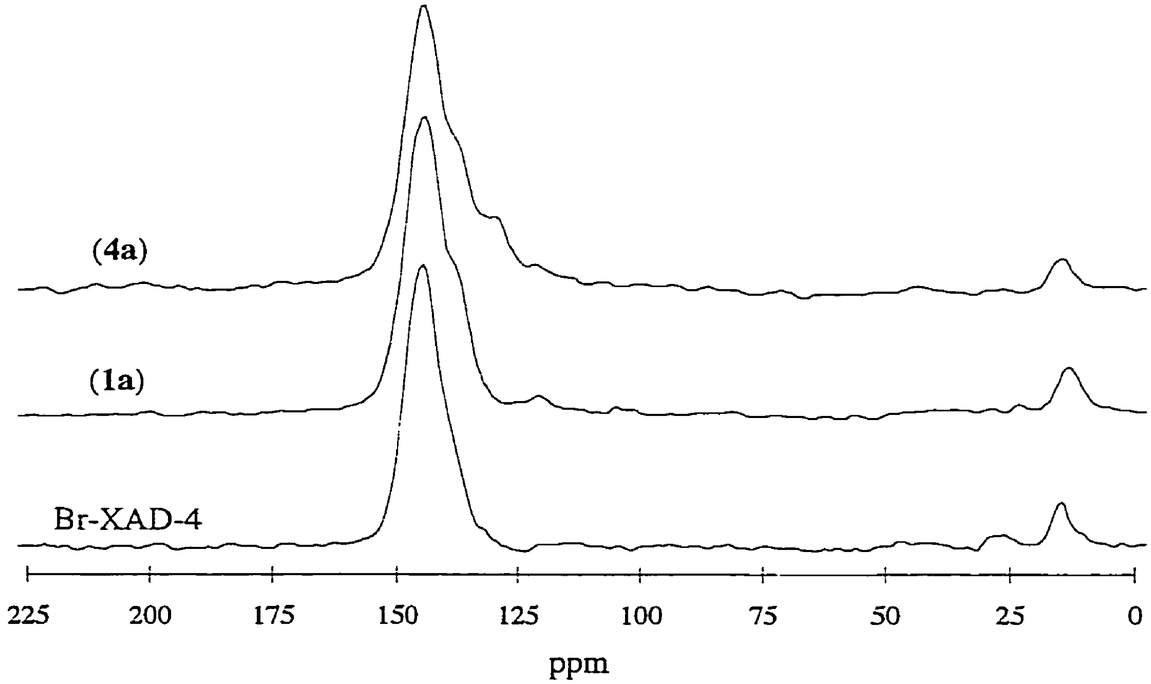


Fig. 5.5b. ^{13}C CP-MAS-DD NMR spectra of brominated XAD-4 and thiol-modified XAD-4-Br.

5.3.5 Potential applications of modified resins and suggestions for further investigations

We have prepared resins which may have potential applications as adsorbents or solid-phase reagents. Modification can change properties of the resins, such as hydrophilicity, which may change behaviour in separation applications such as chromatography [3]. XAD-4 was previously modified for these applications using traditional methodologies [45]. No one has previously modified the vinylbenzene groups of XAD-4 to change its sorption properties.

This modification could also be expanded to other vinyl-containing polymers, such as rubbers or block copolymers, possibly changing various physical characteristics. Linear poly(divinylbenzene) could also be modified to further aid in structure elucidation in comparison of the use of thiol and disulfide for modification.

The use of solvent is not necessary for liquid disulfides; however, due to the noxious qualities of disulfides, solvent use is recommended in order to minimize the volume of disulfide used. Other solvents which could be tried include carbon disulfide or acetic acid [28]. Increasing the amount of iodine used (from 0.1 equiv per vinyl group to as much as 1 equiv) may increase the percent conversion; this could be examined in future studies.

The reaction of allyl disulfide with iodine may lead to a cross-linked resin, rubber or dendrimeric structure since it contains both alkene and disulfide moieties. Variation of reaction conditions such as time, stoichiometries of disulfide and iodine, and the use of solvent may influence structure.

Other disulfides which could be tried include thiocyanogen, $(SCN)_2$, isopropyl-xanthogen disulfide, lipoic acid and its derivatives, tetramethylene disulfide, dithioglycolic acid and its derivatives, methyl disulfide, *n*-butyl disulfide, benzothiazoyl disulfide, *o*-tolyl disulfide, 2,6-xylyl disulfide, 2,3,5,6-tetramethyl phenyl disulfide, carboxyphenyl disulfide and its ethyl ester, 2-hydroxymethyl phenyl disulfide, and halogenated disulfides, including trifluoromethyl disulfide, 2,4,5-trichlorophenyl disulfide, chloromethyl phenyl disulfide, and bromomethyl phenyl disulfide. Many of these have been used in reactions with alkenes, and many have chain transfer constants comparable to those of the disulfides we studied (table 5.2) [19, 20, 23-26, 28, 29]. The presence of these functional groups may change the resin's qualities (such as hydrophobicity), or introduce functionalities such as carboxylic acids, or precursors to other groups. Comparison of degree of functionalization with the use of cyclic disulfides, halogenated disulfides, and disulfides with bulky groups could be made. The addition of carboxylic acids to the vinyl groups may also be possible, as done by Holmberg with dithioglycolic acid [28].

5.4. Conclusions

Amberlite XAD-4, a commercially-available styrenic copolymer, can be modified by disulfide addition to the accessible pendant vinylbenzene groups. We have demonstrated that disulfide addition uses a simple one-step reaction with yields as high as 55%. The most important variables for high conversions of the vinyl groups are the solubility of the disulfide in an appropriate dry solvent, and its ease of cleavage of the S-S bond. Further work with regard to expanding the choice of disulfides and polymers is encouraged.

5.5. Acknowledgements

We wish to thank Rohm and Haas Company for donation of 5 kg of Amberlite XAD-4, and for providing some information used in this paper. Solid phase ^{13}C NMR spectra were taken by Dr. F.G. Morin of the Department of Chemistry, McGill University. M. Petrucci, E. Schultz, and Dr. F. Sauriol helped take liquid state ^{1}H and ^{13}C NMR's. Elemental analyses were performed in part by M. Soon, Department of Oceanography, University of British Columbia. Some repeats of preparations were done by S. Pierre. Some of the infrared spectra were taken by M. Ruzicka, K. Schantz and N. Walicki. Thanks also go to Dr. R.B. Lennox, Dr. D.N. Harpp, and Dr. D.S. Argyropoulos for helpful discussion. Funding for this project was provided by a Natural Sciences and Engineering Research Council of Canada Strategic Grant. Special thanks go to Dr. S. Meyerson and Dr. E.K. Fields for personal correspondence and permission to present some of their previously unpublished data.

5.6. References

[1] J.P. Gao, F.G. Morin and G.D. Darling, Macromolecules, 26 (1993), 1196.

[2] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted May 1997. Chapter 4 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[3] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted April 1997. Chapter 2 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[4] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted April 1997. Chapter 3 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[5] R. Kunin, Amberhilites (produced by Rohm and Haas Co.), Number 161 (spring 1979).

[6] R. Kunin, Amberhilites (produced by Rohm and Haas Co.), Number 163 (winter 1980).

[7] E.F. Meitzner and J.A. Oline, U.S. Patent 4,382,124, issued May 3, 1983.

[8] Food and Drug Administration, U.S. Government, 173.65, page 100 in "Code of Federal Regulations", 21, Food and Drugs. Parts 170 to 199, revised April 1, 1994.

[9] R.L. Albright, React. Polym., 4 (1986), 155.

[10] Supelco Product Catalogue, 1995, page 264.

[11] N.A. de Munck, M.W. Verbruggen and J.J.F. Scholten, J. Mol. Catal., 10 (1981), 313.

[12] J.P.C. Bootsma, B. Eling and G. Challa, React. Polym., 3 (1984), 17.

[13] M Periyasamy, W.T. Ford and F.J. McEnroe, J. Polym. Sci., Polym. Chem. Ed., 27 (1989), 2357.

[14] M.C. Faber, H.J. van den Berg, G. Challa and U.K. Pandit, React. Polym., 11 (1989), 117.

[15] Z. Zhengpu, P. Hodge and P.W. Stratford, React. Polym., 15 (1991), 71.

[16] J.L. Kice, in O.H. Muth and J.E. Oldfield (Editors), Symposium: Sulfur in Nutrition, The AVI Publishing Company, Inc., Westport, 1970. Section 2, Chapter 2, pages 8-12.

[17] C. Von Sonntag and H.P. Schuchmann, in S. Patai (Editor), The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulfur Analogues,

Supplement E, Part 2. John Wiley and Sons, Chichester, 1980. Chaper 22, page 932.

[18] D.I. Davies and M.J. Parrott, Free Radicals in Organic Synthesis. Springer-Verlag, Berlin, 1978. p. 113.

[19] F.W. Stacey and J.F. Harris, Jr., in A.C. Cope (Editor-in-Chief), Organic Reactions. Volume 13. John Wiley and Sons, Inc., New York, 1963. pages 207-208.

[20] G. Haran and D.W.A. Sharp., J.C.S. Perkin I, (1972), 34.

[21] A.V. Tobolsky and B. Baysal, J. Am. Chem. Soc., 75 (1953), 1757.

[22] T. Otsu, J. Polym. Sci., 21 (1956), 559.

[23] R.M. Pierson, A.J. Costanza and A.H. Weinstein, J. Polym. Sci., 17 (1955), 221.

[24] Y. Nambu, M.H. Acar, T. Suzuki and T. Endo, Makromol. Chem., 189 (1988), 495.

[25] K. Endo, K. Murata and T. Otsu, Macromolecules, 25 (1992), 5554.

[26] M Opresnik and A. Sebenik, Polym. Int., 36 (1995), 13.

[27] G.A. Crosby, N.M. Weinshenker and H.S. Uh, J. Am. Chem. Soc., 97 (1975), 2232.

[28] B. Holmberg, Arkiv. Kemi., Mineral. Geol., 12B, number 48, (1938) (in German); Chem. Abstr. 32 (1938), 4155.

[29] B. Holmberg, Arkiv. Kemi., Mineral. Geol., 13B, number 14, (1940) (in German); Chem. Abstr. 34 (1940), 2341.

[30] H.J. Schneider, J.J. Bagnell and G.C. Murdoch, J. Org. Chem., 26 (1961), 1987.

[31] G.W. Francis and K. Veland, J. Chromotogr., 219 (1981), 379.

[32] S. Meyerson and E.K. Fields, Prepr., Div. Pet. Chem., Am. Chem. Soc., 24 (1979), 27; Chem. Abstr. 94 (1981), 174510x.

[33] Personal communication with S. Meyerson and E.K. Fields, May-June, 1996. Data presented here published with permission.

[34] M.C. Caserio, C.L. Fisher and J.K. Kim, J. Org. Chem., 50 (1985), 4390.

[35] D.A. McCaulay and A.P. Lien, U.S. Patent, 2,519,586, issued August 22, 1950; Chem. Abstr. 44 (1950), 10728c.

[36] Rohm and Haas Company, "Amberlite XAD-4. Polymeric Adsorbent." product literature, June 1993.

[37] D.R. Lide and G.W.A. Milne (Editors), Handbook of Data on Organic Compounds. 3rd Ed. CRC Press, Inc., Boca Raton, 1994. Volume 1, page 513;

Volume 2, pages 1239, 1243-1244; volume 3, pages 2520-2523, 2526-2527; and volume 5, pages 4376-4378.

[38] M. Bartholin, G. Boissier and J. Dubois, Makromol. Chem., 182 (1981), 2075.

[39] M.B. Smith, Organic Synthesis, McGraw-Hill, Inc., New York, 1994. page 125.

[40] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym, submitted May 1997. Chapter 7 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[41] E. Kobayashi, T. Obata, S. Aoshima and J. Furukawa, Polym. J., 22 (1990), 803.

[42] C.J. Pouchert (Editor), The Aldrich Library of FT-IR Spectra, Edition 1. Aldrich Chemical Company, Inc., Milwaukee, 1985. Volume 1, pages 255, 257; 258, 266-269, 974, 1173, 1177, 1182, 1183, 1185, 1196, 1197, 1210, 1330, 1341, 1386; and Volume 3, page 349.

[43] J.B. Lambert, H.F. Shurvell, D.A. Lightner and R.G. Cooks, Introduction to Organic Spectroscopy, MacMillan Publishing Co., New York, 1987. pages 197, 201, 211, 219, 222.

[44] C.J. Pouchert and J. Behnke (Editors), The Aldrich Library of ^{13}C and ^{1}H FT-NMR Spectra, Edition 1. Aldrich Chemical Company, Inc., Milwaukee, 1993. Volume 1, pages 428, 430, 431, 465; and Volume 2, pages 65, 440.

[45] T.A. Armer, Ph.D. Thesis, Tulane University, Diss. Abstr. Int. B 43 (6) (1982), 1910; Chem. Abstr. 98 (1983), 35435w.

Chapter 6

Epoxidation of the Pendant Vinylbenzene Groups of Commercial poly(Divinylbenzene-*co*-Ethylvinylbenzene).

Forward to Chapter 6

The content of the following section is comprised of a paper with the same title which will be submitted to the journal Reactive and Functional Polymers (K.L. Hubbard, G.D. Darling and J.A. Finch, expected submission June 1997).

The previous sections focused on modification of poly(divinylbenzene-*co*-ethylvinylbenzene) by the addition of thiols and disulfides to the pendant vinylbenzene groups, producing resins with mono- and disubstituted thioether-linked functionalities. This chapter expands on the methods used to modify poly(divinylbenzene-*co*-ethylvinylbenzene), by epoxidation of the pendant vinylbenzene groups to produce a functional resin with epoxy groups which has the potential to act as a precursor for the introduction of other functionalities. Many methods which were either not previously used with a polymer system, or were used with a few polymers, or were traditional polymer epoxidation methods, are compared in the modification of commercial poly(divinylbenzene-*co*-ethylvinylbenzene). Commercial poly(divinylbenzene-*co*-ethylvinylbenzene) has not previously been used to prepare resins with epoxy groups by oxidation of the pendant vinylbenzene groups.

Abstract

Amberlite XAD-4, the commercial form of poly(divinylbenzene-*co*-ethylvinylbenzene), was modified by the oxidation of its pendant vinylbenzene groups. Of several methods used, only oxidation with dimethyldioxirane in acetone produced pendant epoxides without further rearrangement. Attempted conversion to episulfide groups led to ring-opening with a mixture of functional groups.

Keywords: Amberlite XAD-4, poly(divinylbenzene-*co*-ethylvinylbenzene), epoxidation, pendant vinyl groups

6.1. Introduction

This paper discusses the modification of vinyl groups in a polystyrene-like matrix. Commercial poly(divinylbenzene-*co*-ethylvinylbenzene) was modified by the oxidation of the pendant vinylbenzene groups. Variation of reaction conditions and reagents were studied. Conversion of the epoxide to episulfide was attempted.

Previously, our group modified laboratory-made poly(divinylbenzene-*co*-ethylvinylbenzene) by the anti-Markovnikov radical addition of a few simple thiols to the pendant vinylbenzene groups [1]. We have recently expanded upon this work to include the use of a commercial resin, Amberlite XAD-4, as well as a greater range of thiols and conditions [2]. Further work studied the addition of various disulfides and analogous thiols [3].

One advantage of modifying XAD-4 by epoxidation of the vinylbenzene groups to prepare functional resins is that only a one-step modification of a commercially-available matrix is needed. The reaction conditions are generally straightforward and purification of the modified resin is simple.

6.1.1 Commercial poly(divinylbenzene-*co*-ethylvinylbenzene)

Copolymers of divinylbenzene and ethylvinylbenzene have a cross-linked structure with pendant vinylbenzene and ethylbenzene groups (figure 6.1). The degrees of functionalization are indicated by the symbols X_{CL}, X_{VB}, and X_{EB}, (CL for cross-linked, VB for vinylbenzene, and EB for ethylbenzene). The randomly-occurring repeat units are meta- and para-disubstituted.

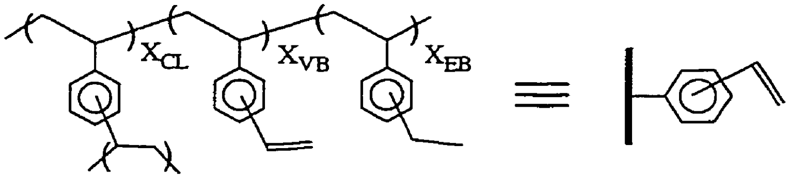


Fig. 6.1. Structure of poly(divinylbenzene-*co*-ethylvinylbenzene).

Amberlite XAD-4 (Rohm and Haas Company) is a macroporous resin prepared from 80 to 85 wt % divinylbenzene and 15 to 20 wt % ethylvinylbenzene [4-10]. Since XAD-4 has a high surface area (725 to 1040 m^2/g) and porosity (0.98 to 1.55 mL/g), vinyl groups should be accessible to reagents used during modification which will promote high conversions to functional groups [4, 5, 10-12]. The vinyl content ranges from 29 to 41% (2.2 to 3.1 mmol/g) depending on lot [5]. Besides ourselves, only five research groups have mentioned the presence of vinyl groups in XAD-4 [12-16], and of these, only two actually modified the resin by reaction with the vinyl functionality [15, 16].

6.1.2 Introduction of epoxy groups into polymeric substrates, and subsequent reactions

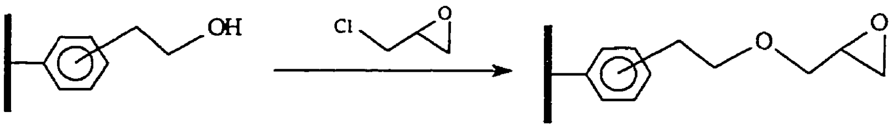
A styrenic resin with epoxy groups can act as a precursor for many functional polymers. Previously, work on epoxide-containing polymers has included ring-opening reactions with amines, carboxylic acids, and other nucleophiles [17].

Many preparations of polymers with epoxy groups have been done previously. Pendant vinyl groups of a styrenic resin were epoxidized using *m*-chloroperbenzoic acid (*m*CPBA) to form poly(*p*-oxirane-styrene) [18]. Some ring-opening of the epoxide occurred. Poly(*p*-oxirane-styrene) was also prepared by reaction of polystyrene carboxaldehyde with trimethyl sulfonium chloride using phase transfer conditions [18]. The epoxide groups were further reacted with amines such as dimethylamine.

Cross-linked poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) was prepared using suspension polymerization to produce a resin with 60% epoxy content (degree of functionalization) [19]. Amines which were then reacted with the epoxy group included 2-aminomethyl pyridine and 2-aminothiophenol to form chelating resins with degrees of functionalization of 33% and 19% respectively.

Further work was done using poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) [20, 21]. Conversion of the epoxy groups to thiirane groups was accomplished by reaction with thiourea in the presence of dilute sulfuric acid [20]. Characterization of both the epoxy and thiirane resins included solid-state ^{13}C CP-MAS NMR, infrared (FTIR) and Raman spectroscopy [20]. NMR spectral peaks for the epoxy were seen at 48 ppm, and for the thiirane at 30.5 and 38.3 ppm. The FTIR spectra had peaks for the epoxy at 850, 910, 1340, and 1480 cm^{-1}, and for the thiirane at 620, 910, 1330, and 1440 cm^{-1}. Addition of various azoles to either the epoxy resin or thiirane resin was done with conversions ranging from 50 to 78% [20]. A benzimidazole-containing ligand was also added either through addition of the pre-synthesized ligand or by a multi-step polymer modification [21]. Addition of the ligand to the resins led to 18.7% (epoxy resin) and 27.1% (thiirane resin) conversions compared to 10.7% conversion of the epoxy group to the functional group through the multi-step modification.

Styrenic resins with pendant epoxy groups were prepared from poly(hydroxyethylstyrene) [22]. Two methods were used: the addition of epichlorohydrin under basic phase transfer conditions, and the addition of epichlorohydrin with boron trifluoride-etherate, followed by cyclization of the chlorinated alcohol derivative with sodium methoxide (scheme 6.1). The latter method gave a higher yield of epoxy groups (1.5 mmol/g compared to 1.25 mmol/g for the first method). However, the first method was reported to be easier and more reproducible. Reactions of the epoxy groups included with various concentrations of hydrochloric acid to produce either the chlorinated alcohol derivative (0.25 M HCl) or the chlorinated alcohol derivative with some diol groups (0.05 M HCl), with dilute sulfuric acid (0.05 to 0.25 M) to produce only the diol, and additions of either aldehydes, chlorinated alcohols, carboxylic acids, or amines.



Scheme 6.1. Preparation of styrenic resin with epoxy groups [22].

Styrene-butadiene-styrene linear block copolymer was epoxidized with hydrogen peroxide (H_2O_2) and a phase transfer catalyst, methyltrioctylammonium tetrakis(diperoxotungsten)phosphate (3-) [23]. A biphasic mixture of 30% H_2O_2 and either toluene or 1,2-dichloroethane was used, with toluene giving better results. The order of reactivity of double bonds in the butadiene block toward epoxidation was cis-1,4 > trans-1,4 >> 1,2.

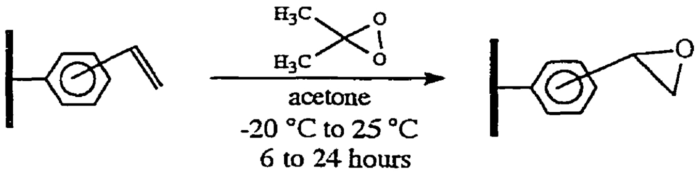
The previous method was attempted with no success to epoxidize a block copolymer consisting of styrene and 1,2-butadiene units [24]. The polymer was epoxidized successfully with *m*CPBA in toluene. Other solvents tried included dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$), with toluene giving the best results. The epoxy groups were then modified with various nucleophiles such as diethylamine, ethylenediamine, 2-mercaptobenzothiazole, and 2-mercaptopyridine, benzoic acid and various acid chlorides, to produce amphiphilic block copolymers.

Poly(β-malic acid) with pendant allyl groups was epoxidized with *m*CPBA, as well as dimethyldioxirane (DMD) [25]. The polymer, dissolved in anhydrous CH_2Cl_2, was reacted at room temperature either with *m*CPBA (1.3-2 equiv, 1.5 to 10 days, yield 40-100%) or with a solution of DMD in acetone (6 equiv, 1 day, 100% yield).

Dimethyldioxirane has also been used in the oxidation of polymer-containing silanes to form polymer-containing silanols [26, 27]. DMD has also been use to bleach Kraft pulps [28]. We have not found any other references to the use of DMD in epoxidation of polymeric substrates (besides [25]).

Epoxidation of polybutadiene and styrene-butadiene-styrene block copolymers was done using monoperoxyphthalic acid (MPPA) [29]. Either dioxane or dioxane-$CHCl_3$ (1:2 v/v) were used as solvent, with temperatures ranging from 25 °C to 50 °C, and reaction times up to 100 minutes. Polybutadiene was epoxidized with as much as 54% conversion at 50 °C in 40 minutes using dioxane as the solvent.

We are the first to take advantage of the ideal characteristics of XAD-4 to prepare functional resins by conversion of the vinylbenzene groups to epoxides and present our results on modifying XAD-4 with a variety of reaction conditions, including with dimethyldioxirane (scheme 6.2). Many different epoxidation techniques were attempted. Some methods have been previously used in polymer modification, as noted above, while others have not, and were adapted from syntheses involving small molecules.



Scheme 6.2. Epoxidation of vinylbenzene groups of XAD-4 with dimethyldioxirane.

6.1.3 Introduction of thiirane groups into polymeric substrates

We also wanted to prepare thiirane-containing resins by modification of the pendant vinylbenzene groups. The most straightforward technique would be conversion of the epoxide to the thiirane. Previously, resins based on glycidyl methacrylate (2,3-epoxypropyl methacrylate), were converted to thiirane resins using either thiourea or potassium thiocyanate [30]. Reaction conditions which were varied included solvent and temperature. The optimal conditions were with a water-dioxane solvent mixture (1:1 v/v), 10 equiv thiourea, 90 °C, and 1 day to produce a resin with 3.3 mmol thiirane/g (87% conversion of epoxide groups). An alternative method used dilute sulfuric acid to catalyze the addition of 5 equiv thiourea in water at room temperature for 6 hours, with a yield of 3.0 mmol thiirane/g. The optimal conditions when potassium thiocyanate was used were: 10 equiv KSCN, dioxane as the solvent, 100 °C, and 1 day with a yield of 2.9 mmol thiirane/g (76% conversion).

6.2. Experimental

6.2.1 Materials

Unless otherwise noted, all materials were purchased from Aldrich Chemical Company and used as received. The same lot (#1090-7-1473) of Amberlite XAD-4 was used throughout this study, obtained from Rohm and Haas Co. XAD-4 comes imbibed with sodium chloride and sodium carbonate to retard bacterial growth [31]. Unless otherwise noted, all resins were pretreated by Soxhlet extraction with acetone for several days, followed by drying under vacuum overnight at 60 °C. Water was doubly-distilled.

6.2.2 Epoxidation of pendant vinylbenzene groups

Work-up for most reactions involved filtering the resin, washing with solvent and then Soxhlet extraction for several days with a variety of solvents. The solvents used for Soxhlet extraction of modified resins included methanol (MeOH), dichloromethane (CH_2Cl_2), water, ethanol-dioxane azeotrope (90.7:9.3 w/w, bp 78.1 °C), water-dioxane azeotrope (18.4:81.6 w/w, bp 87.8 °C), or acetone. The purified resins were dried under vacuum at 70 °C for one day.

6.2.2.1 Epoxidation with hydrogen peroxide and acetonitrile, benzonitrile, or trichloroacetonitrile

Using methods which were modified from epoxidations of small molecules, including styrene, epoxidation was done using hydrogen peroxide and acetonitrile [32, 33], benzonitrile [34], or trichloroacetonitrile [35]. The pH of the H_2O_2 was adjusted with potassium carbonate (K_2CO_3). Typical modified procedures follow.

In a 100 mL 2-neck round bottom flask with magnetic stirring bar and condenser, 1 g of resin (2.5 mmol vinyl), 20 mL methanol, 30% H_2O_2 (3 mL, 25 mmol, 10 equiv per vinyl group, pH 8-8.5) and either acetonitrile (3 mL, 50 mmol, 20 equiv per vinyl group) or benzonitrile (5 mL, 50 mmol, 20 equiv per vinyl group) were added. The stirring mixture was heated to 65 °C, and additional amounts of H_2O_2 (10 equiv) and nitrile (20 equiv) were added at 30 minute intervals over 3 hours (total of 6 additions). The resin was then filtered and purified with Soxhlet extraction using methanol.

A similar method was used for epoxidation using trichloroacetonitrile and hydrogen peroxide. The reactions conditions included: 1 g of resin, 50 mL methanol, 30% H_2O_2 (3 mL, 25 mmol, 10 equiv per vinyl group, pH 7.5-8), trichloroacetonitrile (5 mL, 50 mmol, 20 equiv per vinyl group), and temperature 75 °C. Additional amounts of H_2O_2 (10 equiv) and nitrile (20 equiv) were added at 6 hour intervals over 1 day (total of 4 additions).

6.2.2.2 Epoxidation with hydrogen peroxide and ethyl chloroformate

We adapted a small molecule epoxidation method which generates *O*-ethylperoxycarbonic acid in situ by the reaction of hydrogen peroxide with ethyl chloroformate [36]. The pH of the H_2O_2 was adjusted to 9.5 with sodium phosphate (Na_3PO_4).

In a 50 mL round bottom flask with magnetic stirring bar, 1 g of resin (2.5 mmol vinyl), 15 mL dichloromethane, and 30% H_2O_2 (4 mL, 38 mmol, 15 equiv per vinyl group, pH 9.5) were cooled to 0 °C with an ice bath. Ethyl chloroformate (1.2 mL, 13 mmol, 5 equiv per vinyl group) was added dropwise. The stirring mixture was allowed to warm to room temperature and taken off after one day. The resin was then filtered and purified with Soxhlet extraction using methanol, then acetone.

6.2.2.3 Epoxidation with hydrogen peroxide and methyltrioctylammonium tetrakis(diperoxotungsten)phosphate (3-)

The phase transfer epoxidation catalyst, methyltrioctylammonium tetrakis(diperoxotungsten)phosphate (3-), was prepared using the method of Venturello [37]. Reaction was done in either toluene or 1,2-dichloroethane. In a typical reaction, resin (5 g, 12.5 mmol vinyl groups) was swelled in 50 mL toluene, and catalyst (2.8 g, 1.3 mmol, 0.1 equiv per vinyl group) and 30% H_2O_2 (15 mL, 125 mmol, 10 equiv per vinyl group) were added. The mixture was stirred at 85 °C for one day, with additional H_2O_2 (15 mL) added after 12 hours. The resin was then filtered and purified with Soxhlet extraction using ethanol-dioxane azeotropic mixture, then acetone.

Reactions using an excess of the catalyst and no H_2O_2 were done in both toluene and 1,2-dichloroethane. Resin (0.5 g, 1.25 mmol vinyl groups) and catalyst (4.5 g, 1.9 mmol, 1.5 equiv per vinyl group) were swelled in 30 mL solvent. The reaction proceeded at 85 °C (toluene) or 70 °C (1,2-dichloroethane) for one day. The resin was then filtered and purified with Soxhlet extraction using dichloromethane, then acetone.

6.2.2.4 Epoxidation with *m*-chloroperbenzoic acid (*m*CPBA)

Epoxidation with *m*CPBA was done using two methods. In both methods, *m*CPBA was added to a chilled mixture of resin in solvent (0 °C) and the mixture was allowed to warm to room temperature. The first method was adapted from that of Ziffer using a biphasic system [38]. A mixed solvent of dichloromethane and water (2:1 v/v, water adjusted to pH 8 with $NaHCO_3$) was used with two additions of *m*CPBA (1 equiv per vinyl group for each addition), one at the beginning and one after 1.5 hours. The reaction continued after the second addition for another 1.5 hours.

The second method used either chloroform, toluene or dichloromethane, and one addition of *m*CPBA (1.05 equiv per vinyl group). The reaction ran at room temperature for either 1.5 hours or 1 day. With both methods, Soxhlet extraction was done using dichloromethane followed by ethanol.

6.2.2.5 Epoxidation with magnesium monoperoxyphthalate (MMPP)

Reactions with MMPP were done with many solvents including: *N,N*-dimethylformamide, ethanol, dioxane, chloroform, water, and solvent mixtures such as dioxane-chloroform (1:2 v/v), chloroform-water (1:8 v/v), isopropanol-water (1:8 v/v), methanol-water (1:8 v/v), and ethanol-water (1:8 v/v). A typical reaction involved stirring resin (1 g, 2.5 mmol vinyl groups), MMPP (7.7 g of 80% MMPP, 13 mmol, 5 equiv per vinyl group), and 85 mL solvent for 2 days at temperatures ranging from 50 °C to 100 °C. In some reactions, poly(ethylene glycol) (M.W. 600) was also added (12-25 wt % to resin). The resin was then filtered and purified with Soxhlet extraction using water-dioxane azeotropic mixture, then acetone.

6.2.2.6 Epoxidation with peracetic acid

Resin (1 g, 2.5 mmol vinyl groups) was swelled in dichloromethane (15 mL) and cooled to 0 °C. Peracetic acid (2.5 mL of a 32% solution, 10 mmol, 4 equiv per vinyl group) was added and the mixture stirred for 6 hours. Other solvents used were ethanol and chloroform. The resin was purified by Soxhlet extraction with acetone.

6.2.2.7 Epoxidation with dimethyldioxirane (DMD)

Two methods of epoxidation with DMD were used. The first involved the in situ generation of DMD, as previously described [39]. Essentially, resin, buffered water (pH 7.5, phosphate buffer) and acetone (22-27 equiv per vinyl group) were mixed, and small quantities of Oxone (3-5 equiv per vinyl group in total, $2KHSO_5$-$KHSO_4$-$K2SO_4$) were added. To maintain the pH at 7.5, a pH stat method was used with potassium hydroxide solution (0.5-10 M) as titrant. Soxhlet extraction was done with water, followed by acetone.

The second method used a prepared acetone solution of DMD. The method of DMD preparation was a variation of Adam's method [40]. A 5 L glass reaction vessel was fitted with a mechanical stirrer, a water condenser was attached and connected with glass tubing in sequence to a dry ice-acetone condenser, followed by a cold trap (dry ice-acetone), and then a water aspirator. The dry ice-acetone condenser had a receiving flask in a dry ice-acetone bath. The reaction vessel was cooled to less than 10 °C with an ice-water bath. Water (250 mL), reagent grade acetone (190 mL), and $NaHCO_3$ (60 g) were added and stirred vigorously (650 rpm). Oxone was added at 3 minute intervals in 5 portions (24 g each). After the last addition, the water aspirator was turned on and a yellow solution of DMD in acetone slowly distilled and was collected in the receiving flask. Some DMD solution was also collected in the trap. The DMD was stored at -20 °C until used, within a few days. The concentration of DMD was 0.05 M, as measured by iodometric titration [28].

In all reactions with acetone solutions of DMD, work-up involved evaporation of the acetone followed by drying in vacuo at 70 °C for one day. Resin (0.5 g, 1.25 mmol vinyl groups) was mixed with DMD solution (30 mL, 1.5 mmol, 1.2 equiv per vinyl group). The mixture was left for one day at -20 °C and then for an additional 8 hours at room temperature or just at room temperature for 8 hours. An alternate method involved contacting several smaller volumes of DMD solution followed by evaporation each time after a 45 minute contact. Resin (0.5 g, 1.25 mmol vinyl groups) was mixed a total of 6 times with fresh DMD solution (5 mL each, 1.75 mmol in total, 1.4 equiv per vinyl group in total) at room temperature.

6.2.3 Acid-catalyzed reaction of epoxy groups with *N,N*-dimethylthioformamide

One sample of XAD-4 epoxidized with DMD was further reacted to convert the epoxide groups to thiirane groups. A method previously used to convert styrene epoxide to the thiirane was adapted for use with a polymeric system [41]. Epoxidized resin (epoxy-XAD-4, 1 g, 2.4 mmol epoxy groups) was swelled in 1,2-dichloroethane (25 mL), and *N,N*-dimethylthioformamide (TDMF, 4 mL, 24 mmol, 10 equiv per epoxy group) was added, followed by trifluoroacetic acid (as a solution in 1,2-dichloroethane, 0.5 mmol, 0.2 equiv per epoxy group). The mixture was then heated for 3 hours at 60 °C under nitrogen. Soxhlet extraction was done using acetone, tetrahydrofuran, and then acetone again for one day each.

6.2.4 Characterization

6.2.4.1 Elemental analysis

Samples were sent to Robertson Microlit Laboratories (Madison, NJ) to be analyzed for sulfur or oxygen, where applicable.

6.2.4.2 Infrared spectroscopy

The unmodified resin was characterized using infrared spectroscopic analysis to measure the vinyl group content [5, 42]. Modified resins were characterized to determine reduction of vinyl peaks and introduction of peaks due to the modifying groups. Samples were ground into powder with FTIR-grade potassium bromide (KBr) and disks were prepared. Fourier transform infrared absorbance spectra were taken with a Bruker IFS 66 spectrometer, using a DTGS detector and 2 cm^{-1} resolution, with 120 to 200 scans.

6.2.4.3 Raman spectroscopy

Fourier transform Raman spectra were taken using a Bruker IFS 88 spectrometer with FRA-105 Raman module using a Nd^{+3}:YAG laser (1064.1 nm). Samples were ground into powder and packed lightly into an aluminum sample cup. The number of scans ranged from 250 to 5000, with a 4 cm^{-1} resolution. It should be noted that when spectra were taken with samples in glass melting point tubes had fluorescence due to the glass, obscuring most peaks, so this method was not used.

6.2.4.4 ^1H and ^{13}C NMR spectroscopy

Solid-phase ^{13}C NMR spectra were obtained with a Chemagnetics Inc. CMX-300 instrument. ^{13}C CP-MAS (cross-polarization magic angle spinning) NMR spectra were obtained at 75.3 MHz with contact time of 3 ms, recycle delay of 1 s, number of transients of 2000-8000, and spectral window 30 kHz. The FID was sampled with 256 points, zero-filled to 2048 points and apodized with 50 Hz of line-broadening before Fourier transformation. The spinning speed was 4000 Hz. Spinning sidebands were eliminated by the application of the TOSS pulse sequence. Proton decoupling was done at a field strength of 60 kHz. The ^{13}C CP-MAS-DD (DD is dipolar dephasing) NMR spectra were obtained similarly, with a dephasing time (τ) of 45 μs. Samples were referenced to hexamethylbenzene.

One sample of XAD-4 epoxidized with DMD was swelled in deuterated chloroform. ^{1}H and ^{13}C NMR spectra were measured on a Jeol 270 MHz spectrometer referenced to tetramethylsilane.

6.3. Results and Discussion

6.3.1 Characteristics of starting materials

Previously, we characterized the starting material with regard to vinyl content, surface area, porosity, and monomer content and the results are fully presented elsewhere [4]. Table 6.1 summarizes these characteristics. The vinyl content was calculated using FTIR spectroscopy [4, 42]. The degree of functionalization (X_{VB}, %) is the percentage of repeat units which have vinylbenzene groups, and the degree of cross-linking (X_{CL}, %) is the percentage of repeat units which cross-link the resin. The pore size distribution is based on the percent of the total pore volume with pores of a given diameter.

Table 6.1. Characteristics of XAD-4 (data from [4])

Surface Area (m^2/g)	Total Pore Volume (mL/g)	Pore Size (nm)	Degree of Functionalization (X_{VB}, %)	Degree of Cross-Linking (X_{CL}, %)	Vinyl Content (mmol/g)
831	1.181	< 6 (17.3%) 6-10 (20.5%) 10-20 (59.5%)	33 ± 1	47 ± 2	2.5 ± 0.1

6.3.2 Epoxidation of XAD-4

6.3.2.1 Comparison of epoxidation techniques

Spectroscopic analyses aided in determining the conversion of vinylbenzene groups to styrene oxide (epoxy) groups. The methods which led to reductions in vinylbenzene content, as seen by comparison of the infrared spectra, are listed in table 6.2. Of these, the methods which produced resins with epoxy groups were reaction with either *m*CPBA (in dichloromethane) or dimethyldioxirane (DMD, as acetone solution). The DMD method gave no reactive by-products, only acetone. Use of *m*CPBA could lead to ring-opening by any *m*-chlorobenzoic acid present [18]. This is of particular concern since the matrix is cross-linked, and the acid may not elute out of (or even back into) the bead before reacting with epoxy groups.

The method using *m*CPBA with reaction times of 1.5 hours showed only slight reductions in vinyl peaks in the FTIR spectra, whereas reactions run for one day showed significant reductions in vinyl peaks. The method using a biphasic solvent system (H_2O-CH_2Cl_2) also had some reduction in vinyl peaks, but with the presence of side-products resulting from ring-opening of epoxy groups. This method had previously been used to prepare styrene oxide from styrene, with 95% yield [38].

Table 6.2. Methods which gave reductions of vinylbenzene groups

Resin and Label	Modification reagent used	Notes
1 H_2O_2-CH_3CN	hydrogen peroxide with acetonitrile	results similar for all 3 methods using H_2O_2 and nitriles
2 H_2O_2-PhCN	hydrogen peroxide with benzonitrile	
3 H_2O_2-CCl_3CN	hydrogen peroxide with trichloroacetonitrile	
4 *m*CPBA	*m*-chloroperbenzoic acid	best solvents: CH_2Cl_2, then toluene
5 MMPP	magnesium monoperoxyphthalate	best solvents: MeOH-H_2O, EtOH-H_2O, iPrOH-H_2O
6 CH_3COOOH	peracetic acid	best solvent: CH_2Cl_2
7 DMD	dimethyldioxirane	use of acetone solution of DMD gave 100% conversion
8 TDMF	*N,N*-dimethylthioformamide (thiirane attempt)	reaction of **7** with TDMF

The other methods gave resins with a mixture of functionalities due to incomplete reaction, epoxidation, as well as subsequent ring-opening reactions. The presence of side-products, including diol groups, will be discussed in the section on spectroscopic characterization.

Epoxidation with hydrogen peroxide in the presence of nitriles gave a mixture of functionalities, the nature of which will be discussed later. Styrene was epoxidized in 74% yield using this technique [32]. This method has not previously been used on polymeric systems, as with the method using hydrogen peroxide with ethyl chloroformate which did not give any reduction in vinyl peaks in the infrared spectra. Since these reagents are relatively inexpensive, further investigation of their use is recommended. This could include variation of amounts of reagents used, beyond what was done here. Our experiments used excess quantities of reagents, which likely led to ring-opening.

Epoxidation also failed with use of the tungsten phase transfer catalyst, as was also discovered in the attempted epoxidation of a block copolymer consisting of styrene and 1,2-butadiene units [24]. Styrene was epoxidized in 74% yield using this same catalyst [37]. Since this method uses a biphasic solvent system, penetration of the reagent into the polymer, or regeneration of any catalyst inside the resin with more hydrogen peroxide, may not have occurred.

The method giving complete conversion of vinylbenzene groups to epoxy groups was epoxidation with dimethyldioxirane in acetone. This was determined by the complete absence of vinyl peaks in the infrared, Raman, and ^{13}C NMR spectra, and verified by elemental analysis (table 6.3).

In-situ techniques of preparation of DMD were not successful in the epoxidation of XAD-4, most likely due to the presence of two solvent phases, minimizing penetration of DMD from large volumes of water into the matrix.

The methods which involved either contacting resin with an acetone solution of DMD at -20 °C for one day, followed by allowing the mixture to warm to room temperature for 8 hours, or using repeat contacts of small quantities of fresh solution, were both effective in complete epoxidation of XAD-4. This would suggest that this modification method could be adapted to a column set-up.

As with most of the other methods used in this work, the methods using DMD were adapted from small molecule syntheses. Styrene oxide was prepared by reaction of 1.1 equiv of DMD in acetone with styrene in > 95% yield [42 ,43]. Even with a polymeric system, this method is an effective means of epoxidizing vinylbenzene groups.

Table 6.3 lists the data from the elemental analyses of resin **7** and **8**. Resin **8** was prepared by acid-catalyzed reaction of *N,N*-dimethylthioformamide (TDMF) with epoxy-XAD-4 (**7**), and will be discussed in the next section. The degree of functionalization of epoxy-XAD-4 (X_{epox}) and the percent conversion (Φ) of vinylbenzene (VB) groups to epoxy groups were calculated according to equations 6.1 and 6.2, respectively.

Equation 6.1 $$X_{epox} = \frac{130.6 \times (\text{mol O/g})}{1 - (\text{mol O/g} \times \text{MWO})} \times 100\%$$

Equation 6.2 $$\Phi = \frac{X_{epox}}{X_{VB}} \times 100\%$$

Table 6.3. Elemental contents of resins **7** and **8** (a)

Resin	mmol O/g	mmol S/g	X_{epox}	X_{SHOH}	Φ
7	2.41 ± 0.06	0	32.8 ± 0.9%	0	99%
8	2.48 ± 0.05	1.44 ± 0.04	~15% (b)	~20%	61%

(a) XAD-4 lot #1090-7-1473 (X_{VB} = 33 ± 1 %) used to prepare **7**. No nitrogen present.
(b) Combination of epoxide and group(s) resulting from rearrangement of epoxide.

An analogous resin to epoxidized XAD-4, poly(*p*-oxirane-styrene), was prepared from cross-linked polystyrene [18]. However, a 4-step modification of polystyrene was required, starting with chloromethylation of polystyrene, conversion to the phosphonium salt, elimination to *p*-vinylbenzene groups, then epoxidation with *m*CPBA which was accompanied by ring-opening. The alternate 3-step procedure involved oxidation of chloromethylated polystyrene to form resins with benzaldehyde groups, followed by reaction with trimethyl sulfonium chloride under phase transfer conditions. Our method involved the one-step epoxidation of commercial poly(divinylbenzene-*co*-ethylvinylbenzene).

The advantage of epoxidation with acetone solutions of DMD is that the modification only needs contact times as short as 8 hours, and work-up simply involves filtration and drying to remove acetone. The only drawback to the use of DMD is that only dilute solutions (0.04- 0.12 M) can be prepared due to the instability of this cyclic peroxide [44].

Thus, XAD-4 was successfully modified by complete reaction of the vinylbenzene groups with dimethyldioxirane to form a resin (epoxy-XAD-4, **7**), with 2.4 mmol epoxy/g.

6.3.2.2 Attempted conversion of epoxide to episulfide

Epoxy-XAD-4 (**7**) was reacted with *N,N*-dimethylthioformamide using acid catalysis. This method has previously been used with success to convert styrene oxide to the thiirane in 92% yield [41], but never attempted on a polymer matrix.

Table 6.3 compares the elemental contents of resins **7** and **8**. Resin **8** had the mole content of oxygen calculated by difference of the carbon, hydrogen, nitrogen and sulfur contents (wt %). Based on the elemental contents, all the functional groups present had oxygen, and these included mercaptoethanol groups (e.g. R–CHSH–CR'OH, where R or R' is phenyl or H), accounting for approximately 20% of the repeat units, while approximately 15% were oxygen-containing, most likely either as epoxide or acetophenone groups. It is likely that the catalyst, trifluoroacetic acid, caused ring-opening, and rearrangement of the epoxy group. No nitrogen was present in either resin **7** or **8**. The functional groups present will be further discussed in the section on spectroscopic characterization. Approximately 61% of the epoxide groups reacted with *N,N*-dimethylthioformamide.

Alternate methods which have been used to convert polymer-bound epoxy groups to thiirane groups should also be attempted. These include use of thiourea or potassium thiocyanate [30]. Previously, styrene sulfide was prepared by reaction of styrene oxide with potassium thiocyanate in water-dioxane with 72% yield [45].

6.3.3 Spectroscopic characterization

The modified resins were characterized and compared to the starting material using infrared, Raman and ^{13}C NMR spectroscopy. Peak assignments were done by comparison to analogous model compounds [46, 47], and with the help of reference books on spectroscopy [48, 49].

6.3.3.1 Infrared spectroscopy

Figure 6.2 compares the FTIR absorbance spectrum of XAD-4 and those of XAD-4 modified by the reagents listed in table 6.2, indicated with a label corresponding to the method used (listed in table 6.2). This includes the resin formed by reaction of epoxy-XAD-4 (**7**) with *N,N*-dimethylthioformamide (TDMF, **8**) is also shown. Only spectra of modified resins with noticeable changes are shown.

The infrared spectral peaks have previously been assigned for unmodified poly(divinylbenzene-*co*-ethylvinylbenzene) (XAD-4) [5, 42]. Tables 6.4a and 6.4b note any peaks which appear in the spectra of the modified resins.

On comparison of the spectra for XAD-4 and the modified resins, the five peaks due to the vinyl groups (1630, 1410, 1015, and 990 cm^{-1}) decrease in relation to the degree of functionalization. The peak at 905 cm^{-1} is due to both vinyl groups and disubstituted phenyls, so it is never completely eliminated.

Table 6.4a. Infrared peak assignments for modified resins (**1-5**)

Resin	Band (cm^{-1})	Assignment	Reference	Notes
1	3578	O-H stretch	[48], p. 188	vinyl peaks less (than XAD-4), diol present
	1116	C-O stretch, secondary alcohol	[48], p. 207	
	1067 or 1048	C-O stretch, primary alcohol	[48], p. 207	
2	3587	O-H stretch	[48], p. 188	vinyl peaks less, spectrum same as **1** with stronger peak at 1115 cm^{-1}, diol present
	1115	C-O stretch, secondary alcohol	[48], p. 207	
	1067 or 1048	C-O stretch, primary alcohol	[48], p. 207	
3	3586	O-H stretch	[48], p. 188	vinyl peaks less, spectrum same as **1** with stronger peak at 1115 cm^{-1}, diol present
	1116	C-O stretch, secondary alcohol	[48], p. 207	
	1067 or 1049	C-O stretch, primary alcohol	[48], p. 207	
4	3565	O-H stretch	[48], p. 188	almost no vinyl peaks, epoxy and alcohol group
	1255	ring breathing of epoxy group	[49], p. 113 [18]	
	1120	C-O stretch, secondary alcohol	[48], p. 207	
5	3586	O-H stretch	[48], p. 188	almost no vinyl peaks MMPP embedded, diol present
	1727	C=O stretch	[48], p. 195	
	1421, 1374			
	1285	C-O stretch of carboxylic acid	[48], p. 207	
	1256	ring breathing of epoxy group	[49], p.113 [18]	some epoxy groups
	1120	C-O stretch, secondary alcohol	[48], p. 207	
	1072	C-O stretch, primary alcohol	[48], p. 207	
	873			
	747	ortho disubstitution (of MMPP)	[48], p. 197	

Resins **1**, **2**, and **3** had similar spectra. The vinyl peaks decreased from **1** to **2** to **3**, and the peak at 1115 cm^{-1} (C-O stretch) increased from **1** to **3**, indicating a higher conversion of vinylbenzene groups to functional groups, most likely the diol.

Resins **4** and **7** had similar spectra, both with peaks corresponding to epoxy groups (1255 cm^{-1}). Resin **7** had no vinyl peaks, whereas resin **4** had very small peaks due to the vinylbenzene groups, as well as peaks which indicated that ring-opening of the epoxy group had occurred.

The spectra of resins **5** and **6** were similar. No epoxy peaks were visible, and, since there were significant reductions in vinyl peaks, epoxidation followed by ring-opening reactions most likely occurred. Resin **5** may have had MMPP physically embedded in the resin, while resin **6**, formed by reaction of XAD-4 with peracetic acid, probably had alcohol (possibly including diol groups) and ester (acetate) groups.

Table 6.4b. Infrared peak assignments for modified resins (**6**-**8**)

Resin	Band (cm^{-1})	Assignment	Reference	Notes
6	3567	O-H stretch	[48], p. 188	almost no vinyl peaks
	1740	C=O stretch	[48], p. 195	may have diol, alcohol, acetate groups
	1373	CH_3 symmetrical deformation	[48], p. 175	
	1239	antisymmetric C-O-C stretch, acetate ester	[48], p. 207	
	1158	C-O stretch, secondary alcohol	[48], p. 207	
	1064	C-O stretch, primary alcohol	[48], p. 207	
7	1253	ring breathing of epoxy group	[49], p. 113 [18]	no vinyl peaks, epoxy group
8	3567	O-H stretch	[48], p. 188	no vinyl peaks, no epoxy peak
	1789	C=O stretch, possibly aromatic ester	[48], p. 195	possible functionalities: thio-alcohol, diol, ketone, ester
	1732	C=O stretch	[48], p. 195	
	1683	C=O stretch, possibly aromatic ketone (acetophenone group)	[48], p. 195	
	1225		[46], Vol. 1, p. 262	Like mercaptoethanol: ~1225 cm^{-1}, 1169 cm^{-1}, 1049 cm^{-1}
	1169			
	1064	C-O stretch	[48], p. 207	
	1043	C-O stretch, primary alcohol	[48], p. 207	

Resin **8**, the product of reaction of **7** with *N,N*-dimethylthioformamide in the presence of trifluoroacetic acid, did not have any peaks (1440, 1330, 910, and 620 cm^{-1} [20]) corresponding to a thiirane group. It seems to have a mixture of functionalities including a mercaptoethanol group, and either acetophenone, diol, or ester groups.

As will be discussed in the next section, Raman spectra were taken of **7** and **8**, and compared to that of XAD-4.

6.3.3.2 Raman spectroscopy

Figure 6.3 compares the Raman spectra of XAD-4, XAD-4 epoxidized with dimethyldioxirane (DMD, **7**), and the resin prepared by reaction of epoxy-XAD-4 (**7**) with *N,N*-dimethylthioformamide (TDMF, **8**), in an attempt to convert the epoxide to the thiirane group. The Raman spectral peak assignments for XAD-4 are presented elsewhere [5].

No vinyl peaks were seen (1632, 1409, and 1209 cm^{-1}) in the spectra of the modified resins. Resin **7** had peaks corresponding to the epoxy group at 1470, 1388, and 1255 cm^{-1} [48, p. 180; 50, vol. 4, p. 3803, Raman peaks for styrene oxide].

The Raman spectrum of resin **8** had no epoxy peaks, but new peaks at 2573 cm^{-1} (S-H stretch) [48, p. 181], 674 and 620 cm^{-1} (C-S stretches) [48, p. 181]. No other peaks which could aid in determination of the other functionalities were visible.

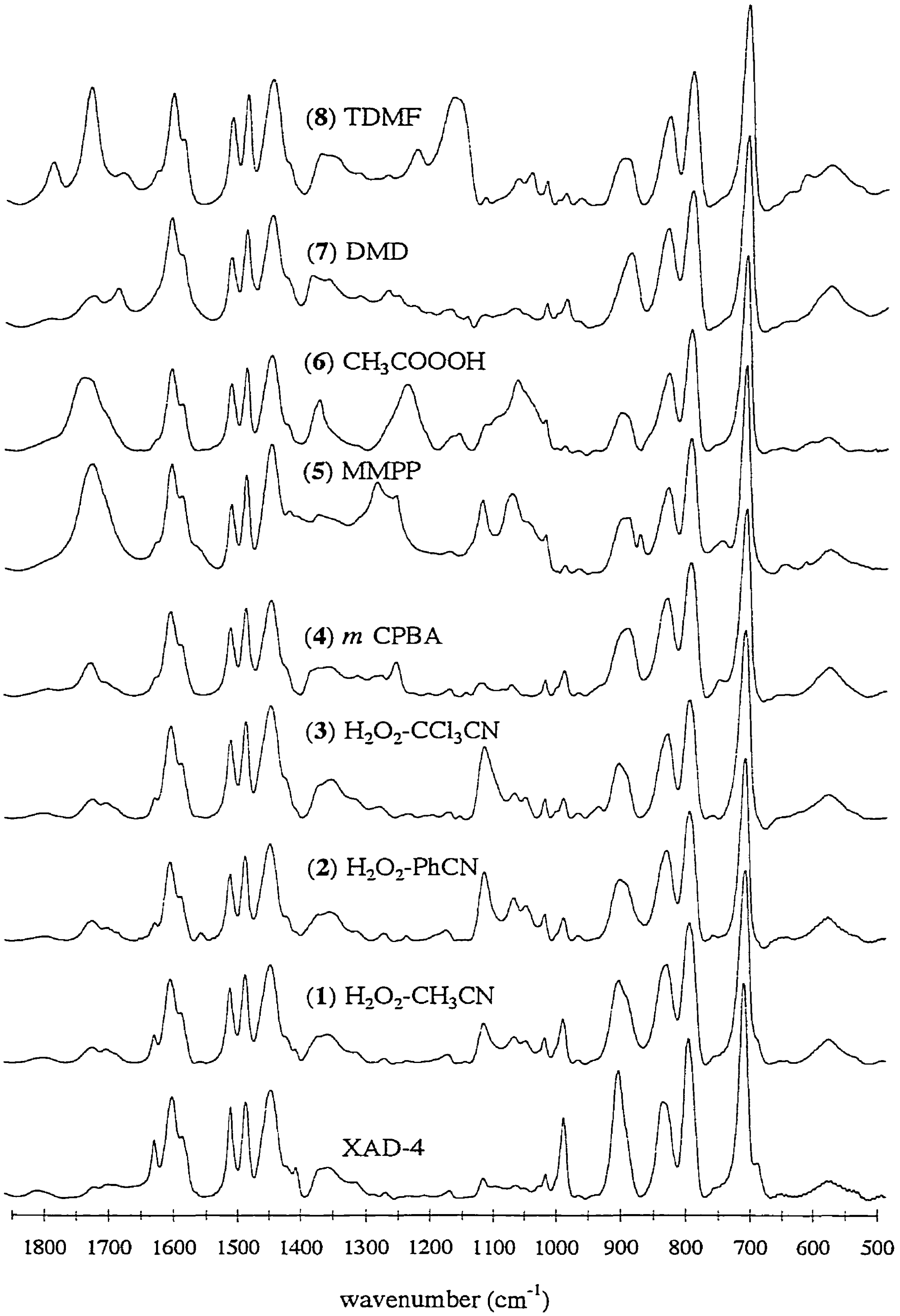


Fig. 6.2. FTIR absorbance spectra of XAD-4 and modified resins (**1**-**8**).

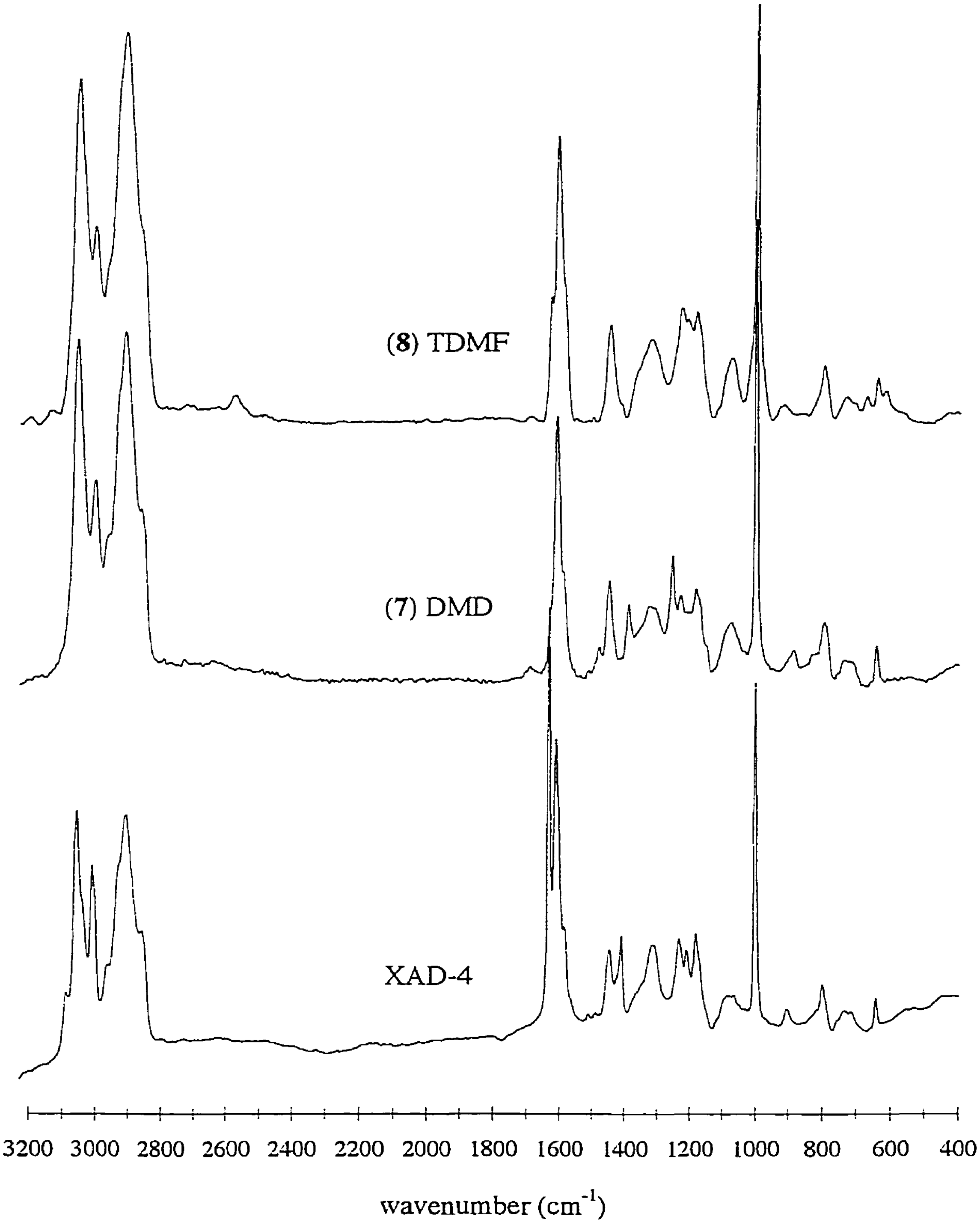


Fig. 6.3. Raman spectra of XAD-4 and modified resins (**7** and **8**).

6.3.2.3 ^{13}C NMR spectroscopy

The ^{13}C NMR spectral peak for unmodified XAD-4 have previously been assigned [5]. Dipolar dephasing eliminated the peaks due to the vinyl carbons, the epoxy carbons, and the polymer backbone (CH_2, CH, phenyl CH).

Figure 6.4 shows the solid-phase ^{13}C CP-MAS NMR spectra for XAD-4 and for the modified resins. The labels used are the same as for the IR and Raman spectra (table 6.2). As was seen with the infrared and Raman spectra, the intensity of the vinyl peaks were less (137 ppm and 114 ppm) for all modified resins in comparison to XAD-4. Table 6.5 lists the ^{13}C CP-MAS NMR peak assignments for modified XAD-4 and for analogous model compounds [47]. Peaks due to the polymer backbone are excluded from table 6.5.

For the dipolar dephased NMR spectra, the only peaks visible in most cases corresponded to those of the resin backbone: 144, 137, 30, and 16 ppm. Peaks due to the carbons of the modified dimethylene spacer (i.e. the epoxy group) were generally not seen in the dipolar dephased spectra due to limited mobility.

Besides solid-phase NMR spectroscopy, liquid NMR techniques were used for resin **7**. A sample was swelled in deuterated chloroform using a new NMR tube (i.e. not previously in contact with solvents such as acetone). The only peaks visible were for chloroform and acetone. Acetone peaks were not seen in the solid-phase ^{13}C NMR spectra for any of the resins. Although the resins were dried at 60 °C under vacuum, some acetone remained entrapped in the polymer, giving infrared peaks in the carbonyl stretching region (~ 1700 cm^{-1}).

The NMR spectral data indicate that the best method to prepare epoxy-XAD-4 is by epoxidation of XAD-4 with dimethyldioxirane (resin **7**). No other functionalities were seen since the reaction generates a non-reactive by-product (acetone). Epoxidation with *m*CPBA (resin **4**) was also successful, but some ring-opening of the epoxy groups occurred due to the presence of *m*-chlorobenzoic acid. Even lightly cross-linked resins modified by epoxidation of vinylbenzene groups with *m*CPBA had ring-opening occurring [18].

The spectra of the other resins (**1**, **2**, **3**, **5**, **6**) showed other peaks which would indicate ring-opening reactions of epoxy groups. The spectrum of resin **8**, the product of reaction of epoxy-XAD-4 (**7**) with *N,N*-dimethylthioformamide (TDMF), had no peaks due to either epoxy or thiirane groups, and likely functionalities include (1-mercapto-2-hydroxyethyl)benzene and acetophenone groups.

Table 6.5. ^{13}C CP-MAS NMR peak assignments for modified XAD-4

Resin	Peak (ppm) (a)	^{13}C NMR peak assignments for model compounds (b)	Notes
1	85.5, 67.5	140.43, 128.39*, 127.80*, 126.02*, 74.67*, 67.93 (c)	diol group
2	85.2, 67.2	(c)	diol and some epoxy group
	54.4 (a)	137.53, 128.41*, 128.09*, 125.40*, 52.30*, 51.15 (d)	
3	84.7, 67.5	(c)	diol and some epoxy group
	55.5 (a)	(d)	
4	55.5 (a)	(d)	epoxy group
	67.9 (a), 26.0 (a)	145.78, 128.37*, 127.31*, 125.33*, 70.24*, 25.09* (e)	small peaks at 67.9 ppm and 26.0 ppm due to alcohol side-product
5	74.7, 67.9 (a)	(c)	diol group
6	~ 170	170.71, 135.90, 128.49*, 128.17*, 66.24, 20.95* (f)	small bump at 170 ppm may be due to acetate group
		170.84, 137.76, 128.81*, 128.43*, 126.49*, 64.87, 35.09, 20.90* (g)	combination of functionalities including ester-alcohol, diol, diester
	109.5 (a)	108.40, 64.46, 25.62* (h)	peak at 109.5 ppm may be due to $C(OR)_2$ group, formed by reaction of diol with acetone during purification
	79.5-62.5	(c, e)	
	26.0 (a)		
7	51.2 (a)	(d)	epoxy group
8	~ 200	197.93, 137.14, 133.01*, 128.51*, 128.24*, 26.52* (i)	small bump at 170 ppm may be due to acetophenone group
	~160		small bump at 160 ppm may be due to adsorbed DMF
	67.8, 26.4 (a)	63.95, 27.54 (j) (e)	mercaptoethanol group, probably (1-mercapto-2-hydroxyethyl)benzene
		36.0*, 27.2 (k)	no thiirane group

(a) Also visible in ^{13}C CP-MAS-DD spectrum.
(b) Data from [47], unless otherwise noted, * means odd parity (i.e. CH, CH_3).
(c) 1-Phenyl-1,2-ethanediol, [47, Vol. 2, p. 393].
(d) Styrene oxide, [47, Vol. 2, p. 219].
(e) *sec*-Phenethyl alcohol, [47, Vol. 2, p. 327].
(f) α-Methylbenzyl acetate, [47, Vol. 2, p. 1201].
(g) Phenethyl acetate, [47, Vol. 2, p. 1203].
(h) 2,2-Dimethyl-1,3-dioxolane, [47, Vol. 1, p. 396].
(i) Acetophenone, [47, Vol. 2, p. 802].
(j) 2-Mercaptoethanol, [47, Vol. 1, p. 422].
(k) Styrene sulfide, peaks of thiirane carbons, [41].

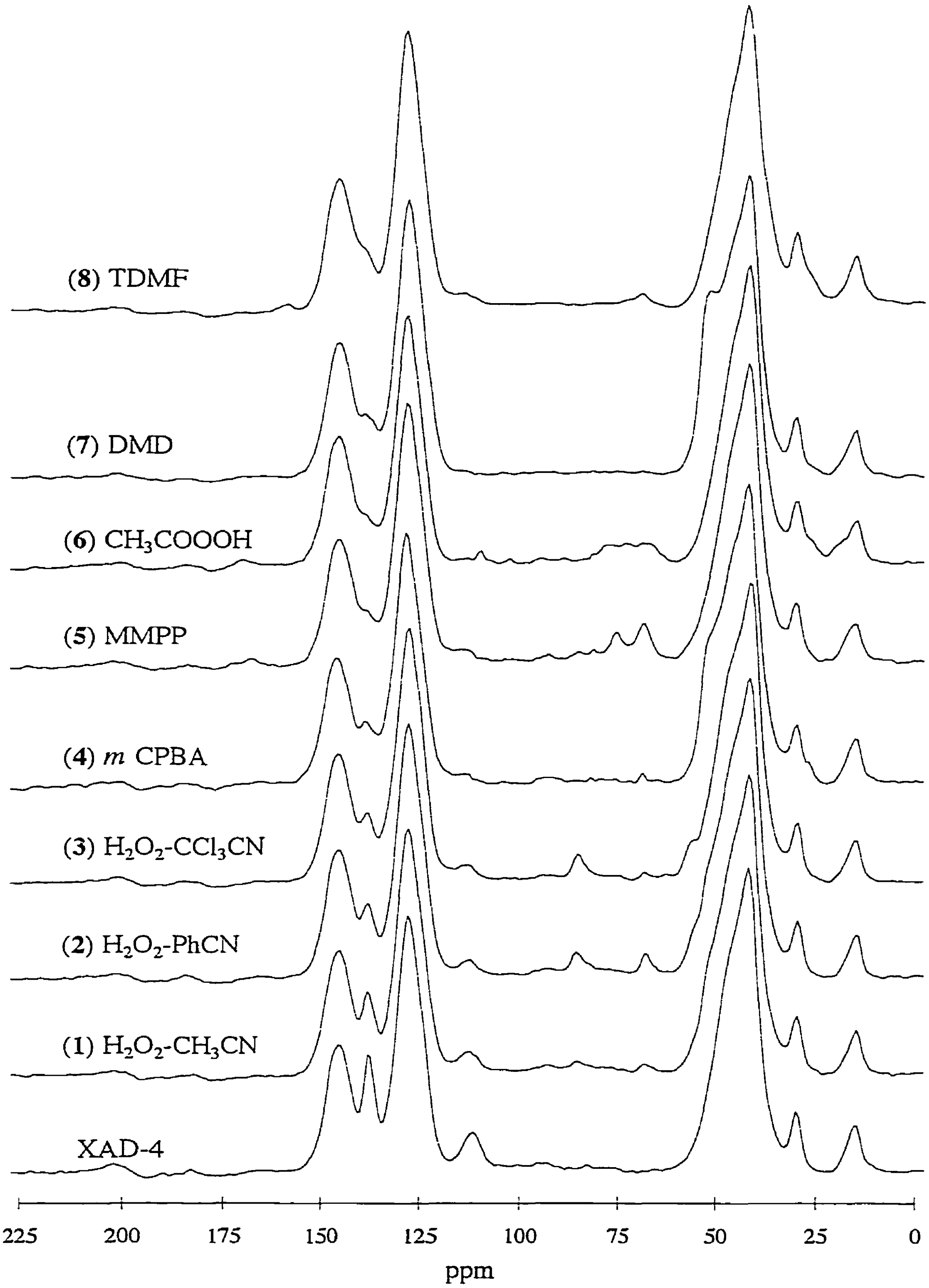


Fig. 6.4. ^{13}C CP-MAS NMR spectra of XAD-4 and modified resins (**1**-**8**).

6.3.4 Potential applications of modified resins and suggestions for further investigations

We have prepared resins which may have potential applications as adsorbents or solid-phase reagents. Modification can change properties of the resins, such as hydrophilicity, which may change behaviour in separation applications such as chromatography [5]. XAD-4 was previously modified for these applications using traditional methodologies [51]. No one has previously modified the vinylbenzene groups of XAD-4 to change its sorption properties.

Linear poly(divinylbenzene) could also be modified using the methodologies described in this paper. This may also aid in structure elucidation, and comparison of epoxidation methods to cross-linked XAD-4. For example, though epoxidation with the tungsten phase transfer catalyst was unsuccessful with XAD-4, it may work with the linear polymer, as it did for a styrene-butadiene-styrene linear block copolymer [23].

Modification of XAD-4 with DMD could be done using column techniques, which could be transferable to a larger (industrial) scale. The other modification methods which led to epoxy groups, but with subsequent ring-opening reactions, should be further investigated because these reactions have simple conditions and potentially low cost.

Since resins with thiirane groups can act as reactive polymers in the preparation of functional polymers [20, 30], further methods to prepare thiirane-XAD-4, either from epoxy-XAD-4 or XAD-4 should be investigated.

Polymers with epoxide and thiirane groups can be modified by addition of various nucleophiles. Applications of these modified resins include use as coordinating polymers [19, 20, 24, 30]. We have recently developed a simple screening method involving pH titration to elucidate a potential ligand's ability to complex various transition metals [52]. This method can be used as the first step in the development of coordinating or ion exchange resins. In order to properly gauge a ligand's behaviour, models which emulate how the ligand is attached to the resin should be studied. Some of the ligands studied have been used to modify resins by reaction with epoxy groups [19, 24]. These ligands include: ethylenediamine [24], 2-mercaptobenzothiazole [24], 2-aminomethylpyridine [19], and 2-aminothiophenol [19]. Any of the ligands mentioned in these references [19, 24, 30, 52] could be used to modify epoxy-XAD-4. Thus a coordinating resin with an alcohol group and ligand can be prepared in two steps.

Epoxy-XAD-4 could also be used in the preparation of solid-phase catalysts for various reactions including lipase hydrolysis. Styrene oxide has been used to prepare various azacrown ethers which were studied for lipase-catalyzed hydrolysis of 2-cyano-1-methylethyl acetate [53]. It was found that the azacrown ethers enhanced both the enantioselectivity and reaction rate. Epoxy-XAD-4 could be used to prepare polymer-supported analogues of these azacrown ethers by the one step addition of the commercially-available precursor azacrown ethers.

6.4. Conclusions

Amberlite XAD-4, a commercially-available styrenic copolymer, can be modified by epoxidation of the completely accessible pendant vinylbenzene groups. We have demonstrated that dimethyldioxirane in acetone can be used in a simple one-step reaction with complete conversion to epoxy groups, with a degree of functionalization of 33%. Styrenic resins with epoxy groups could be used for the preparation of functional resins with many diverse applications.

6.5 Acknowledgements

We wish to thank Rohm and Haas Company for donation of 5 kg of Amberlite XAD-4, and for providing some information used in this paper. Solid phase ^{13}C NMR spectra were taken by Dr. F.G. Morin of the Department of Chemistry, McGill University. Dr. F. Sauriol helped take liquid state ^{1}H and ^{13}C NMR spectra. Some of the infrared spectra were taken by M. Ruzicka. Thanks also go to B. Stranix, Dr. D.S. Argyropoulos, Dr. R.B. Lennox, and Dr. D.N. Harpp for helpful discussion. Dr. E. Sun helped with the generation of dimethyldioxirane solutions. Special thanks go to Dr. R.W. Murray for comments on DMD chemistry. Funding for this project was provided by a Natural Sciences and Engineering Research Council of Canada Strategic Grant.

6.6 References

[1] J.P. Gao, F.G. Morin and G.D. Darling, Macromolecules, 26 (1993), 1196.

[2] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted May 1997. Chapter 4 of the doctoral thesis of K.L. Hubbard, McGill Univeristy, June 1997.

[3] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted May 1997. Chapter 5 of the doctoral thesis of K.L. Hubbard, McGill Univeristy, June 1997.

[4] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted April 1997. Chapter 2 of the doctoral thesis of K.L. Hubbard, McGill Univeristy, June 1997.

[5] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted April 1997. Chapter 3 of the doctoral thesis of K.L. Hubbard, McGill Univeristy, June 1997.

[6] R. Kunin, Amberhilites (produced by Rohm and Haas Co.), Number 161 (spring 1979).

[7] R. Kunin, Amberhilites (produced by Rohm and Haas Co.), Number 163 (winter 1980).

[8] E.F. Meitzner and J.A. Oline, U.S. Patent 4,382,124, issued May 3, 1983.

[9] Food and Drug Administration, U.S. Government, 173.65, page 100 in "Code of Federal Regulations", 21, Food and Drugs. Parts 170 to 199, revised April 1, 1994.

[10] R.L. Albright, React. Polym., 4 (1986), 155.

[11] Supelco Product Catalogue, 1995, page 264.

[12] N.A. de Munck, M.W. Verbruggen and J.J.F. Scholten, J. Mol. Catal., 10 (1981), 313.

[13] J.P.C. Bootsma, B. Eling and G. Challa, React. Polym., 3 (1984), 17.

[14] M Periyasamy, W.T. Ford and F.J. McEnroe, J. Polym. Sci., Polym. Chem. Ed., 27 (1989), 2357.

[15] M.C. Faber, H.J. van den Berg, G. Challa and U.K. Pandit, React. Polym., 11 (1989), 117.

[16] Z. Zhengpu, P. Hodge and P.W. Stratford, React. Polym., 15 (1991), 71.

[17] J. Kalal, F. Svec and V. Marousek, J. Polym. Sci., Polym. Symp., 47 (1974), 155.

[18] J.M.J. Frechet and E. Eichler, Polym. Bull. (Berlin), 7 (1982), 345.

[19] D. Lindsay and D.C. Sherrington, React. Polym., 3 (1985), 327.

[20] P.M. van Berkel, W.L. Driessen, J. Reedijk, D.C. Sherrington and A. Zitsmanis, React. Funct. Polym., 27 (1995), 15.

[21] P.M. van Berkel, D.J. Dijkstra, W.L. Driessen, J. Reedijk and D.C. Sherrington, React. Funct. Polym., 28 (1995), 39.

[22] V. Migonney, M.D. Lacroix, C. Douzon and M. Jozefowicz, J. Appl. Polym. Sci., 46 (1992), 1151.

[23] X. Jian and A.S. Hay, J. Polym. Sci., Polym. Chem. Ed., 29 (1991), 1183.

[24] M. Antonietti, S. Forster, J. Hartmann and S. Oestreich, Macromolecules, 29 (1996), 3800.

[25] M. Leboucher-Durand, V. Langlois and P. Guerin, React. Funct. Polym., 31 (1996), 57.

[26] S. Lu, E.M. Pearce and T.K. Kwei, Macromolecules, 26 (1993), 3514.

[27] S. Lu, M.M. Melo, J. Zhao, E.M. Pearce and T.K. Kwei, Macromolecules, 28 (1995), 4908.

[28] J. Bouchard, C. Maine, R.M. Berry and D.S. Argyropoulos, Can. J. Chem., 74 (1996), 232.

[29] W.K. Huang, G.H. Hsiue and W.H. Hou, J. Polym. Sci., Polym. Chem. Ed., 26 (1988), 1867.

[30] B.D. Moore, D.C. Sherrington and A. Zitsmanis, J. Mater. Chem., 2 (1992), 1231.

[31] Rohm and Haas Company, "Amberlite XAD-4. Polymeric Adsorbent." product literature, June 1993.

[32] G.B. Payne, P.H. Deming and P.H. Williams, J. Org. Chem., 26 (1961), 659.

[33] R.D. Bach and J.W. Knight, Org. Synth., 60 (1981), 63.

[34] G.B. Payne, Tetrahedron, 18 (1962), 763.

[35] L.A. Arias, S. Adkins, C.J. Nagel and R.D. Bach, J. Org. Chem., 48 (1983), 888.

[36] R.D. Bach, M.W. Klein, R.A. Ryntz and J.W. Holubka, J. Org. Chem., 44 (1979), 2569.

[37] C. Venturello and R. D'Aloisio, J. Org. Chem., 53 (1988), 1553.

[38] M. Imuta and H. Ziffer, J. Org. Chem., 44 (1979), 1351.

[39] R. Curci, M. Fiorentino and L. Troisi, J. Org. Chem., 45 (1980), 4758.

[40] W. Adam, J. Bialas amd L. Hadjiarapoglou, Chem. Ber., 124 (1991), 2377.

[41] T. Takido, Y. Kobayashi and K. Itabashi, Synthesis, (1986), 779.

[42] M. Bartholin, G. Boissier and J. Dubois, Makromol. Chem., 182 (1981), 2075.

[43] A.L. Baumstark and P.C. Vasquez, J. Org. Chem., 53 (1988), 3437.

[44] R. W. Murray, Chem. Rev., 89 (1989), 1187.

[45] J.M. Stewart, J. Org. Chem., 28 (1963), 596.

[46] C.J. Pouchert (Editor), The Aldrich Library of FT-IR Spectra, Edition 1. Aldrich Chemical Company, Inc., Milwaukee, 1985. Volume 1, pages 262, 269, 837, 848, 1063, 1156; and Volume 2, pages 15, 16, 191, 442.

[47] C.J. Pouchert and J. Behnke (Editors), The Aldrich Library of ^{13}C and ^{1}H FT-NMR Spectra, Edition 1. Aldrich Chemical Company, Inc., Milwaukee, 1993. Volume 1, pages 396, 422; and Volume 2, pages 219, 327, 393, 802, 1201, 1203.

[48] J.B. Lambert, H.F. Shurvell, D.A. Lightner and R.G. Cooks, Introduction to Organic Spectroscopy, MacMillan Publishing Co., New York, 1987. pages 175, 180-81, 188, 195, 207, 210.

[49] R.M. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric Identification of Organic Compounds, 5th Edition, John Wiley and Sons, Inc., New York, 1991. page 113.

[50] D.R. Lide and G.W.A. Milne (Editors), Handbook of Data on Organic Compounds. 3rd Ed. CRC Press, Inc., Boca Raton, 1994. Volume 4, page 3803.

[51] T.A. Armer, Ph.D. Thesis, Tulane University, Diss. Abstr. Int. B 43 (6) (1982), 1910; Chem. Abstr. 98 (1983), 35435w.

[52] K.L. Hubbard, G.D. Darling and J.A. Finch, Minerals Eng., 10 (1997), 41.

[53] T. Itoh, Y. Takagi, T. Murakami, Y. Hiyama and H. Tsukube, J. Org. Chem., 61 (1996), 2158.

Chapter 7

Bromohydration and Bromination of the Pendant Vinylbenzene Groups of Commercial poly(Divinylbenzene-*co*-Ethylvinylbenzene) Resins. Further Reactions of the (1,2-Dibromoethyl)benzene Groups with Thiourea, and with *N,N*-Dimethylthioformamide with Subsequent Methanolysis to Produce Thiol-Containing Styrenic Resins.

Forward to Chapter 7

The content of the following section is comprised of a paper with the same title which was submitted to the journal Reactive and Functional Polymers (K.L. Hubbard, G.D. Darling and J.A. Finch, submitted May 1997).

The goal of this chapter was to expand the types of groups modifying the commercial form of poly(divinylbenzene-*co*-ethylvinylbenzene), in particular with vicinal disubstituted functionalities. These groups included (1-hydroxy-2-bromoethyl)benzene, (1,2-dibromoethyl)benzene, and resins with isothiouronium bromide or (1,2-dimercaptoethyl)benzene, the latter two produced by modification of brominated XAD-4. Resins with (1,2-dimercaptoethyl)benzene groups are desired because of their potential for use as chelating resins in heavy metal removal from various wastewaters. Bromohydration and the method of conversion (using *N,N*-dimethylthioformamide) of brominated groups to thiol groups have not previously been used with a polymer matrix.

Abstract

Amberlite XAD-4, the commercial form of poly(divinylbenzene-*co*-ethylvinylbenzene), was modified by bromohydration and bromination of its pendant vinylbenzene groups. The vinylbenzene groups were completely converted to (1,2-dibromoethyl)benzene groups, with a degree of functionalization of 35%. Bromohydration of XAD-4 created a resin with (1-hydroxy-2-bromoethyl)benzene groups, with a degree of functionalization of 24%. Further modifications to the (1,2-dibromoethyl)benzene groups of the brominated resin were done using thiourea, which led to a resin with a mixture of functional groups, including isothiouronium bromide; and using *N,N*-dimethylthioformamide with subsequent methanolysis, which led to a resin with thiol groups.

Keywords: Amberlite XAD-4, poly(divinylbenzene-*co*-ethylvinylbenzene), pendant vinyl groups

7.1. Introduction

This paper discusses several modifications of vinylbenzene groups in a polystyrene-like matrix. Starting with the commercial form of poly(divinylbenzene-*co*-ethylvinylbenzene), XAD-4, we have bromohydrated the vinylbenzene groups to form (1-hydroxy-2-bromoethyl)benzene groups, and have also brominated the vinylbenzene groups to form (1,2-dibromoethyl)benzene groups. The brominated resin was then reacted with thiourea, and also with *N,N*-dimethylthioformamide with subsequent methanolysis to form resins with thiol groups.

7.1.1 Review of our previous work, including characterization of XAD-4

Previously, our group modified laboratory-made poly(divinylbenzene-*co*-ethylvinylbenzene) by the addition of a few simple thiols to the pendant vinylbenzene groups [1]. We have recently expanded upon this work to include the use of a commercial resin, Amberlite XAD-4, as well as a greater range of thiols and conditions [2]. Further work studied the addition of various disulfides and analogous thiols to the pendant vinylbenzene groups of XAD-4 [3], and the epoxidation of XAD-4 [4].

Cross-linked copolymers of divinylbenzene and ethylvinylbenzene have meta- and para-disubstituted vinylbenzene and ethylbenzene groups (figure 7.1). The degrees of functionalization are indicated by the symbols X_{CL}, X_{VB}, and X_{EB}, (CL for cross-linked, VB for vinylbenzene, and EB for ethylbenzene).

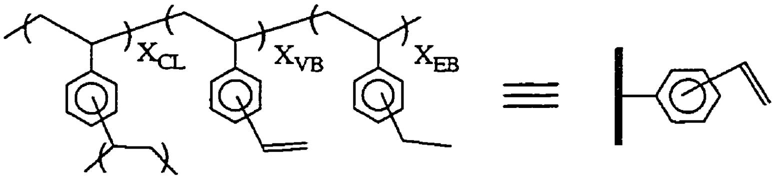


Fig. 7.1. Structure of poly(divinylbenzene-*co*-ethylvinylbenzene).

Amberlite XAD-4 (Rohm and Haas Company) is a macroporous resin prepared from 80 to 85 wt % divinylbenzene and 15 to 20 wt % ethylvinylbenzene [5-11]. Since XAD-4 has a high surface area (725 to 1040 m^2/g) and porosity (0.98 to 1.55 mL/g), vinyl groups are accessible to reagents used during modification, which promotes their high conversions to functional groups [5, 6, 11-13]. The vinyl content ranges from 29 to 41% (2.2 to 3.1 mmol/g) depending on lot [6]. Besides ourselves, only five research groups have mentioned the presence of vinyl groups in XAD-4 [13-17], and of these, only two modified the resin by reaction with the vinyl functionality [16, 17].

7.1.2 Review of bromohydrin preparation

Small molecule bromohydrins have been prepared by the reaction of alkenes with hydrobromous acid, formed by mixing bromine and potassium bromide in water or with *N*-bromoacetamide and water in dioxane [18]. 2-Bromo-1-phenylethanol was prepared from styrene using these methods with 96% and 83% yields, respectively. *N*-bromosuccinimide (NBS, 1 equivalent) and water have also been used to prepare 2-bromo-1-phenylethanol from styrene in 82% yield [19]. The reaction was done at room temperature for 35 minutes with water as the solvent. This same preparation was also done using dimethyl sulfoxide (DSMO) as the solvent, with 2 equivalents of water and 2 equivalents of NBS and a nitrogen atmosphere, to produce 2-bromo-1-phenylethanol in 76% yield [20, 21]. Other solvents used to prepare bromohydrins include *tert*-butanol and tetrahydrofuran (THF) [22].

To our knowledge, polymers containing bromohydrins have not previously been prepared.

7.1.3 Review of bromination of polymers

Various polymers have had bromine groups introduced by a variety of methods including addition of bromine to vinyl groups, and by electrophilic addition to aromatic groups. For example, a polycarbonate having pendant vinyl groups prepared by the copolymerization of carbon dioxide with butadiene monoxide (BMO) was brominated in chloroform at room temperature to produce a polymer with 1,2-dibromoethyl groups [23].

Polystyrene resins have been modified by bromination in the presence of ferric ion, which was optionally followed by lithiation with subsequent reaction of the lithiated resin with 1,2-dibromoethane to produce a resin with 2-bromoethylbenzene groups [24]. Aryl-brominated polystyrene was also reacted with sulfur, followed by reduction of any disulfides formed with lithium aluminum hydride, to produce a resin with 2.9 mmol thiol/g [24].

Styrenic resins with bromo-alkyl spacers have been prepared by addition of ω-bromoalkenes with polystyrene in the presence of trifluoromethanesulfonic (triflic) acid [25]. The degree of functionalization of the ω-bromoalkylated polystyrenes was 38%.

Polystyrene resins with pendant sulfone groups having vinyl groups were prepared in a three-step modification of polystyrene ($P-SO_2CH_2CH=CH_2$), and subsequently brominated across the vinyl group [26].

Chloromethylated polystyrene was modified to have 1,2-dibromoethyl groups by reaction with allylamine, followed by brominations of the vinyl groups [27]. The 1,2-dibromoethyl groups were then reacted with sodium hydrosulfide to produce a resin with vicinal dithiol groups.

A polymer with (1,2-dibromoethyl)benzene groups was prepared by the copolymerization of styrene or *meta*-divinylbenzene with *meta*-(1,2-dibromoethyl)styrene [28]. The 1,2-dibromo-monomer was prepared by selectively brominating one vinyl group of *meta*-divinylbenzene using pyridinium hydrobromide perbromide. The (1,2-dibromoethyl)benzene groups of the copolymers formed were then converted to vinyl groups by heating in the presence of sodium iodide to eliminate bromine.

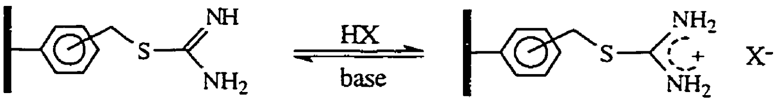
XAD-2, a copolymer of styrene, divinylbenzene and ethylvinylbenzene [6], was brominated in the presence of ferric chloride to produce a resin with 4.0 mmol Br/g [29, 30]. The only spectral data given was an infrared peak at 603 cm^{-1} [29]. The structure of the modified resin was given as: XAD-2–CH_2CH_2Br [30]. Since XAD-2 has vinyl groups [5], the brominated XAD-2 likely had (1,2-dibromoethyl)benzene groups and bromobenzene groups.

XAD-2 and XAD-4 have previously been hydrobrominated [16]. Anti-Markovnikov and Markovnikov hydrobrominations were performed; the first method used radical addition of hydrogen bromide (HBr) to form $-CH_2CH_2Br$ groups, and the second method used electrophilic addition of HBr to form $-CHBrCH_3$ groups. Anti-Markovnikov addition of HBr to the pendant vinyl groups gave 0.95 mmol Br/g for XAD-2 and 1.95 mmol Br/g for XAD-4, and Markovnikov addition of HBr to the pendant vinyl groups gave 2.01 mmol Br/g for XAD-4. This would have meant that the degree of functionalization of vinyl groups was 13.5% for XAD-2 and 30.2% for XAD-4 [6].

A polystyrene resin with bromobenzene groups is commercially-available as Sepabeads SP-206 and SP-207, part of the Diaion resin series from Mitsubishi Chemical [31]. It is claimed that this resin has a greater hydrophobicity (and thus greater selectivity for non-polar molecules) than regular styrenic resins.

7.1.4 Modifications of resins with thiourea

Resins have been modified with thiourea [32-36]. Macroreticular resins with isothiourea groups and isothiouronium groups (scheme 7.1) have been used for the extraction of platinum group metals [32]. The free-base isothiourea groups can coordinate with metal cations, and the isothiouronium groups will bind anionic metal complexes by anion exchange [32].



Scheme 7.1. Interconversion of isothiourea groups and isothiouronium groups [32].

Pendant chloromethyl groups of cross-linked polyepichlorohydrin (PECH) were reacted with either thioglycolic acid, potassium hydrosulfide (KSH), sodium hydrosulfide (NaSH), or thiourea to produce sulfur-containing resins [33]. Reaction of PECH with thioglycolic acid formed thioether linkages with the resin, producing a resin with carboxylic acid groups. Reactions of PECH with KSH and NaSH did not form resins with free thiol groups. Thiourea was reacted with PECH using a solvent mixture of *N,N*-dimethylformamide (DMF) and ethanol, or DMF with 2M HCl. A mixture of functional groups was present including thiol, isothiouronium, and dimethylamino. In all cases, most of the isothiouronium groups were hydrolyzed, as seen by comparison of the sulfur and nitrogen contents: 7.8 mmol S/g (25 wt % S), 3.4 mmol N/g (4.8 wt % N), giving a maximum of 1.7 mmol isothiouronium groups/g, and as much as 6.1 mmol thiol/g. The use of HCl increased the reaction rates, but did not affect the sulfur-nitrogen ratios.

XAD-2 and XAD-4, and other styrenic resins were used to prepare coordinating resins [34]. The styrene units were chloromethylated, aminated with hexamethylenetetramine and then converted to the polymer-bound thiourea functionality by reaction with NH_4SCN. The introduction of spacer groups was accomplished by modification with either 1,2-diaminoethane or 1,3-diaminopropane, instead of by amination. Unlike the previous examples, the thiourea group was linked through the amine to the resin.

7.1.5 Thiol-containing resins

One of our research goals was to prepare thiol-containing resins by modification of XAD-4. We have recently accomplished this by the one-step anti-Markovnikov radical addition of dithiols to the pendant vinylbenzene groups of laboratory-made poly(divinylbenzene-*co*-ethylvinylbenzene) [1] and XAD-4 [2]. Thiols used included: 1,2-ethanedithiol, 1,3-propanedithiol, 1,4-butanedithiol, sodium 2,3-dimercapto-1-propanesulfonate, 2-mercaptoethyl sulfide, and 2,3-dimercapto-1-propanol [1, 2]. One of the thiols was consumed in the formation of the thioether linkage to the resin. Resins modified with mercaptoacetic acid were hydrolyzed to form resins with (2-mercaptoethyl)benzene groups [1].

The preparation of mercaptan-containing polymers has been reviewed [35]. Thiol-containing resins are generally prepared by reaction of thiourea with halogen-containing groups, forming isothiouronium halide groups, followed by hydrolysis. Copolymers of 4-chloromethylstyrene and styrene were modified by this method [36]. The isothiouronium-containing resins were hydrolyzed under basic conditions to produce resins with degrees of functionalization of thiol groups between 14 and 54%, depending on the mole fraction of chloromethyl groups in the starting polymer (incomplete conversions of chloromethyl groups were seen).

Copolymers of 4-chloromethylstyrene and *N*-vinyl-2-pyrrolidone were also used to prepare thiol-containing resins [36]. The chloromethyl groups were reacted with *N,N*-dimethylthioformamide (TDMF, 100 equiv per chloromethyl group) at 80 °C under nitrogen for 3 hours, followed by methanolysis at 60 °C under nitrogen for 1 hour. The chloromethyl groups were completely converted to iminium salts (96-100% conversions), and the iminium salts were completely hydrolyzed to produce resins with disulfide and thiol groups. The proportion of thiol to disulfide (and thus yield of conversion of chloromethyl to thiol groups) increased as the mole fraction of chloromethyl groups in the starting polymers decreased. The polymer with the highest amount of thiol groups was prepared from a copolymer with a mole fraction of 57% to 43% for 4-chloromethylstyrene to *N*-vinyl-2-pyrrolidone. The thiol resin had a degree of functionalization of thiol groups of 38%, representing a 67% conversion from the chloromethyl groups.

XAD-4 was modified by acetylation, followed by hydrolysis to the benzyl alcohol functionality, then esterification with thioglycolic acid to produce a resin with thioglycoloylmethyl groups [37]. The infrared spectra were shown for each intermediate resin, and vinyl peaks were visible in the spectrum of the starting material. In the spectrum of the modified resin, weak peaks between 2600-2700 cm^{-1} may be attributed to the presence of thiol groups, although this was not mentioned in the paper. Reduction of the vinyl peaks in the spectra for the modified resins was also not noted by the authors, nor the presence of side-products attributed to reactions with vinyl groups.

Polystyrene resins were modified to have either thiophenol groups or benzylmercaptan groups [38]. Polystyrene was brominated, lithiated, and then reacted with elemental sulfur and reduced with lithium aluminum hydride [28, 38]. Direct lithiation, without prior bromination, of polystyrene was also done to form resins with thiophenol groups [38]. The first method gave resins with as much as 2.85 mmol SH/g, and the second method gave resins with as much as 1.98 mmol SH/g. To prepare resins with benzylmercaptan groups, chloromethylated polystyrene was reacted with thiourea, followed by base hydrolysis under nitrogen to form resins with 2.04 mmol SH/g [38]. When hydrolysis was done in air, no thiols were detected. Chloromethylated polystyrene was also reacted with 1,4-butanedithiol, using basic phase transfer conditions, under nitrogen to form resins with 3.5 mmol SH/g [39].

Resins with vicinal dithiols were prepared by the copolymerization of 2,3-epithiopropyl methacrylate and ethylene glycol dimethacrylate, followed by reaction with hydrogen sulfide [40]. A polystyrene resin containing vicinal thiols attached through a small spacer group to the styrene unit was prepared by a three-step modification of chloromethylated polystyrene, as mentioned previously [29].

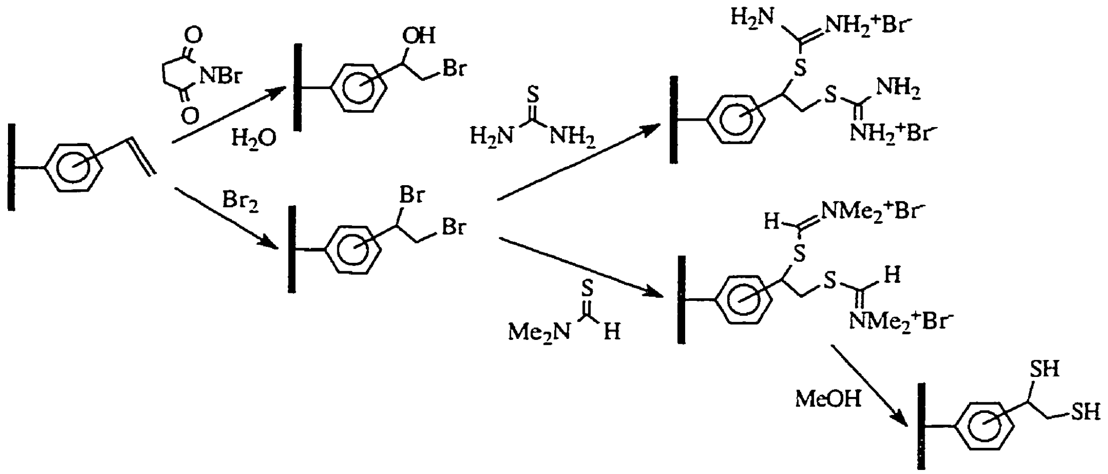
A thiol-containing polystyrene resin with 5.4 mmol SH/g is commercially-available as Duolite ES465 [33]. Duolite GT-73 is a similar product available from Rohm and Haas [41]. Sulfur analysis of this resin gave a sulfur content of 6.6 mmol S/g (dry resin) [42].

Polystyrene resins with (1,2-dimercaptoethyl)benzene groups have not been previously prepared, although the analogous small molecule (phenylethane-1,2-dithiol) has been prepared by the reduction of the corresponding trithiocarbonates [43].

7.1.6 Modifications of commercial poly(divinylbenzene-*co*-ethylvinylbenzene) in this paper

We are the first to take advantage of the ideal characteristics (high porosity and surface area, accessible vinylbenzene groups) of XAD-4 to prepare functional resins by modification of the vinylbenzene groups through the addition of thiols, disulfides, epoxidation, and other reactions [2-4]. We present our results on modifying XAD-4 with *N*-bromosuccinimide in water to produce the bromohydrin-containing resin, and with bromine to produce the (1,2-dibromoethyl)benzene-containing resin, as well as further reactions with brominated XAD-4, as seen in scheme 7.2.

One advantage of using these methods to prepare functional resins is that only one- or two-step modifications of a commercially-available preformed matrix are needed. The reaction conditions are usually straightforward, and of short duration. Purification of the modified resin is also simple. Introduction of a wide range of functionalities is possible.



Scheme 7.2. Modifications to poly(divinylbenzene-*co*-ethylvinylbenzene).

7.2. Experimental

7.2.1 Materials and methods

Unless otherwise noted, all materials were purchased from Aldrich Chemical Company and used as received. The same lot (#1090-7-1473) of Amberlite XAD-4 was used throughout this study, obtained from Rohm and Haas Co. XAD-4 comes imbibed with sodium chloride and sodium carbonate to retard bacterial growth [44]. Unless otherwise noted, all resins were pretreated by Soxhlet extraction with acetone for several days, followed by drying under vacuum overnight at 60 °C. Water was doubly-distilled.

Work-up for all reactions involved filtering the resin, washing with solvent and then Soxhlet extraction for several days with a variety of solvents. The solvents used for Soxhlet extraction of modified resins included methanol (MeOH), dichloromethane (CH_2Cl_2), water, ethanol-dioxane azeotrope (90.7:9.3 w/w, bp 78.1 °C), water-dioxane azeotrope (18.4:81.6 w/w, bp 87.8 °C), or acetone. The purified resins were dried under vacuum (70 °C) for one day.

7.2.2 Bromohydration of XAD-4

In a 50 mL 2-neck round bottom flask with magnetic stirring bar, 1 g of XAD-4 (2.5 mmol vinyl groups), *N*-bromosuccinimide (NBS, 1.1 to 2 equiv per vinyl group), 25 mL of solvent, and 1 to 25 mL water were stirred at room temperature for 7 to 24 hours under nitrogen. Solvents used included dimethyl sulfoxide (DMSO), ethanol, *tert*-butanol, tetrahydrofuran (THF), acetone, dioxane, and water. In most experiments, Soxhlet extraction was performed using acetone, then water-dioxane azeotrope and then acetone, each for one day.

7.2.3 Bromination of XAD-4

XAD-4 was brominated using a slight excess (1.1 equiv) of bromine. In a 1 L round bottom flask equipped with magnetic stirring bar, XAD-4 (50 g, 125 mmol vinyl groups) in 500 mL of carbon tetrachloride was cooled to 0 °C. Bromine (7 mL, 140 mmol) in 20 mL CCl_4 was added, and the reaction stirred in the dark at room temperature overnight. The resin was filtered and Soxhlet extracted for one day with CH_2Cl_2, followed by drying under vacuum at 60 °C overnight. The reaction was also done using CH_2Cl_2.

7.2.4 Reactions of brominated XAD-4

7.2.4.1. Addition of thiourea to (1,2-dibromoethyl)benzene groups

A typical reaction involved stirring 5 g brominated XAD-4 (3.99 mmol Br/g), thiourea (12 g, 160 mmol, 8 equiv per Br), and solvent (95-200 mL) at 80 °C for 2 to 4 days. Solvents used included: THF-ethanol (15:4 v/v), DMSO, H_2O-ethanol (6:1 to 35:1 v/v), ethanol, methanol, DMSO-H_2O (1:1 v/v), and dioxane-acetone (1:1 v/v). In most experiments, Soxhlet extraction was performed using water or water-dioxane azeotrope and then acetone, each for one day.

7.2.4.2. Addition of *N,N*-dimethylthioformamide to (1,2-dibromoethyl)benzene groups and methanolysis

Brominated XAD-4 (0.5 g, 3.76 mmol Br/g), *N,N*-dimethylthioformamide (TDMF, 5 mL, 58 mmol, 31 equiv per Br) were stirred under nitrogen 80 °C for 3 hours. Some reactions used tetrahydrofuran (10 mL) as the solvent, with a reaction temperature of 66 °C. Soxhlet extraction was done under nitrogen using THF or the resin was reacted with methanol.

Methanolysis was performed on some resins using a variety of methods. The filtered resin (0.5 g) could be stirred in methanol (20 mL) under nitrogen for 1-2 hours at 60 °C. Optionally, methanol could be added to the TDMF reaction mixture without first filtering the resin (1 pot). Methanolysis was also done by Soxhlet extraction (with methanol) of the filtered resin under nitrogen for one day. In most cases, the resins were purified by Soxhlet extraction under nitrogen using methanol for one day, then THF for 2 days.

One resin had both the reaction with TDMF and methanolysis performed twice to determine if multiple reactions would increase yield. The first reaction sequence used THF, and at the end of 3 hours, methanol was added. The second reaction sequence also used THF, which was removed by filtration before methanolysis.

7.2.5 Characterization

7.2.5.1 Elemental analysis

Samples were sent to the University of British Columbia or Robertson Microlit Laboratories (Madison, NJ) to be analyzed for sulfur, nitrogen, oxygen, and bromine where applicable.

7.2.5.2 Infrared spectroscopy

The unmodified resins were characterized using infrared spectroscopic analysis to measure the vinyl group content [6, 45]. Modified resins were characterized to determine reduction of vinyl peaks and introduction of peaks due to the modifying groups. Samples were ground into powder with FTIR-grade potassium bromide (KBr) and disks were prepared. Fourier transform infrared absorbance spectra were taken with a Bruker IFS 66 spectrometer, using a DTGS detector and 2 cm^{-1} resolution, with 120 to 200 scans.

7.2.5.3 Raman spectroscopy

Fourier transform Raman spectra were taken using a Bruker IFS 88 spectrometer with FRA-105 Raman module using a Nd^{+3}:YAG laser (1064.1 nm). Samples were ground into powder and packed lightly into an aluminum sample cup.

The number of scans ranged from 250 to 5000, with a 4 cm^{-1} resolution. It should be noted that spectra taken with samples held in glass melting point tubes had fluorescence due to the glass, obscuring most peaks, so this method was not used.

7.2.5.4 ^{13}C NMR spectroscopy

Solid-phase ^{13}C NMR spectra were obtained with a Chemagnetics Inc. M-100 instrument. ^{13}C CP-MAS (cross-polarization magic angle spinning) NMR spectra were obtained at 25.1 MHz with a contact time of 2 ms, pulse delay of 2 s, spinning rate of 3-4 kHz, and high-power proton decoupling during acquisition. The ^{13}C CP-MAS-DD (DD is dipolar dephasing) NMR spectra were obtained similarly, with a dephasing time (τ) of 45 μs.

7.3. Results and Discussion

7.3.1 Characteristics of starting materials

Previously, we characterized the starting material with regard to vinyl content, surface area, porosity, and monomer content and the results are fully presented elsewhere [6]. Table 7.1 summarizes these characteristics. The vinyl content was calculated using FTIR spectroscopy [6, 45]. The degree of functionalization (X_{VB}, %) is the percentage of repeat units which have vinylbenzene groups, and the degree of cross-linking (X_{CL}, %) is the percentage of repeat units which cross-link the resin. The pore size distribution is based on the percent of the total pore volume with pores of a given diameter.

Table 7.1. Characteristics of XAD-4 (data from [6])

Surface Area (m^2/g)	Total Pore Volume (mL/g)	Pore Size (nm)	Degree of Functionalization (X_{VB}, %)	Degree of Cross-Linking (X_{CL}, %)	Vinyl Content (mmol/g)
831	1.181	< 6 (17.3%) 6-10 (20.5%) 10-20 (59.5%)	33 ± 1	47 ± 2	2.5 ± 0.1

7.3.2 Modification of XAD-4

7.3.2.1 Calculation of the degree of functionalization

The general equation for calculating the degree of functionalization of modified XAD-4 (X_{fg}) is based on the average MW per repeat unit of unmodified resin (130.6 for 80% DVB content), the mole content of functional group (mol fg/g, calculated from elemental analysis), and the molecular weight (MW fg) of the modifying group (equation 7.1). For example, the degree of functionalization of brominated XAD-4 ($X_{1,2\text{-}Br}$) was calculated based on the bromine content. Since each functional group contains two bromine atoms ($-CHBrCH_2Br$), the (mol fg/g) equals (mol Br/g ÷ 2) and the (MW fg) equals (MW Br x 2), simplifying equation 7.1 to equation 7.2. Similarly, the calculation for the degree of functionalization of bromohydrated XAD-4 (functional group $-CHOHCH_2Br$, $X_{1,2\text{-}OHBr}$) is shown in equation 7.3. The oxygen content could be used instead of the bromine content. The percent conversion (Φ) of vinyl groups (double bonds) to modified groups is given in equation 7.4.

Equation 7.1
$$X_{fg} = \frac{130.6 \times (\text{mol fg/g})}{1 - (\text{mol fg/g} \times \text{MW fg})} \times 100\%$$

Equation 7.2
$$X_{1,2\text{-}Br} = \frac{130.6\ \text{g/mol} \times (\text{mol Br/g} \div 2)}{1 - (\text{mol Br/g} \times \text{MW Br})} \times 100\%$$

Equation 7.3
$$X_{1,2\text{-}BrOH} = \frac{130.6\ \text{g/mol} \times (\text{mol Br/g})}{1 - (\text{mol Br/g} \times \text{MW OHBr})} \times 100\%$$

Equation 7.4
$$\Phi = \frac{X_{fg}}{X_{VB}} \times 100\%$$

7.3.2.2 Bromohydration of XAD-4

The resins were characterized by infrared analysis to qualitatively determine reduction in vinylbenzene groups. The methods giving the greatest reduction in vinyl peaks in the FTIR spectra used large proportions of water. This probably ensured penetration of water into the polymer matrix. Table 7.2 compares the results of the two syntheses with the greatest reductions in vinyl groups.

Table 7.2. Results of bromohydration of XAD-4 with *N*-bromosuccinimide (a)

Resin	Reaction Conditions	$C_{1,2\text{-OHBr}}$ (mmol/g)	$X_{1,2\text{-OHBr}}$ (%)	Φ
1 XAD-4-OHBr	1 g XAD-4 10 mL H_2O	1.54 ± 0.01 mmol Br/g	24% (Br result)	73% (Br)
	10 mL acetone 1.1 equiv NBS Soxhlet: acetone, H_2O-dioxane, acetone	1.6 ± 0.1 mmol O/g	25% (O result)	75% (O)
2 XAD-4-OHBr	1 g XAD-4 (b) 20 mL H_2O	1.80 ± 0.01 mmol Br/g	29% (Br result)	87% (Br)
	1.1 equiv NBS Soxhlet: acetone	1.20 ± 0.04 mmol O/g	18% (O result)	54% (O)

(a) Both reactions were done under nitrogen at room temperature for 1 day.
(b) XAD-4 was not pretreated by Soxhlet extraction with acetone, only dried in vacuo. Imbibed with NaCl and Na_2CO_3.

The oxygen and bromine contents (mol %) of resin **1** were comparable, with a degree of functionalization of 24-25%, and conversion of vinyl groups by as much as 75%. In contrast, resin **2** had more bromine than oxygen, indicating the presence of more than one type of functional group, including the bromohydrin, but also most likely the (1,2-dibromoethyl)benzene group ($X_{1,2\text{-Br}}$ as much as 11%). Resin **2** was prepared from XAD-4 which had not been purified by Soxhlet extraction to remove the salts. This was done to determine if the reaction could be performed with water as the sole solvent since XAD-4 can be wetted when imbibed with salts. Since NBS is more soluble in acetone than water, formation of bromine may have occurred before the NBS could have penetrated the resin and reacted to form the bromohydrin group when water was used. The NBS was used as received; further purification may have improved yields.

The small molecule analogue, 2-bromo-1-phenylethanol, has been prepared previously from styrene [18-21]. The reaction done with styrene using hydrobromous acid (formed by mixing bromine and potassium bromide in water or with *N*-bromoacetamide and water in dioxane [18]) was not attempted because of the possibility of side-products including (1,2-dibromoethyl)benzene groups. *N*-bromosuccinimide with water has also been used to prepare 2-bromo-1-phenylethanol from styrene in 82% yield, which is close to our yield of 75% for resin **1** [19]. This same reaction was also done on styrene using dimethyl sulfoxide (DSMO) as the solvent, with a 76% yield [20, 21]. However, we did not get as good a result with use of DMSO in comparison to resins **1** and **2** (based on reduction of vinyl peaks in FTIR spectra). Other solvents that we used included *tert*-butanol and tetrahydrofuran (THF). The use of alcohol (ethanol, *tert*-butanol) formed ethers on the resins. In the case of *tert*-butanol, the FTIR spectrum had a strong peak at 1368 cm^{-1}, which is attributed to the *tert*-butyl group. Since water was only present in small quantities for this experiment, the *tert*-butanol may have acted as a reagent. In comparison to the result for resin **1**, the reaction using THF did not have as great a reduction of vinyl peaks in the FTIR spectrum, although the other peaks were comparable. The reaction using dioxane also did not give as great a reduction in vinyl groups, as well, peaks were seen at 602 and 571 cm^{-1} which are attributed to the presence of the dibromo groups (as will be seen later).

7.3.2.3 Bromination of XAD-4

We previously modified XAD-4 by bromination in order to study the distribution of vinyl groups within the resin [5]. The bromine contents, listed in table 7.3, were in close agreement to the vinyl content calculated using the FTIR spectroscopic technique of the starting XAD-4 (table 7.1), X_{VB}, 33 ± 1 %. This would indicate that the vinylbenzene groups were converted entirely to (1,2-dibromoethyl)benzene groups without further cross-linking or other side-reactions.

Table 7.3. Results of bromination of XAD-4 (a)

Resin	Reaction Conditions	$C_{1,2\text{-Br}}$ (mmol/g)	$X_{1,2\text{-Br}}$ (%)	Φ
3	100 g XAD-4	2.00 ± 0.01 mmol fg/g	39%	100%
XAD-4-Br	750 mL CH_2Cl_2			
	1.1 equiv Br_2	3.99 ± 0.01 mmol Br/g		
4	50 g XAD-4	1.88 ± 0.01 mmol fg/g	35%	100%
XAD-4-Br	500 mL CCl_4			
	1.1 equiv Br_2	3.76 ± 0.01 mmol Br/g		

(a) Both reactions were done at room temperature for 1 day.

Faber and co-workers modified XAD-2 and XAD-4 by anti-Markovnikov hydrobromination, using radical addition of hydrogen bromide (HBr), to form $-CH_2CH_2Br$ groups [16]. The bromine content was 0.95 mmol Br/g for XAD-2 and 1.95 mmol Br/g for XAD-4. Using our formula to calculate degree of functionalization, we find that the degree of functionalization of hydrobrominated groups, and thus vinyl groups, was 13.5% for XAD-2 and 30.2% for XAD-4.

They mentioned that the vinyl content was 0.7 mmol/g for XAD-2 and 1.95 mmol/g for XAD-4; however, based on the degrees of functionalization, we calculate that the vinyl contents were closer to 1.0 mmol/g and 2.3 mmol/g respectively [5]. The vinyl content of XAD-4 is comparable to our findings (table 7.1) [6].

The preparation of brominated XAD-4 is a simple one-step procedure which produced a functional polymer which could be further modified by reaction of the (1,2-dibromoethyl)benzene groups as will be seen in the following sections.

7.3.2.4 Reaction of brominated XAD-4 with thiourea

Brominated XAD-4 was reacted with thiourea (TU) under a variety of reaction conditions. Results of three typical reactions are given in table 7.4. Since thiourea has two nitrogen atoms, the nitrogen content was divided by two in order to calculate the isothiouronium bromide content. The sulfur content was always greater than the calculated TU content, indicating that hydrolysis or alcoholysis occurred. The degree of uncontrolled hydrolysis/alcoholysis increased from resins **5** through to **7**, as seen by the nitrogen and bromine contents (table 7.4). The infrared spectra of each resin further supports this, as will be seen later on. Not all of the bromine was replaced, leading to a range of functional groups, such as (1,2-dibromoethyl)benzene, (1,2-di(isothiouronium)ethyl)benzene, (1-isothiouronium-2-bromoethyl)benzene, (1-bromo-2-(isothiouronium)ethyl)benzene, as well as the hydrolyzed analogues.

As mentioned in the introduction, chloromethyl groups of cross-linked polyepichlorohydrin (PECH) were reacted with thiourea using a solvent mixture of *N,N*-dimethylformamide (DMF) and ethanol, or DMF with 2M HCl [33]. As with the resins we prepared, these resins had a mixture of functional groups including thiol, isothiouronium, and dimethylamino (from the solvent), and in all cases, most of the isothiouronium groups were hydrolyzed, as seen by comparison of the sulfur and nitrogen contents: 7.8 mmol S/g, 3.4 mmol N/g, giving a maximum of 1.7 mmol isothiouronium groups/g, and as much as 6.1 mmol thiol/g.

Although we did not do further modifications with the thiourea-modified resins, the isothiouronium groups could have been hydrolyzed to thiol groups using basic phase-transfer conditions, as others have done [36, 38]. An alternate method of converting the brominated XAD-4 to a thiol-containing resin is presented in the following section. The advantage over the use of thiourea is that the modifying reagent is a liquid and can be used in the absence of solvent.

Table 7.4. Results of reaction of brominated XAD-4 with thiourea

Resin	Reaction Conditions	Elemental Contents (mmol/g) (a)
5	5 g XAD-4-Br (**3**) (b)	2.07 ± 0.01 mmol N/g
XAD-4-TU	75 mL THF, 20 mL EtOH (95%)	(1.04 ± 0.01 mmol TU/g)
	8 equiv thiourea (TU) per Br	1.50 ± 0.03 mmol S/g
	80 °C, 3 days	2.34 ± 0.01 mmol Br/g
6	1 g XAD-4-Br (**3**) (b)	1.24 ± 0.02 mmol N/g
XAD-4-TU	100 mL EtOH (95%)	(0.62 ± 0.01 mmol TU/g)
	8 equiv thiourea (TU) per Br	1.1 ± 0.1 mmol S/g
	78 °C, 2 days	1.70 ± 0.01 mmol Br/g
7	1 g XAD-4-Br (**4**) (c)	1.4 ± 0.2 mmol N/g
XAD-4-TU	30 mL H_2O, 5 mL EtOH (95%)	(0.7 ± 0.1 mmol TU/g)
	8 equiv thiourea (TU) per Br	1.51 ± 0.03 mmol S/g
	80 °C, 3 days	0.98 ± 0.03 mmol Br/g

(a) Thiourea has 2N and 1S, the isothiuronium salt has 2N:1S:1Br.
(b) XAD-4-Br (**3**) had 3.99 mmol Br/g (2.00 mmol fg/g, see table 7.3).
(c) XAD-4-Br (**4**) had 3.76 mmol Br/g (1.88 mmol fg/g, see table 7.3).

7.3.2.5 Addition of *N,N*-dimethylthioformamide to brominated XAD-4 and methanolysis

Brominated XAD-4 was reacted with *N,N*-dimethylthioformamide to produce a resin with iminium bromide groups (scheme 7.2). Methanolysis converted the iminium bromide to thiol groups. The results of several preparations of thiol-containing XAD-4 (XAD-4-SH), as well as the intermediate (XAD-4-TDMF), are shown in table 7.5.

As with the resins modified with thiourea, the unequal nitrogen and sulfur contents of the *N,N*-dimethylthioformamide-modified resins (**8** and **10**) indicated that hydrolysis/alcoholysis had occurred. When methanolysis was performed, the nitrogen and bromine contents decreased further and the sulfur content increased, as would be expected (as seen for resins **8** and **9**).

Approximately 75% of the bromine was replaced by sulfur in resin **9**. As will be further discussed in the section of the infrared spectra, the functional groups most likely consisted of (1,2-dimercaptoethyl)benzene, (1-mercapto-2-bromoethyl)benzene, some (1,2-dibromoethyl)benzene, and possibly (1-bromo-2-mercaptoethyl)benzene groups.

Table 7.5. Results of reaction of brominated XAD-4 with *N,N*-dimethylthioformamide with subsequent methanolysis

Resin	Reaction Conditions	Elemental Contents (mmol/g) (a)
8 XAD-4-TDMF	0.5 g XAD-4-Br (**4**) (b) 5 mL TDMF (31 equiv per Br) 80 °C, nitrogen, 3 hours (no methanolysis)	0.15 ± 0.01 mmol N/g 2.19 ± 0.01 mmol S/g 1.25 ± 0.01 mmol Br/g
9 XAD-4-SH	0.5 g XAD-4-Br (**4**) (b) 5 mL TDMF (31 equiv per Br) 80 °C, nitrogen, 3 hours, filter, wash with THF Methanolysis: 20 mL MeOH 60 °C, nitrogen, 1 hour	0.07 ± 0.01 mmol N/g 2.40 ± 0.03 mmol S/g 0.92 ± 0.02 mmol Br/g
10 XAD-4-TDMF	0.5 g XAD-4-Br (**4**) (b) 5 mL TDMF (31 equiv per Br) 10 mL THF 66 °C, nitrogen, 3 hours (no methanolysis)	0.09 ± 0.01 mmol N/g 0.80 ± 0.02 mmol S/g
11 XAD-4-SH	0.5 g XAD-4-Br (**4**) (b) 5 mL TDMF (31 equiv per Br) 80 °C, nitrogen, 3 hours, add 20 mL MeOH 60 °C, nitrogen, 1 hour	0.08 ± 0.01 mmol N/g 2.50 ± 0.02 mmol S/g 1.07 ± 0.01 mmol Br/g
12 XAD-4-SH	0.5 g XAD-4-Br (**4**) (b) 3 mL TDMF (18 equiv per Br) 80 °C, nitrogen, 3 hours, Soxhlet extraction with MeOH under nitrogen, 1 day	0.10 ± 0.01 mmol N/g 2.07 ± 0.01 mmol S/g 0.99 ± 0.03 mmol Br/g
13 XAD-4-SH	1 g XAD-4-Br (**4**) (b) 10 mL TDMF (31 equiv per Br) 10 mL THF 66 °C, nitrogen, 3 hours, add 30 mL MeOH 60 °C, nitrogen, 1 hour	0.08 ± 0.01 mmol N/g 0.86 ± 0.01 mmol S/g 2.33 ± 0.01 mmol Br/g
14 XAD-4-SH	0.5 g **13** XAD-4-SH 5 mL TDMF (31 equiv per original Br) 10 mL THF 66 °C, nitrogen, 3 hours, add 20 mL MeOH 60 °C, nitrogen, 2 hours	1.02 ± 0.03 mmol S/g 2.10 ± 0.01 mmol Br/g

(a) *N,N*-Dimethylthioformamide (TDMF) has 1N and 1S, the salt has 1N:1S:1Br.
(b) XAD-4-Br (**4**) had 3.76 mmol Br/g (1.88 mmol fg/g, see table 7.3).

The use of tetrahydrofuran (THF) as solvent led to much lower sulfur contents of the modified resins, as seen for resins **10**, **13** and **14** (table 7.5). As well, the use of slightly lower amounts of *N,N*-dimethylthioformamide (TDMF) also led to slightly lower sulfur contents as seen for resin **12**. Repeating the modification on a resin which had previously been modified did lead to an increase in the sulfur content and a decrease in the bromine content as seen when resin **13** was re-modified to prepare resin **14**. This may have been due to a longer reaction period overall, or to steric and electronic effects: the intermediate iminium bromide may have prevented the addition of more TDMF to surrounding bromine groups. Multiple contacts including methanolysis each time would form the less bulky and neutrally-charged thiol group, allowing further modification to take place.

The methanolysis step was done either after filtration and rinsing off excess TDMF from the resin (resin **9**), or by addition of methanol directly to the reaction (resins **11**, **13**, **14**), or by Soxhlet extraction with methanol (resin **12**). It would seem from the results that filtration is not necessary when TDMF is used neat. Soxhlet extraction with methanol is also sufficient.

Overall, longer contact times with neat TDMF, Soxhlet extraction using methanol under nitrogen, and repeated cycles would probably increase the conversion of bromine groups by more than 75%.

Table 7.6 compares our results of the introduction of thiol groups to poly(divinylbenzene-*co*-ethylvinylbenzene) by the anti-Markovnikov radical addition of thiols to the pendant vinylbenzene groups [1, 2] and by the conversion of the (1,2-dibromoethyl)benzene groups of brominated XAD-4 with results of other researchers in the preparation of thiol-containing resins.

Copolymers of 4-chloromethylstyrene and *N*-vinyl-2-pyrrolidone were also used to prepare thiol-containing resins by reaction of the chloromethyl groups with 100 equivalents *N,N*-dimethylthioformamide using the same reaction conditions that we used [36]. The chloromethyl groups were completely converted to iminium salts (96-100% conversions), whereas we still had some bromine-containing groups in our modified resins (table 7.5). Use of a higher amount of TDMF may have improved conversions in our case.

While our resins did not have the highest sulfur contents, they were comparable to most of the other experimental resins. As well, our resins have the advantage of having a vicinal dithiol group, which can coordinate with metals more strongly due to the chelation effect. Our method of preparation is also simpler: bromination of XAD-4, followed by reaction with *N,N*-dimethylthioformamide with subsequent methanolysis. This last step could be done as the purification step, for example, Soxhlet extraction with methanol under an inert atmosphere. The modification of XAD-4 by thiol addition [2] is only a one-step process. The use of dithiols such as 1,2-ethanedithiol, etc., and 2-mercaptoethyl sulfide, also introduces spacer groups which may make the ligands more accessible to ions. Resins modified with sodium 2,3-dimercapto-1-propanesulfonate not only have thiol groups, but also sulfonate salts which make the resin hydrophilic.

Table 7.6. Comparison of methods of introduction of thiol-containing groups onto various polymers

Method	Result (mmol S/g)	Reference
Anti-Markovnikov addition of dithiols to pendant vinylbenzene groups of poly(divinylbenzene-*co*-ethylvinylbenzene). a) sodium 2,3-dimercapto-1-propanesulfonate b) 2-mercaptoethyl sulfide c) 2,3-dimercapto-1-propanol	a) 0.6 mmol fg/g b) 1.4 mmol fg/g c) 1.6 mmol fg/g	[2]
Conversion of the (1,2-dibromoethyl)benzene groups of brominated XAD-4 with *N,N*-dimethylthioformamide followed by methanolysis.	2.40	this work
Polystyrene was brominated, lithiated, reacted with S_8 and reduced with $LiAlH_4$ to produce resins with thiophenol groups.	2.85	[28, 38]
Polystyrene was lithiated, reacted with S_8 and reduced with $LiAlH_4$ to produce resins with thiophenol groups.	1.98	[38]
Chloromethylated polystyrene was reacted with thiourea, followed by base hydrolysis under nitrogen to form resins with benzylmercaptan groups.	2.04	[38]
Chloromethylated polystyrene was reacted with 1,4-butanedithiol, using basic phase transfer conditions.	3.5	[39]
Duolite GT-73 (Rohm and Haas) (Commercial polystyrene resin with thiophenol groups)	6.6	[42]
Chloromethylated polystyrene was modified to have pendant 1,2-dibromoethyl groups which were reacted with NaSH to produce resins with vicinal thiol groups.	6.3 (calculated from: 20.2% S)	[29]

7.3.3 Spectroscopic characterization

The modified resins were spectroscopically characterized and compared to the starting material using infrared, Raman and ^{13}C NMR spectroscopy.

7.3.3.1 Infrared spectroscopy

Infrared spectroscopy was used to compare the functionalities of XAD-4 to bromohydrated XAD-4 (XAD-4-OHBr), and to brominated XAD-4 (XAD-4-Br) (figure 7.2). The infrared spectral peaks have previously been assigned for XAD-4 [6, 45].

On comparison of the spectra for XAD-4 and the modified resins, the five peaks due to the vinyl groups decrease in relation to the degree of functionalization. The peak at 905 cm^{-1} is due to both vinyl groups and disubstituted phenyls, so it is never completely eliminated.

For the modified XAD-4, the vinyl peaks (1630, 1410, 1015, 990 cm^{-1}) are decreased significantly (figure 7.2). The spectrum of XAD-4-OHBr (**1**) has new peaks due to (1-hydroxy-2-bromoethyl)benzene groups at 3549 (O-H), 1255, 1215, 1121, 1068 cm^{-1} (C-O, secondary alcohol), 873, and 574 cm^{-1} (C-Br) [46, 47]. The spectrum of XAD-4-OHBr (**2**) was similar to that of **1**, with additional peaks at 1722, 1686, and 599 cm^{-1}. These peaks are possibly due to residual succinimide (1722 and 1686 cm^{-1}) [48], and the presence of (1,2-dibromoethyl)benzene groups (599 and 573 cm^{-1}) [48]. From the elemental analyses (table 7.2), resin **1** had only the bromohydrin group present, whereas resin **2** had bromohydrin and (1,2-dibromoethyl)benzene groups.

Resins **3** and **4**, both brominated XAD-4 (XAD-4-Br), had identical infrared spectra. The FTIR spectrum of resin **4** is compared to those of XAD-4 and resin **1** in figure 7.2. In comparison to the spectrum of XAD-4, the peak at 900 cm^{-1} is reduced, with a second peak at 892 cm^{-1} visible. Peaks due to the (1,2-dibromoethyl)benzene functionality are seen (1236, 1215, 1176, 1130, 602 (C-Br), and 571 cm^{-1} (C-Br)) [47, 48]. In comparison to the spectral peaks assignments of hydrobrominated XAD-4 [16], the –CH_2Br group had a C-Br stretch at 571 cm^{-1} and the –CHBr group had a C-Br stretch at 602 cm^{-1}.

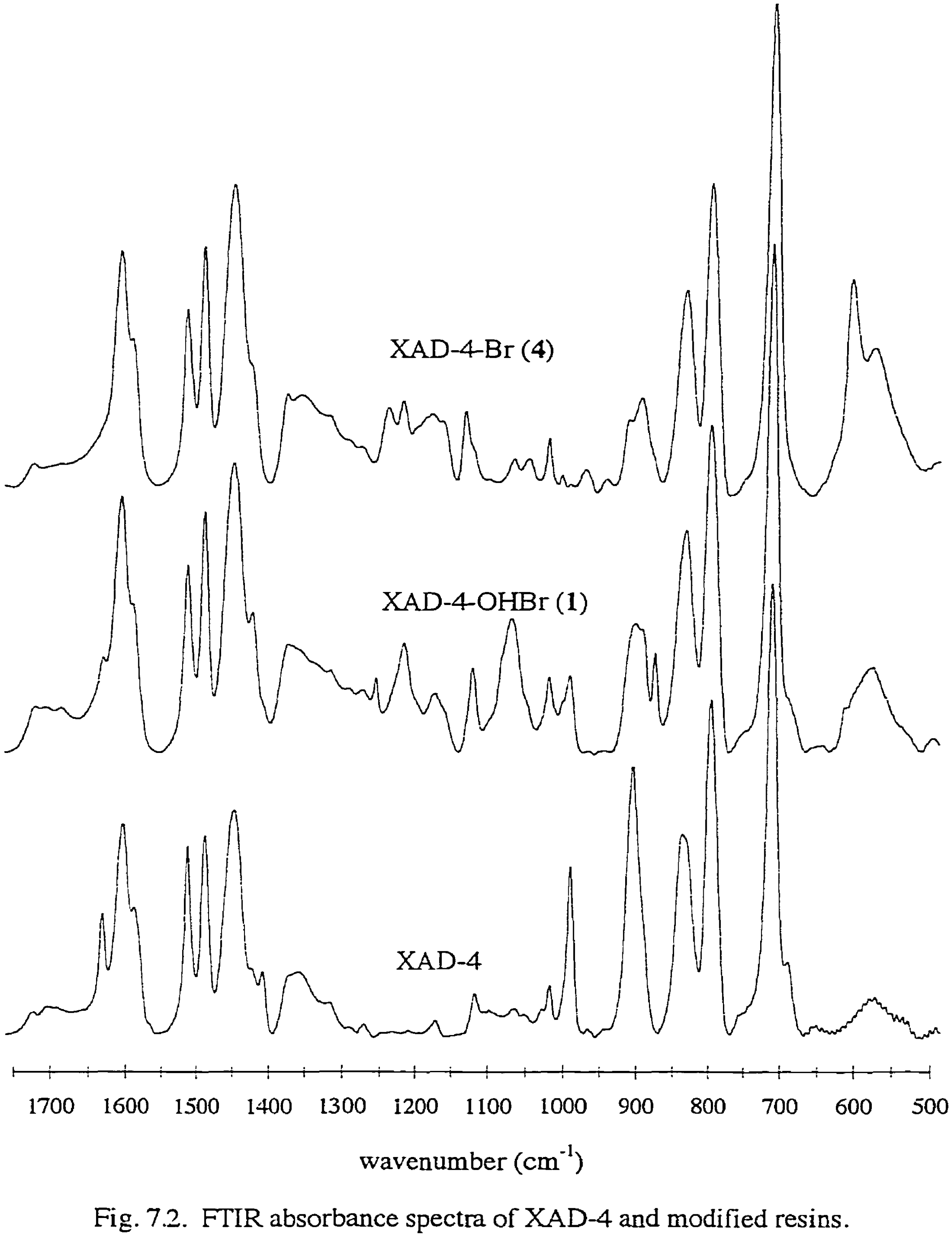


Fig. 7.2. FTIR absorbance spectra of XAD-4 and modified resins.

The infrared spectrum of brominated XAD-4 (XAD-4-Br, **4**) is compared to those of brominated XAD-4 modified with thiourea (XAD-4-TU, **5**, **6**, **7**), and with *N,N*-dimethylthioformamide (XAD-4-TDMF, **8**) followed by methanolysis (XAD-4-SH, **9**), in figure 7.3. For the modified resins (XAD-4-TU, XAD-4-TDMF, and XAD-4-SH), reductions in the C-Br peaks at 602 and 571 cm^{-1} are seen. In all cases (**5**, **6**, **7**, **8**, **9**), the peak at 602 cm^{-1} is reduced to a greater extent than that at 571 cm^{-1}, indicating that the secondary benzylic bromide (Ph–CHBr–) is more reactive than the bromomethyl ($-CH_2Br$) group.

The spectra for the XAD-4-TU resins (**5**, **6** and **7**, figure 7.3) are similar. On comparison of the elemental contents (table 7.4), the resins showed a decrease in nitrogen and bromine contents from **5** through to **7**. It would appear that the isothiouronium groups were hydrolyzed. The sulfur contents are higher in all cases than the thiourea content, calculated by division of the nitrogen content by 2 (table 7.4). Resin **7**, which was prepared in water, had the lowest thiourea and bromine contents. On comparison of the FTIR spectra of these resins (figure 7.3), the peak at 1650 cm^{-1}, which is likely due to C=N of the isothiouronium group [46], decreases from resin **5** to **7**. For **6**, an additional peak at 1685 cm^{-1} was seen which may have been due to N-OH [47]. Other peaks in the spectra of resins **5**, **6** and **7** were: 1472, 1254, 1120, 1019, and 873 cm^{-1}. Resin **6** had an additional peak at 1270 cm^{-1}. The peaks in the spectrum of **7** were less prominent than for **5** and **6**, in agreement with a loss of isothiouronium groups. Other side-functionalities such as cyclic structures may have also been present.

As mentioned in the introduction, other researchers have modified cross-linked polyepichlorohydrin (PECH) resins with thiourea using a solvent mixture of *N,N*-dimethylformamide (DMF) and ethanol, or DMF with 2M HCl [33]. The product had a mixture of functional groups including thiol and isothiouronium, and in all cases, most of the isothiouronium groups were hydrolyzed, as seen by comparison of the sulfur and nitrogen contents. This is a similar situation as we encountered.

As with the resins modified with thiourea, the spectrum of the *N,N*-dimethylthioformamide-modified resin (XAD-4-TDMF, **8**, figure 7.3) showed a decrease of peaks associated with the (1,2-dibromoethyl)benzene group: 1236, 1215, 1130, 602, and 571 cm^{-1}. The peak at 1674 cm^{-1} was due to C=N of the iminium bromide [46, 49]. As with the thiourea-modified resins, the nitrogen content was less than the sulfur content, indicating hydrolysis. This modification technique has been done with benzyl bromide, forming benzyl mercaptan in 100%

yield [49]. However, the intermediate was not isolated, instead, a one-pot reaction was done, first forming the adduct with TDMF, followed by methanolysis.

Compared to the spectrum of XAD-4-TDMF (**8**), the peak due to C=N at 1674 cm^{-1} was weaker in the spectrum of XAD-4-SH (**9**), as were the nitrogen and bromine contents (table 7.5). As with **8**, the peaks due to C-Br were reduced significantly. Since the secondary benzylic bromide (Ph–CHBr–) is more reactive than the bromomethyl (–CH_2Br) group and approximately 75% of the bromine was replaced by sulfur-containing groups in XAD-4-SH (**9**), the functional groups present would most likely include (1,2-dimercaptoethyl)benzene, (1-mercapto-2-bromoethyl)benzene, and some (1,2-dibromoethyl)benzene groups.

7.3.3.2 Raman spectroscopy

Figure 7.4 compares the Raman spectra of XAD-4 and the resins modified with *N*-bromosuccinimide and water (XAD-4-OHBr, **1**), bromine (XAD-4-Br, **4**), and *N,N*-dimethylthioformamide (XAD-4-TDMF, **8**) followed by methanolysis (XAD-4-SH, **9**). The Raman spectra of the thiourea-modified resins were similar to that for the *N,N*-dimethylthioformamide-modified resin and are not shown. No thiol peaks were visible for the spectra of XAD-4-TU (**5**, **6**, **7**). The peak assignments for XAD-4 have been determined and are presented elsewhere [6].

As for the infrared spectra, the decrease of vinyl peaks (3008, 1632, 1409, and 1209 cm^{-1}) was notable for the spectra of the modified resins compared to XAD-4.

In the Raman spectrum of XAD-4-OHBr (**1**), new peaks were seen at 835 (C-C-O symmetric stretch, [47]), 678, and 581 cm^{-1} (C-Br stretch, [47]).

The Raman spectrum of XAD-4-Br (**4**) had a greater peak intensity at 1236 cm^{-1} than for XAD-4. New peaks were seen at 691 and 575 cm^{-1} (C-Br stretches, [47]), and at 406 cm^{-1} (C-C-Br stretch, [47]).

Comparison of the Raman spectrum of brominated XAD-4 (**4**) to those of the *N,N*-dimethylthioformamide-modified resin (XAD-4-TDMF, **8**) and the methanolyzed product (XAD-4-SH, **9**), shows that the peaks due to the (1,2-dibromoethyl)benzene groups are almost eliminated, in contrast to the infrared spectra where some C-Br peaks were still visible (figure 7.3). The Raman spectrum of XAD-4-SH (**9**) had a peak due to the thiol groups visible at 2575 cm^{-1} (S-H stretch, [47]). A peak at 689 cm^{-1} may be due to the thiol group (C-S stretch, [47]) or residual bromine-containing groups (C-Br stretch, [47]).

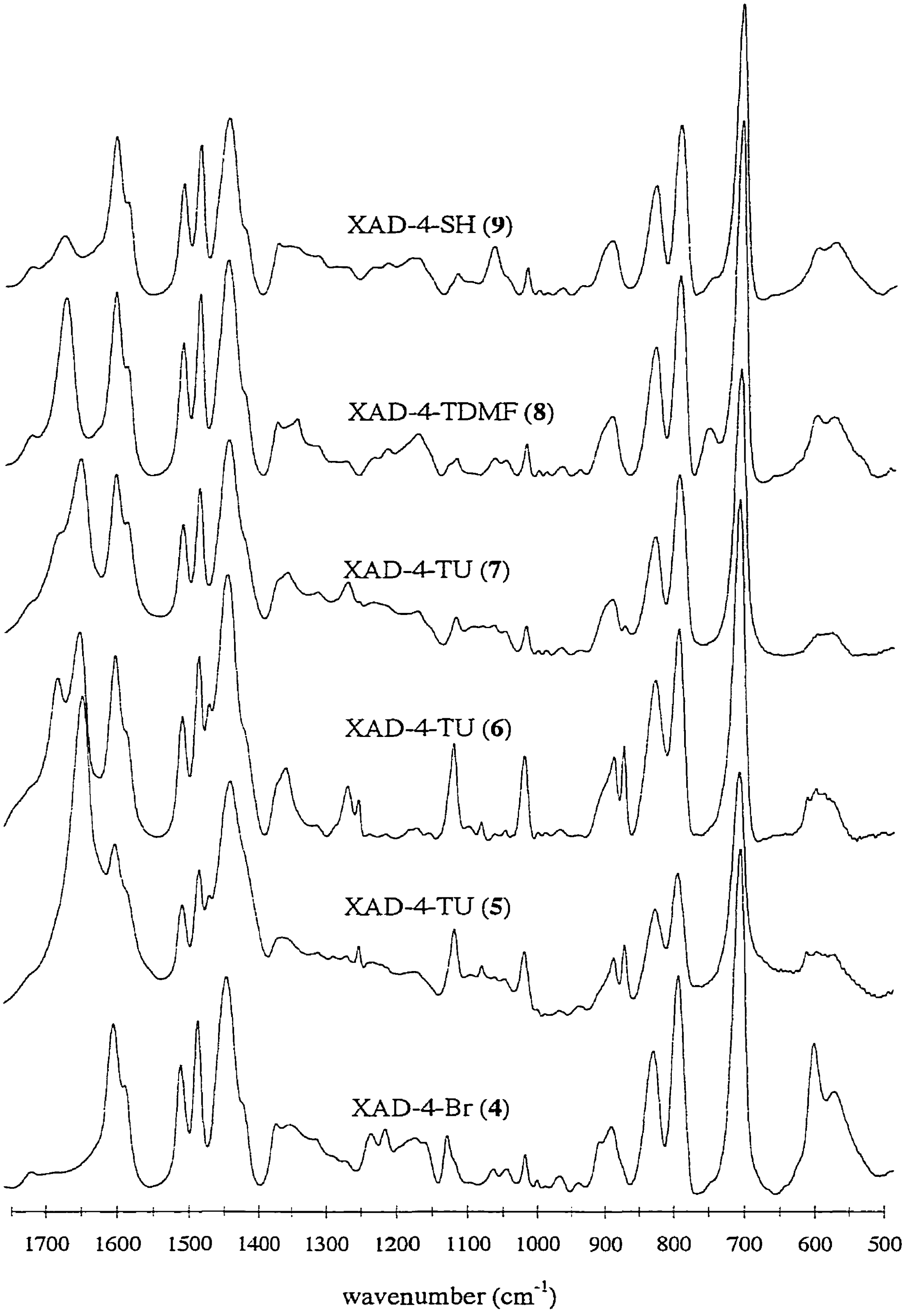


Fig. 7.3. FTIR absorbance spectra of XAD-4-Br and modified XAD-4-Br.

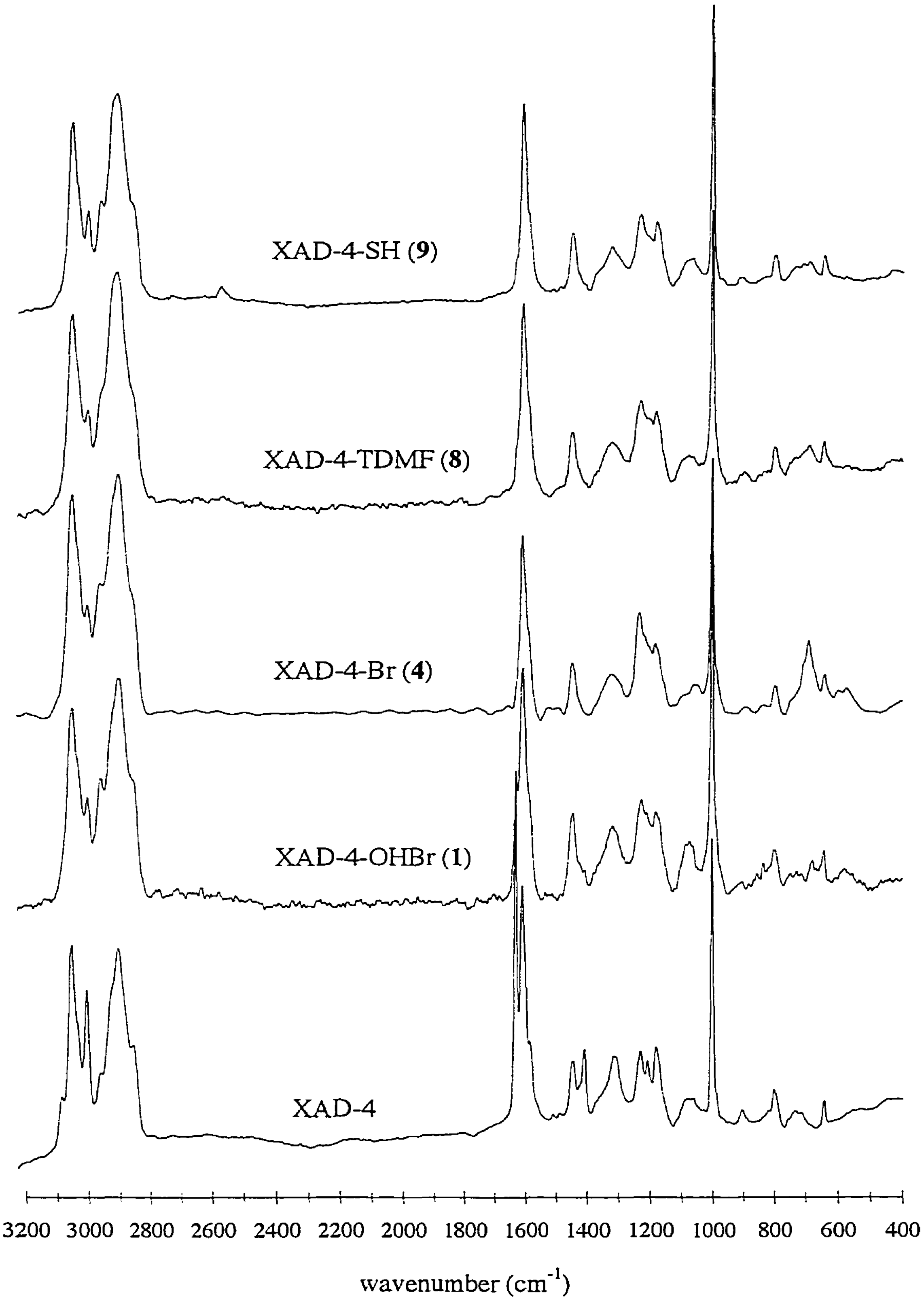


Fig. 7.4. Raman spectra of XAD-4 and modified resins.

7.3.3.3 ^{13}C NMR spectroscopy

Figure 7.5a shows the solid-phase ^{13}C CP-MAS NMR spectra and figure 7.5b shows the solid-phase ^{13}C CP-MAS-DD NMR spectra for XAD-4 and the modified resins XAD-4-OHBr (**1**) and XAD-4-Br (**4**).

The ^{13}C NMR spectral peak assignments for unmodified XAD-4 have also been determined and are presented elsewhere [6]. Dipolar dephasing eliminates the peaks due to the vinyl carbons and the polymer backbone (CH_2, CH, phenyl CH). The peak at 144 ppm corresponds to the (non-hydrogen) substituted phenyl carbons and the peak at 15-16 ppm corresponds to the methyl carbon of the pendant ethylbenzene groups.

As with the infrared and Raman spectra, the intensities of the peaks due to the vinyl group are less in the modified resins (137 ppm and 114 ppm, figure 7.5a). The dipolar-dephased spectra (figure 7.5b) show none of the functional group carbon peaks since they are not mobile enough [1]. This phenomenon was previously seen for resins modified with thiols and disulfides: the dimethylene spacers were not detected in the dipolar dephased spectra [2, 3]. Table 7.7 compares the peak assignments of analogous model compounds with the modified resins [50].

Table 7.7. ^{13}C CP-MAS NMR peak assignments for modified XAD-4

Resin	^{13}C NMR peak assignments of model compounds (a)	C (ppm)	CH_3 (ppm)	CH_2 (ppm)	CH (ppm)
1	62.73, 35.30 (b)	144	15	41, 30	129, 74, 41
4	138.53, 129.07*, 128.76*, 127.57*, 50.85*, 34.99* (c)	144	15	41, 30	129, 41

(a) Data from [50], * means odd parity (i.e. CH, CH_3).

(b) 2-Bromoethanol, [50, Vol. 1, p. 267].

(c) (1,2-dibromoethyl)benzene, [50, Vol. 2, p. 65].

As can be seen, besides the loss of vinyl peaks, the only peak of value is that for the alcohol of XAD-4-OHBr (**1**) at 74 ppm. XAD-4-OHBr (**2**) had identical NMR spectra to resin **1**, including a peak at 74 ppm. The peaks due to the bromine functionalities in the spectra for XAD-4-OHBr (**1**) and XAD-4-Br (**4**) are under the broad peaks of the resin backbone (50 ppm and 35 ppm), and were eliminated with dipolar dephasing.

The NMR spectra of XAD-4-TDMF (**8**) and XAD-4-SH (**9**) were identical to those of XAD-4-Br (**4**), and are not shown. Absence of peaks attributable to the functional groups is due to them lying in the same regions as the backbone, and elimination during dipolar dephasing due to lack of mobility of the relevant carbons.

7.3.4 Potential applications of modified resins and suggestions for further work

We have prepared resins which may have potential applications as coordinating resins, solid-phase protecting groups and adsorbents. The bromohydrated XAD-4 and brominated XAD-4 can act as functional precursors as seen in the modifications of brominated XAD-4. Modification can change properties of the resins, such as hydrophilicity, which may change behaviour in separation applications such as chromatography [5]. XAD-4 was previously modified for these applications using traditional methodologies [51], although no one has previously modified the vinylbenzene groups of XAD-4 for this purpose.

The preparation of resins with free thiol groups is desired because they can act as redox polymers and are excellent for mercury removal [52-54]. Preparations of thiol-containing resins have been multi-step, involving laborious conditions. We were previously able to prepare thiol-containing resins by the use of the one-step addition of compounds having more than one thiol group to the vinyl groups of resins [2]. We also were able to prepare resins by the modification of brominated XAD-4 using simple conditions: reaction with TDMF followed by methanolysis. This promising modification technique may also be applied to other polymers with unsaturation, such as rubbers, or to halogen-containing polymers, such as poly(vinyl chloride). Yields of the modification of brominated XAD-4 with TDMF may be improved by reaction with larger amounts of TDMF, longer reaction times, or multiple reaction cycles.

The introduction of thiourea groups may be more successful and useful as a coordinating resin by attachment through the amine. This was already done to XAD-4 using chloromethylation, amination and then conversion to the polymer-bound thiourea functionality by reaction with NH_4SCN. The introduction of spacer groups was accomplished by modification with either 1,2-diaminoethane or 1,3-diaminopropane, instead of by amination [34]. A similar resin could be prepared by the radical addition of 2-aminoethanethiol to XAD-4 (done previously to produce a resin with 1.3 mmol fg/g, [2]), followed by reaction of the polymer-bound amines with NH_4SCN.

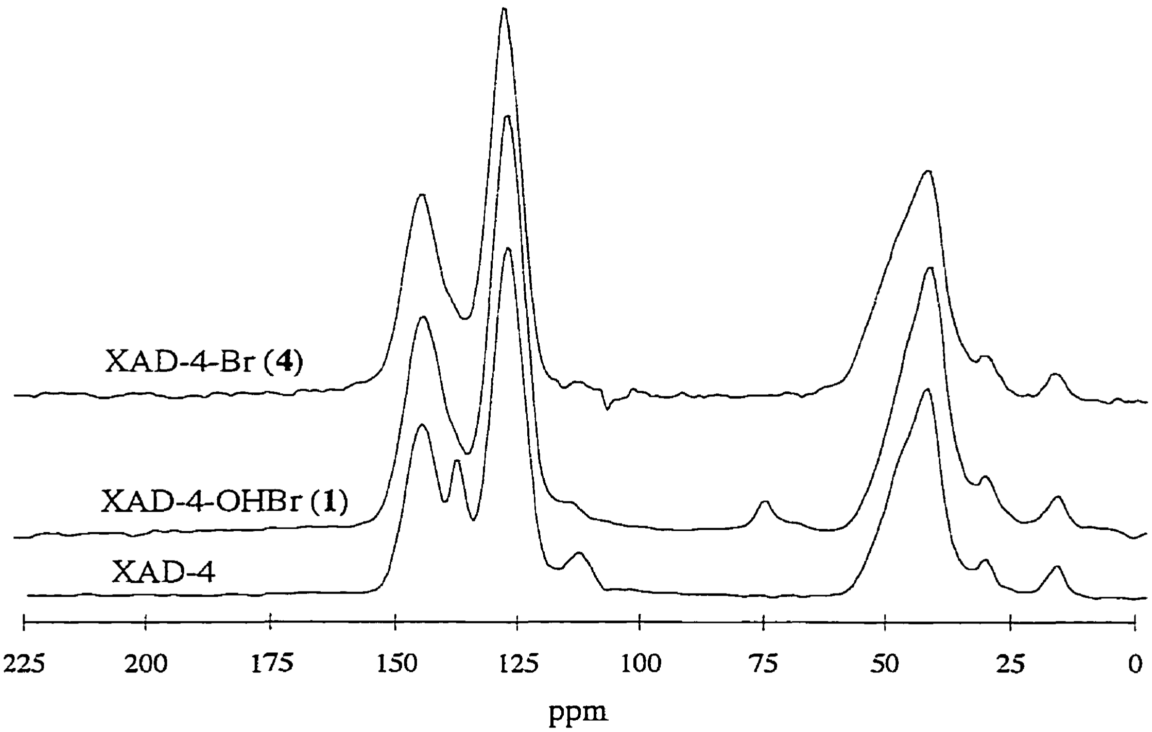


Fig. 7.5a. ^{13}C CP-MAS NMR spectra of XAD-4 and modified resins.

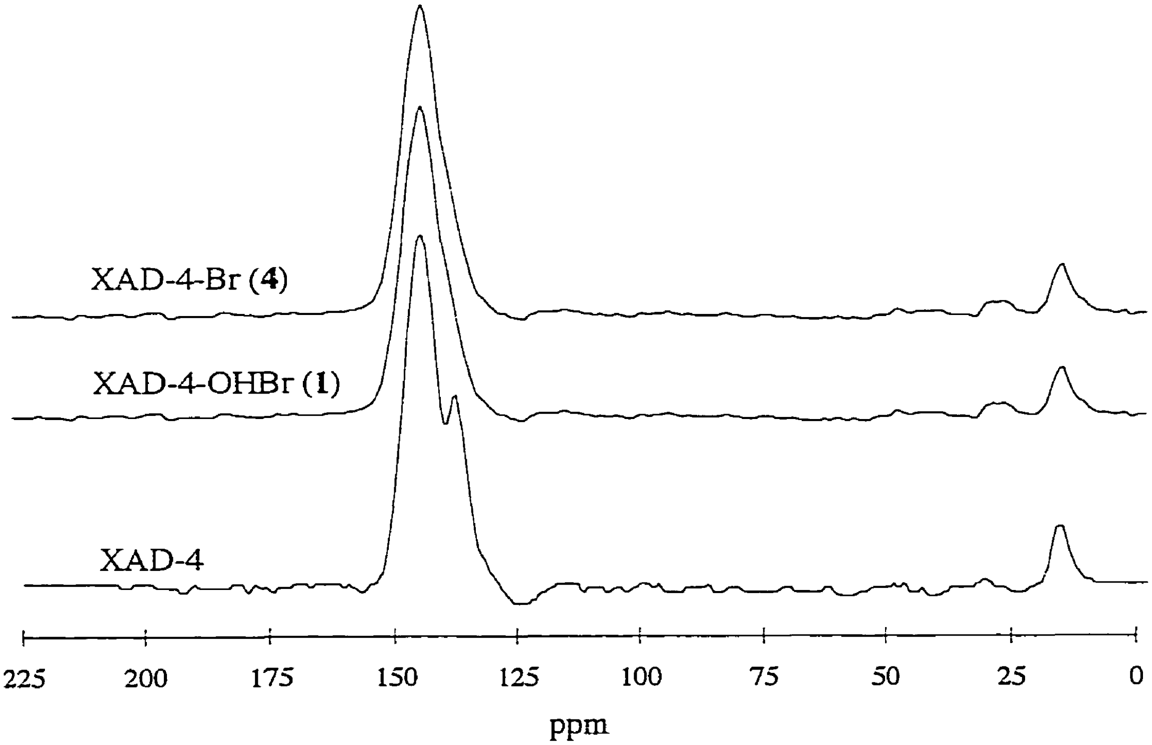


Fig. 7.5b. ^{13}C CP-MAS-DD NMR spectra of XAD-4 and modified resins.

7.4. Conclusions

Several functional polymers were prepared from the commercial resin, XAD-4, by modification to its vinylbenzene groups. Quantitative bromination produced a resin with 3.76-3.99 mmol Br/g ($X_{1,2\text{-Br}}$ 35-39%). Bromohydration of XAD-4 produced resins with (1-hydroxy-2-bromoethyl)benzene groups in 75% conversion with 1.5 mmol fg/g ($X_{1,2\text{-OHBr}}$ 24-25%). Brominated XAD-4 was converted to a resin with as much as 2.5 mmol/g thiol groups by reaction with *N,N*-dimethylthioformamide followed by methanolysis.

7.5. Acknowledgements

We wish to thank Rohm and Haas Company for donation of 5 kg of Amberlite XAD-4, and for providing some information used in this paper. ^{13}C NMR spectra were taken by Dr. F.G. Morin of the Department of Chemistry, McGill University. Elemental analyses were performed in part by M. Soon, Department of Oceanography, University of British Columbia. Some of the infrared spectra were taken by M. Ruzicka. Thanks also go to Dr. R.B. Lennox, Dr. D.N. Harpp, and Dr. D.S. Argyropoulos for helpful discussion. Funding for this project was provided by a Natural Sciences and Engineering Research Council of Canada Strategic Grant.

7.6. References

[1] J.P. Gao, F.G. Morin and G.D. Darling, Macromolecules, 26 (1993), 1196.

[2] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted May 1997. Chapter 4 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[3] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted May 1997. Chapter 5 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[4] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., in preparation. Chapter 6 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[5] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted April 1997. Chapter 2 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[6] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted April 1997. Chapter 3 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[7] R. Kunin, Amberhilites (produced by Rohm and Haas Co.), Number 161 (spring 1979).

[8] R. Kunin, Amberhilites (produced by Rohm and Haas Co.), Number 163 (winter 1980).

[9] E.F. Meitzner and J.A. Oline, U.S. Patent 4,382,124, issued May 3, 1983.

[10] Food and Drug Administration, U.S. Government, 173.65, page 100 in "Code of Federal Regulations", 21, Food and Drugs. Parts 170 to 199, revised April 1, 1994.

[11] R.L. Albright, React. Polym., 4 (1986), 155.

[12] Supelco Product Catalogue, 1995, page 264.

[13] N.A. de Munck, M.W. Verbruggen and J.J.F. Scholten, J. Mol. Catal., 10 (1981), 313.

[14] J.P.C. Bootsma, B. Eling and G. Challa, React. Polym., 3 (1984), 17.

[15] M Periyasamy, W.T. Ford and F.J. McEnroe, J. Polym. Sci., Polym. Chem. Ed., 27 (1989), 2357.

[16] M.C. Faber, H.J. van den Berg, G. Challa and U.K. Pandit, React. Polym., 11 (1989), 117.

[17] Z. Zhengpu, P. Hodge and P.W. Stratford, React. Polym., 15 (1991), 71.

[18] R.E. Buckles and J.E. Maurer, J. Org. Chem., 18 (1953), 1585.

[19] C.O. Guss and R. Rosenthal, J. Amer. Chem. Soc., 77 (1955), 2549.

[20] D.R. Dalton, J.B. Hendrickson and D. Jones, J. Chem. Soc., Chem. Commun., (1966), 591.

[21] D.R. Dalton, V.P. Dutta and D.C. Jones, J. Amer. Chem. Soc., 90 (1968), 5498.

[22] R.P. Hanzlik, Org. Synth. Coll., 6 (1988), 560.

[23] Y. Yoshida, A. Nishiyama and S. Inoue, Polym. J., 14 (1982), 327.

[24] M.J. Farrall and J.M.J. Frechet, J. Org. Chem., 41 (1976), 3877.

[25] M. Tomoi, N. Kori and H. Kachiuchi, React. Polym., 3 (1985), 341.

[26] A.J. Hagen, M.J. Farrall and J.M.J. Frechet, Polym. Bull. (Berlin), 5 (1981), 111.

[27] B.A. Utkelov, E.E. Ergozhin and R.K. Ashkeeva, React. Polym., 14 (1991), 187.

[28] T. Yamamizu, M. Akiyama and K. Takeda, React. Polym., 3 (1985), 173.

[29] M. Martinez, J. Aracil, F. Addo-Yobo and C.N. Kenney, DECHEMA Biotechnology Conferences, 2 (Bioreactors, Downstream Processing, Process and Reactor Modelling, Bioprocesses), (1988), 83; Chem. Abstr. 112 (1990), 18539y.

[30] J.L. Casillas, J.L. Garrido, J. Aracil, M. Martinez, F. Addo-Yobo and C.N. Kenney, Separations for Biotechnology, 2 (Papers presented at the International Symposium on Separations for Biotechnology), 2nd (1990), 285; Chem. Abstr. 114 (1991), 183777y.

[31] Mitsubishi product literature and Supelco Product Catalogue, 1994, p. 280.

[32] A. Warshawsky, in M. Streat and D. Naden (Editors), Ion Exchange and Sorption Processed in Hydrometallurgy, John Wiley and Sons, Chichester, 1987, Chap. 3, page 127.

[33] M.B. Jackson and L.J. Vickers, React. Polym., 8 (1988), 211.

[34] G. Zuo and M. Muhammed, React. Polym., 24 (1995), 165.

[35] C.D.S. Lee and W.H. Daly, in H.J. Cantow et al (Editors), Advances in Polymer Science, Springer-Verlag, Berlin, 1974. Volume 15, page 61.

[36] K. Yamashita, H. Saba and K. Tsuda, J. Macromol. Sci.-Chem., A26 (1989), 1291.

[37] R.J. Phillips and J.S. Fritz, Anal. Chem., 50 (1978), 1504.

[38] J.M.J. Frechet, M.D. de Smet and M.J. Farrall, Polymer, 20 (1979), 675.

[39] J.M.J. Frechet, M.D. de Smet and M.J. Farrall, J. Org. Chem., 44 (1979), 1774.

[40] J. Kalal and V. Marousek, Czech. Patent 166,481, issued June 13, 1973; Chem. Abstr. 87 (1977), 6866e.

[41] Rohm and Haas Company, "Duolite GT-73. Ion Exchange Resin." product literature, 1994.

[42] Previously unpublished result of K.L Hubbard.

[43] H. Hauptmann and F.O. Bobbio, Chem. Ber., 93 (1960), 2187. (in German); Chem. Abstr. 55 (1961), 3648e.

[44] Rohm and Haas Company, "Amberlite XAD-4. Polymeric Adsorbent." product literature, June 1993.

[45] M. Bartholin, G. Boissier and J. Dubois, Makromol. Chem., 182 (1981), 2075.

[46] R.M. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric Identification of Organic Compounds, 5th Edition, John Wiley and Sons, Inc., New York, 1991. pages 111, 112, 127.

[47] J.B. Lambert, H.F. Shurvell, D.A. Lightner and R.G. Cooks, Introduction to Organic Spectroscopy, MacMillan Publishing Co., New York, 1987. pages 178-181, 215.

[48] C.J. Pouchert (Editor), The Aldrich Library of FT-IR Spectra, Edition 1. Aldrich Chemical Company, Inc., Milwaukee, 1985. Volume 1, pages 795, 974.

[49] K. Hattori, T. Takido and K. Itabashi, Nippon Kagaku Kaishi, 1979, 105 (in Japanese); Chem. Abstr. 90 (1979), 137380b.

[50] C.J. Pouchert and J. Behnke (Editors), The Aldrich Library of ^{13}C and ^{1}H FT-NMR Spectra, Edition 1. Aldrich Chemical Company, Inc., Milwaukee, 1993. Volume 1, page 267, volume 2, page 65.

[51] T.A. Armer, Ph.D. Thesis, Tulane University, Diss. Abstr. Int. B 43 (6) (1982), 1910; Chem. Abstr. 98 (1983), 35435w.

[52] H.P. Gregor, D. Dolar and G.K. Hoeschele, J. Am. Chem. Soc., 77 (1955), 3675.

[53] C.G. Overberger and A. Lebovits, J. Am. Chem. Soc., 77 (1955), 3675.

[54] R. Bogoczek and E. Kociolek-Balawejder, Przem. Chem., 65 (1986), 368 (in Polish); Chem. Abstr. 106 (1987), 34148b.

Chapter 8

Modifications to the Pendant (1,2-Dibromoethyl)benzene Groups of Brominated Commercial poly(Divinylbenzene-*co*-Ethylvinylbenzene). Reaction with Amines.

Forward to Chapter 8

The content of the following section is comprised of a paper with the same title which will be submitted to the journal Reactive and Functional Polymers (K.L. Hubbard, G.D. Darling and J.A. Finch, to be submitted June 1997).

The previous sections included modification of poly(divinylbenzene-*co*-ethylvinylbenzene) by bromination of the pendant vinylbenzene groups, producing a resin with (1,2-dibromoethyl)benzene groups. This chapter expands on the methods used to modify brominated poly(divinylbenzene-*co*-ethylvinylbenzene), by reaction with a variety of amines. The goal was to introduce amine-containing functionalities which were vicinal to each other which could interact in metal coordination. This is of interest since coordinating resins are used in water and wastewater treatment to remove metals. The amines used in modification of brominated poly(divinylbenzene-*co*-ethylvinylbenzene) have been studied for their complexing ability with various metals, which is the topic of appendix 1. Commercial poly(divinylbenzene-*co*-ethylvinylbenzene) has not previously been used to prepare resins with vicinal diamine groups by reaction of amines with the (1,2-dibromoethyl)benzene groups of the brominated resin.

Abstract

Amberlite XAD-4, the commercial form of poly(divinylbenzene-*co*-ethylvinylbenzene), was modified by bromination of its pendant vinylbenzene groups. The vinylbenzene groups were completely converted to (1,2-dibromoethyl)benzene groups, with a degree of functionalization of 35%. Further modifications to the (1,2-dibromoethyl)benzene groups of the brominated resin were done using various amines, which led to resin with a mixture of functional groups

Keywords: Amberlite XAD-4, poly(divinylbenzene-*co*-ethylvinylbenzene), pendant vinyl groups, amines

8.1. Introduction

This paper discusses modification of (1,2-dibromoethyl)benzene groups in a polystyrene-like matrix. Starting with XAD-4, we have brominated the vinylbenzene groups to form (1,2-dibromoethyl)benzene groups. The brominated resin was then reacted with various amines.

8.1.1 Review of previous modifications of poly(divinylbenzene-*co*-ethylvinylbenzene)

Previously, our group modified laboratory-made poly(divinylbenzene-*co*-ethylvinylbenzene) by the radical addition of a few simple thiols to the pendant vinylbenzene groups [1]. We have recently expanded upon this work to include the use of a commercial resin, Amberlite XAD-4, as well as a greater range of thiols and conditions [2]. Thiols with amine functionalities such as 2-aminoethanethiol, 2-dimethylaminothiol, 2-aminothiophenol, 4-amino-2-mercaptopyrimidine, and 3-amino-5-mercapto-1,2,4-triazole were used [2]. The molecules were attached to the resin through a thioether linkage. Other work studied the addition of various disulfides and analogous thiols to the pendant vinylbenzene groups of XAD-4 [3], epoxidation of XAD-4 [4], bromohydration of XAD-4 [5], and bromination with subsequent reactions with thiourea or with *N,N*-dimethylthioformamide followed by methanolysis [5].

8.1.2 Review of poly(divinylbenzene-*co*-ethylvinylbenzene), including XAD-4

Cross-linked copolymers of divinylbenzene and ethylvinylbenzene have meta- and para-disubstituted vinylbenzene and ethylbenzene groups (figure 8.1). The degrees of functionalization are indicated by the symbols X_{CL}, X_{VB}, and X_{EB}, (CL for cross-linked, VB for vinylbenzene, and EB for ethylbenzene).

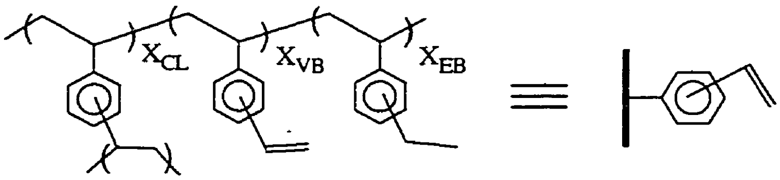


Fig. 8.1. Structure of poly(divinylbenzene-*co*-ethylvinylbenzene).

Amberlite XAD-4 (Rohm and Haas Company) is a macroporous resin prepared from 80 to 85 wt % divinylbenzene and 15 to 20 wt % ethylvinylbenzene [6-12]. Since XAD-4 has a high surface area (725 to 1040 m^2/g) and porosity (0.98 to 1.55 mL/g), vinyl groups are accessible to reagents used during modification which promotes high conversions to functional groups [6, 7, 12-14]. The vinyl content ranges from 29 to 41% (2.2 to 3.1 mmol/g) depending on lot [7]. Besides ourselves, only five research groups have mentioned the presence of vinyl groups in XAD-4 [14-18], and of these, only two actually modified the resin by reaction with the vinyl functionality [17, 18].

8.1.3 Review of modifications of resins with amines

Various polymers have had bromine groups introduced by a variety of methods, which we have reviewed [5]. We have previously brominated XAD-4 to produce a resin with (1,2-dibromoethyl)benzene groups [5]. Brominated XAD-4 was useful in the preparation of resins containing vicinal functional groups such as dithiols [5].

Other researchers have modified styrenic resins and other polymers with amines, including some of the amines that we have used. Generally chloromethylated polystyrene has been reacted with various amines [19-27]. No one has modified resins by reaction of amines with vicinal dihalo groups before. This methodology could be expanded to include the preparation of cyclic functionalities.

XAD-2 and XAD-4, and other styrenic resins were aminated to prepare coordinating resins.[19] The styrene units were chloromethylated, aminated with hexamethylenetetramine and then converted to the polymer-bound thiourea functionality by reaction with NH_4SCN. The introduction of spacer groups was accomplished by modification with either 1,2-diaminoethane or 1,3-diaminopropane, instead of by amination.

Ethylenediamine (ED), diethylenetriamine (DETA), and triethylenetetramine (TT) were fixed to polystyrene resins having between 16 and 100% (degree of functionalization, X_{Cl}) chloromethyl groups [20]. The reaction conditions included using pyridine as the solvent, a reaction time of 4 to 30 hours, a ten-fold excess of amine, and a temperature of 95 °C. The results are shown in table 8.1. We have converted the elemental contents which were given in weight percent to the millimolar amounts and calculated the quantity of functional groups (fg) by dividing by the number of N atoms per molecule (i.e. 2 for ED). It was found that the amines tended to cross-link the resin. TT gave the greatest amounts of cross-linking, followed by DETA. Longer reaction times were needed for the resins with the higher chloromethyl contents: 4 hours for 16%, 8 hours for 50%, and 30 hours for 100% chloromethyl content, respectively.

Table 8.1. Results of reaction of chloromethylated polystyrene with amines (data from [20])

	Resin Used	X_{Cl}	Amine Used	mmol N/g	mmol fg/g	mmol Cl/g
I	1.4 mmol Cl/g	16%	ED	1.81	0.90	0
I	1.4 mmol Cl/g	16%	DETA	2.43	0.81	0
I	1.4 mmol Cl/g	16%	TT	2.50	0.64	0
II	3.6 mmol Cl/g	50%	ED	4.60	2.30	0.020
II	3.6 mmol Cl/g	50%	DETA	5.30	1.76	0.003
II	3.6 mmol Cl/g	50%	TT	6.42	1.61	0.022
III	6.6 mmol Cl/g	100%	ED	7.65	3.83	0.55
III	6.6 mmol Cl/g	100%	DETA	6.66	2.22	1.11
III	6.6 mmol Cl/g	100%	TT	4.47	1.12	2.73

Chloromethylated polystyrene was also reacted with diethylenetriamine (DETA), *N*-(2-(2-pyridyl)ethyl)ethylenediamine, or 2-pyridylmethylamine by swelling in toluene at 60 °C [21]. Thiirane was added to the reaction, the temperature increased to 120 °C and the reaction proceeded for 6 to 30 hours. The

DETA-modified resin reacted with 4 equivalents of thiirane per DETA, or 2 equivalents per free amine ($-NHCH_2CH_2SCH_2CH_2SH$), giving a resin with 1.5 mmol fg/g. The central imino was the site of attachment to the resin.

Diethylenetriamine-containing resins were formed by the reaction of chloromethylated polystyrene with bis(salicylidene-iminate)diethylenetriamine (the Schiff base of DETA) by refluxing in dioxane for 2 days [22, 23]. The Schiff base resin had 2.10 mmol fg/g and hydrolysis was done with 6 M HCl at 60 °C for 6 hours to produce the DETA-containing resin with 3.02 mmol fg/g. Carbon disulfide in sodium ethoxide/ethanol solution was reacted with this resin to give a resin with dithiocarbamate groups (1.8 mmol fg/g).

In contrast, diethylenetriamine was also reacted directly with chloromethylated polystyrene by refluxing in dioxane for 2 days to produce a resin with 2.3 mmol fg/g [23]. The resin had cross-linking due to the amine groups, unlike the resin formed by modifying with the Schiff base followed by hydrolysis.

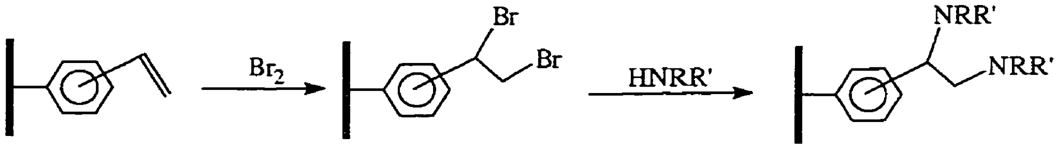
XAD-4 was chloromethylated and modified with anthranilic acid [24-26]. The reaction was done in ether for two days [24], or with ethanol at 55 °C for 3 days, using 1.5 equivalents anthranilic acid [25]. Other solvents used included acetone and *N,N*-dimethylformamide, with reactions done at room temperature for 20 hours [26]. Resins with as much as 0.30 mmol fg/g were produced [26]. The resins were then reacted with rhodium trichloride or palladium dichloride to form hydrogenation catalysts [24-26].

Chloromethylated polystyrene resins were grafted with polyethylenimine blocks which were then reacted with thiirane to form thiol-containing resins [27]. Reaction was also done with carbon disulfide to form resins with dithiocarbamate groups.

8.1.4 Addition of amines to (1,2-dibromoethyl)benzene groups of brominated poly(divinylbenzene-*co*-ethylvinylbenzene)

We are the first to take advantage of the ideal characteristics of XAD-4 to prepare functional resins by modification of the vinylbenzene groups through the addition of thiols, disulfides, epoxidation, and other reactions [2-5] We present our results on modifying the groups (1,2-dibromoethyl)benzene of brominated XAD-4 with a variety of amines (scheme 8.1).

One advantage of using this method to prepare amine-containing resins is that only a two-step modification of a commercially-available preformed matrix is necessary. The reaction conditions are straightforward and of short duration. Purification of the modified resin is also simple. Introduction of a wide range of functionalities is possible.



Scheme 8.1. Modifications to poly(divinylbenzene-*co*-ethylvinylbenzene).

8.2. Experimental

8.2.1 Materials and methods

Unless otherwise noted, all materials were purchased from Aldrich Chemical Company and used as received. The same lot (#1090-7-1473) of Amberlite XAD-4 was used throughout this study, obtained from Rohm and Haas Co. XAD-4 comes imbibed with sodium chloride and sodium carbonate to retard bacterial growth [28]. Unless otherwise noted, all resins were pretreated by Soxhlet extraction with acetone for several days, followed by drying under vacuum overnight at 60 °C. Water was doubly-distilled. Table 8.2 lists the amines used. The salicylaldehyde Schiff base of diethylenetriamine (bis(salicylidene-iminate)diethylenetriamine) was prepared using a published technique [29].

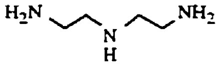
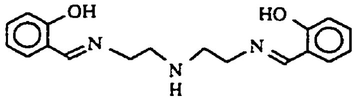
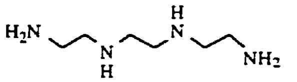
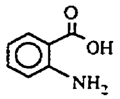
8.2.3 Bromination of XAD-4

XAD-4 was brominated using a slight excess (1.1 equiv) of bromine. In a 1 L round bottom flask equipped with magnetic stirring bar, XAD-4 (100 g, 250 mmol vinyl groups) in 700 mL of dichloromethane was cooled to 0 °C. Bromine (14 mL, 280 mmol) in 50 mL CH_2Cl_2 was added, and the reaction stirred in the dark at room temperature overnight. The resin was filtered and Soxhlet extracted with ethanol-dioxane azeotrope (90.7:9.3 w/w, bp 78.1 °C), then acetone, each for one day, followed by drying under vacuum at 60 °C overnight.

8.2.4 Addition of amines to brominated XAD-4

A typical reaction involved stirring brominated XAD-4 (1 g, 3.99 mmol Br/g), amine (table 8.2, 4-5 equiv per Br), and solvent (50 mL) at 20 to 100 °C for 2 days. Solvents used included: ethanol (100%), dioxane, diethyl ether, acetone, or *N,N*-dimethylformamide.

Table 8.2. Amines used in modification of brominated XAD-4

Amine	Structure	IUPAC Name [CAS number]
1		ethylenediamine (ED) [107-15-3]
2		diethylenetriamine (DETA) [111-40-0]
3		bis(salicylidene-iminate)-diethylenetriamine (SAL)
4		triethylenetetramine hydrate (TT) [112-24-3]
5		anthranilic acid (ANTH) (2-aminobenzoic acid) [118-92-3]
6		2-(aminomethyl)pyridine (AP) [3731-51-9]

Work-up for all reactions involved filtering the resin, washing with solvent and then Soxhlet extraction for several days. Soxhlet extraction was generally performed using ethanol-dioxane azeotrope (90.7:9.3 w/w, bp 78.1 °C) and/or water-dioxane azeotrope (18.4:81.6 w/w, bp 87.8 °C), and then methanol, each for one day. The purified resins were dried under vacuum (70 °C) for one day.

8.2.5 Characterization

8.2.5.1 Elemental analysis

Samples were sent to the University of British Columbia or Robertson Microlit Laboratories (Madison, NJ) to be analyzed for nitrogen and bromine.

8.2.5.2 Infrared spectroscopy

XAD-4 was characterized using infrared spectroscopic analysis to measure the vinyl group content [7, 30]. Brominated XAD-4 and the amine-modified brominated resins were also characterized. Samples were ground into powder with FTIR-grade potassium bromide (KBr) and disks were prepared. Fourier transform infrared absorbance spectra were taken with a Bruker IFS 66 spectrometer, using a DTGS detector and 2 cm^{-1} resolution, with 120 to 200 scans.

8.2.5.3 Raman spectroscopy

Fourier transform Raman spectra were taken using a Bruker IFS 88 spectrometer with FRA-105 Raman module using a Nd^{+3}:YAG laser (1064.1 nm). Samples were ground into powder and packed lightly into an aluminum sample cup. The number of scans ranged from 250 to 5000, with a 4 cm^{-1} resolution.

8.2.5.4 ^{13}C NMR spectroscopy

Solid-phase ^{13}C NMR spectra were obtained with a Chemagnetics Inc. CMX-300 instrument. ^{13}C CP-MAS (cross-polarization magic angle spinning) NMR spectra were obtained at 75.3 MHz with contact time of 3 ms, recycle delay of 1 s, number of transients of 2000-8000, and spectral window 30 kHz. The FID was sampled with 256 points, zero-filled to 2048 points and apodized with 50 Hz of line-broadening before Fourier transformation. Spinning sidebands were eliminated by the application of the TOSS pulse sequence. The spinning speed was 4000 Hz. Proton decoupling was done at a field strength of 60 kHz. The ^{13}C CP-MAS-DD (DD is dipolar dephasing) NMR spectra were obtained similarly, with a dephasing time (τ) of 45 μs. Samples were referenced to hexamethylbenzene.

8.3. Results and Discussion

8.3.1 Characteristics of starting materials

Previously, we characterized the starting material with regard to vinyl content, surface area, porosity and monomer content [7]. Table 8.3 summarizes these characteristics. The vinyl content was calculated using FTIR spectroscopy [7, 30]. The degree of functionalization (X_{VB}, %) is the percentage of repeat units which have vinylbenzene groups, and the degree of cross-linking (X_{CL}, %) is the percentage of repeat units which cross-link the resin. The pore size distribution is based on the percent of the total pore volume with pores of a given diameter.

Table 8.3. Characteristics of XAD-4 (data from [7])

Surface Area (m^2/g)	Total Pore Volume (mL/g)	Pore Size (nm)	Degree of Functionalization (X_{VB}, %)	Degree of Cross-Linking (X_{CL}, %)	Vinyl Content (mmol/g)
831	1.181	< 6 (17.3%) 6-10 (20.5%) 10-20 (59.5%)	33 ± 1	47 ± 2	2.5 ± 0.1

8.3.2 Modification of XAD-4

8.3.2.1 Bromination of XAD-4

8.3.2.1.1 Calculation of the degree of functionalization of brominated XAD-4

The degree of functionalization of brominated XAD-4 (XAD-4-Br, $X_{1,2\text{-}Br}$) was calculated based on the bromine content (equation 8.1) [5].

Equation 8.1 $$X_{1,2\text{-Br}} = \frac{130.6\ \text{g/mol} \times (\text{mol Br/g} \div 2)}{1 - (\text{mol Br/g} \times \text{MW Br})} \times 100\%$$

8.3.2.1.2 Results of bromination of XAD-4

We previously modified XAD-4 by bromination in order to study the distribution of vinyl groups within the resin [7]. The bromine content, ($C_{1,2\text{-}Br}$, in mmol functional groups/g, and $X_{1,2\text{-}Br}$), listed in table 8.4, was slightly higher than the vinyl content calculated using the FTIR spectroscopic technique for the unmodified XAD-4 (table 8.3), X_{VB}, 33 ± 1 %. Since the FTIR method to calculate the vinyl content is only semi-quantitative, it can be assumed that the vinylbenzene groups were converted entirely to (1,2-dibromoethyl)benzene groups without further side-reactions (note: percent conversion of vinylbenzene groups to functional groups represented by Φ). This was confirmed spectroscopically [5, 7].

Table 8.4. Result of bromination of XAD-4

Resin	Reaction Conditions	$C_{1,2\text{-Br}}$ (mmol/g)	$X_{1,2\text{-Br}}$ (%)	Φ (b)
XAD-4-Br	100 g XAD-4 750 mL CH_2Cl_2 1.1 equiv Br_2 20 °C, 1 day	2.00 ± 0.01 mmol fg/g (a) 3.99 ± 0.01 mmol Br/g	39%	100%

(a) $C_{1,2\text{-Br}}$ (mmol fg/g) is the quantity of (1,2-dibromoethyl)benzene groups in mmol/g resin.
(b) Φ is the percent conversion of vinylbenzene groups to functional groups.

The preparation of brominated XAD-4 is a simple one-step procedure which produced a functional polymer which could then be further modified by reaction of the (1,2-dibromoethyl)benzene groups, as will be seen in the following section.

8.3.2.3 Reaction of brominated XAD-4 with amines

Brominated XAD-4 was reacted with several amines using simple reaction conditions. Results of typical reactions are given in table 8.5. The resin with the highest nitrogen content for each amine used is numbered in bold. Since each amine had between one and four nitrogen atoms, the nitrogen content was divided by the number of N atoms in order to calculate the amine (functional group, fg) content.

Not all of the bromine was replaced, leading to a mixture of functional groups, which may have included (1,2-diaminoethyl)benzene, (1,2-dibromoethyl)-benzene, (1-amino-2-bromoethyl)benzene, (1-bromo-2-aminoethyl)benzene, as well as cyclic moieties (where 'amino' represents the amine used in modification). Elimination of hydrogen bromide also led to functionalities such as (2-bromoethenyl)benzene and (1-bromoethenyl)benzene, as well as amine-substituted functionalities. The infrared spectra of each resin further supports this, as will be seen later on.

Table 8.5. Results of reaction of brominated XAD-4 with amines (a)

Resin	Reaction Conditions	Solvents used for Soxhlet extraction	Elemental Contents (mmol/g)	Amine Group Content (mmol fg/g) (b)
1a	5 equiv **1** per Br 50 mL ethanol 55 °C, 2 days	water-dioxane, dioxane, ethanol, methanol	0.603 ± 0.005 mmol N/g 2.885 ± 0.007 mmol Br/g	0.302 ± 0.002 mmol fg/g
2a	5 equiv **2** per Br 50 mL dioxane 100 °C, 2 days	water-dioxane, methanol	1.130 ± 0.003 mmol N/g 1.86 ± 0.02 mmol Br/g	0.377 ± 0.001 mmol fg/g
2b	5 equiv **2** per Br 50 mL ethanol 55 °C, 2 days	water-dioxane, ethanol-dioxane, methanol	0.879 ± 0.006 mmol N/g	0.293 ± 0.002 mmol fg/g
3a	5 equiv **3** per Br 50 mL ethanol 55 °C, 2 days	water-dioxane, ethanol-dioxane, methanol	0.622 ± 0.001 mmol N/g 3.21 ± 0.03 mmol Br/g	0.2073 ± 0.0005 mmol fg/g
3b	5 equiv **3** per Br 50 mL dioxane 100 °C, 2 days	water-dioxane, acetone	0.594 ± 0.008 mmol N/g	0.198 ± 0.003 mmol fg/g
4a	5 equiv **4** per Br 50 mL ethanol 55 °C, 2 days	water-dioxane, ethanol-dioxane, methanol	0.884 ± 0.005 mmol N/g 2.75 ± 0.01 mmol Br/g	0.221 ± 0.001 mmol fg/g
5a	4 equiv **5** per Br 50 mL ethanol 55 °C, 2 days	ethanol-dioxane, methanol	0.37 ± 0.03 mmol N/g 3.593 ± 0.001 mmol Br/g	0.37 ± 0.03 mmol fg/g
5b	4 equiv **5** per Br 50 mL diethyl ether 20 °C, 2 days	ethanol-dioxane, methanol	0 mmol N/g	0 mmol fg/g
5c	4 equiv **5** per Br 50 mL acetone 20°C, 2 days	ethanol-dioxane, methanol	0.033 ± 0.003 mmol N/g	0.033 ± 0.003 mmol fg/g
5d	4 equiv **5** per Br 50 mL DMF 20°C, 2 days	ethanol-dioxane, methanol	0 mmol N/g	0 mmol fg/g
6a	5 equiv **6** per Br 50 mL dioxane 100°C, 2 days	ethanol-dioxane, methanol	1.4751 ± 0.0005 mmol N/g 2.021 ± 0.001 mmol Br/g	0.7375 ± 0.0002 mmol fg/g
6b	5 equiv **6** per Br 50 mL ethanol 55°C, 2 days	ethanol-dioxane, methanol	0.807 ± 0.005 mmol N/g	0.403 ± 0.003 mmol fg/g

(a) Reaction conditions: 1 g XAD-4-Br (3.99 mmol Br/g, 2.00 mmol fg/g) used. The amine used indicated by bold number.

(b) mmol fg/g is mmol N/g divided by number of N atoms per amine.

8.3.3 Spectroscopic characterization

8.3.3.1 Infrared spectroscopy

Infrared spectroscopy was used to compare brominated XAD-4 (XAD-4-Br) to the amine-modified resins (figure 8.2). The FTIR peak assignments for unmodified XAD-4 have been presented elsewhere [7]. Table 8.6 lists the peak assignments for amine-modified brominated XAD-4. Peak assignments were done by comparison to spectra of the amines used to modify XAD-4-Br [31], and with the help of two reference books on spectroscopy [32, 33].

In the infrared spectrum of brominated XAD-4, peaks due to the (1,2-dibromoethyl)benzene functionality are seen (1236, 1215, 1176, 1130, 602 (C-Br), and 571 cm^{-1} (C-Br), figure 8.2) [5, 31, 32]. These peaks are present to varying degrees in the spectra of the modified resins, in correlation to the bromine content (table 8.5). Resin **2a** had the lowest bromine content, and the peaks due to (1,2-dibromoethyl)benzene were the least prominent for the spectra of the modified resins.

All the spectra of the modified resins had peaks at 1473 and 1020 cm^{-1}, and the peak at 891 cm^{-1} was more intense than for the spectrum of XAD-4-Br. The peaks at 1473 and 1020 cm^{-1} were also seen for resins formed by reaction of brominated XAD-4 with thiols using basic conditions (KOH with ethanol, 78 °C, [3]), and have been attributed to the presence of unsaturated groups containing bromine ($Ph\text{-}CH{=}CHBr$ and/or $Ph\text{-}CBr{=}CH_2$) [3, 32]. Unlike the brominated resins which reacted in the presence of KOH [3], no peaks were visible which would indicate the presence of vinylbenzene groups at 1630 and 990 cm^{-1}, with the exception of resin **3a**.

The spectrum of **3a** also had only a small peak at 1684 cm^{-1}, indicating that some of the imine groups of the amine used (bis(salicylidene-iminate)-diethylenetriamine) hydrolyzed, possibly during Soxhlet extraction since a water-dioxane azeotrope was used.

Table 8.6. Infrared peak assignments for amine-modified resins

Resin	Band (cm^{-1})	Assignment	Reference	Notes
1a	1685	C=N stretch	[33], p. 127	imine
	1473 and 1020		[3]	aromatic vinyl bromide
	633	C-Br stretch or $=CH_2$ twisting	[32], p. 177	
2a	1685	C=N stretch	[33], p. 127	imine
	1473 and 1020		[3]	aromatic vinyl bromide
	1121	C-N stretch	[33], p. 124	
	633	C-Br stretch or $=CH_2$ twisting	[32], p. 177	
3a	1684	C=N stretch	[33], p. 127	imine
	1631	C=C stretch	[7]	like unmodified XAD-4
	1472 and 1020		[3]	aromatic vinyl bromide
	754	ortho-disubstituted benzene	[32], p.176	presence of imine of **3**
	633	C-Br stretch or $=CH_2$ twisting	[32], p. 177	
4a	1683	C=N stretch	[33], p. 127	imine
	1473 and 1020		[3]	aromatic vinyl bromide
	633	C-Br stretch or $=CH_2$ twisting	[32], p. 177	
5a	1694 and 1588	C=O stretch, carboxylic acid benzene ring stretch	[32], p. 174 [32], p. 175	presence of **5**
	1472 and 1020		[3]	aromatic vinyl bromide
	750	ortho-disubstituted benzene	[32], p.176	presence of **5**
6a	1685	C=N stretch	[33], p. 127	imine
	1591, 1571, 1434, and 995	pyridine	[31], Volume 2 p. 764	presence of **6**, 2-substituted pyridine
	1473 and 1020		[3]	aromatic vinyl bromide
	1169	C-N stretch	[33], p. 124	
	749	2-substituted pyridine	[33], p. 164	

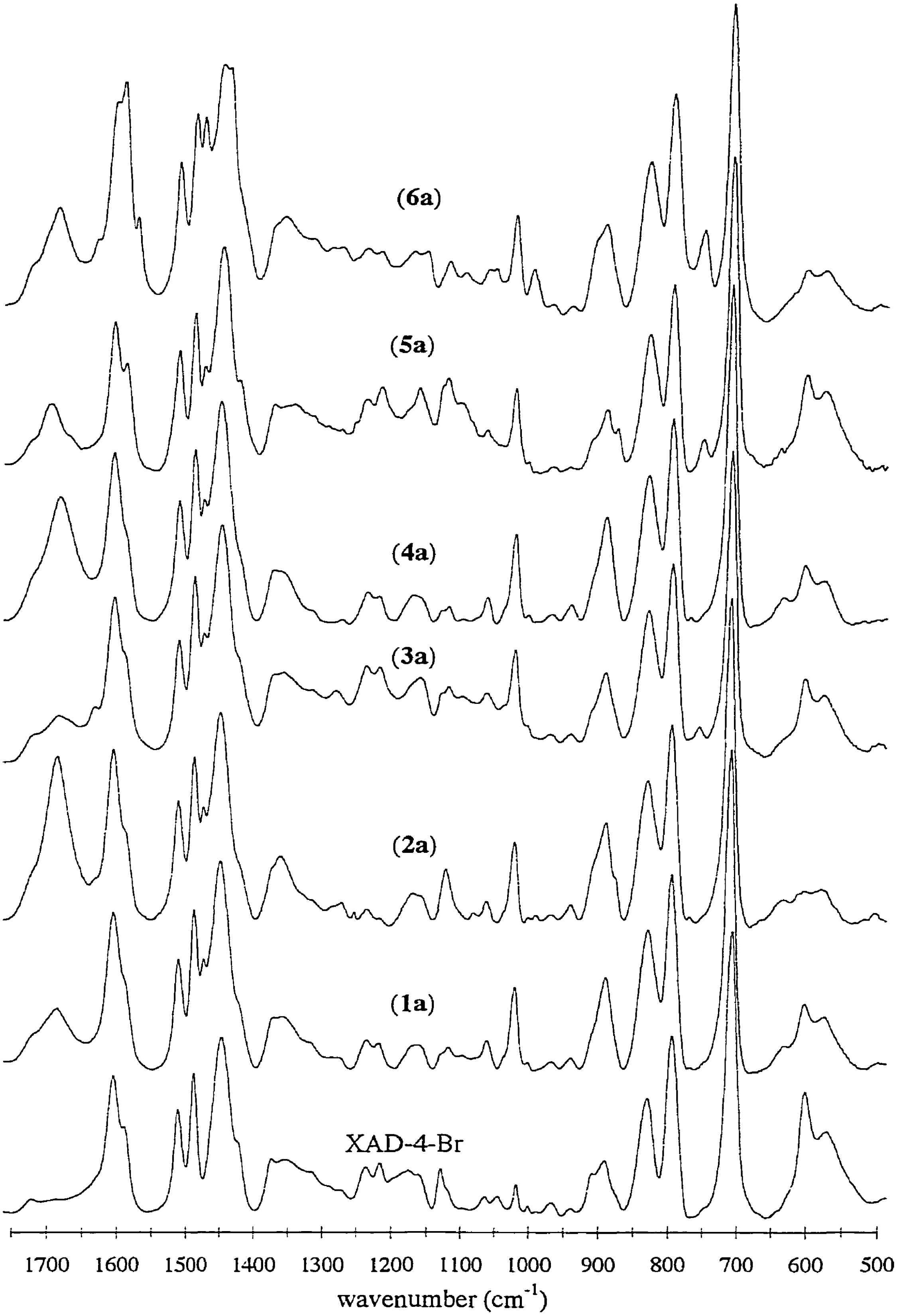
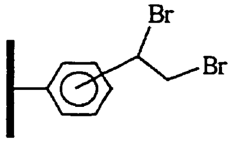


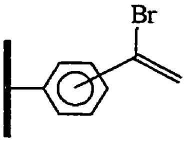
Fig. 8.2. FTIR absorbance spectra of brominated XAD-4 and modified resins.

Table 8.7 lists the possible functionalities which were present on all of the amine-modified brominated poly(divinylbenzene-*co*-ethylvinylbenzene).

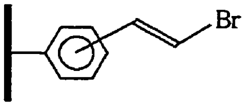
Table 8.7. Possible functional groups of amine-modified brominated XAD-4



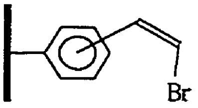
Structure **A**



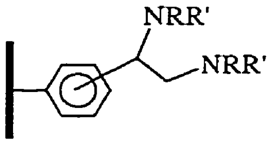
Structure **B**



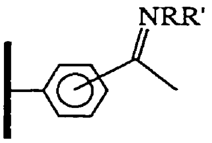
Structure **C**



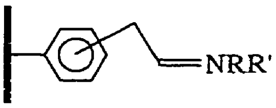
Structure **D**



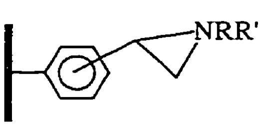
Structure **E**



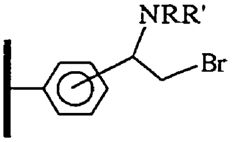
Structure **F**



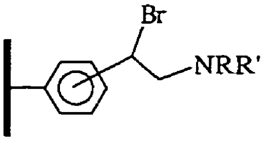
Structure **G**



Structure **H** and other cyclic moieties



Structure **I**



Structure **J**

Structures **B**, **C**, and **D** result from the amines acting as bases, causing elimination of hydrogen bromide (HBr). Structures **F** and **G** could have resulted from addition of one equivalent amine to **A** to form **I** or **J** with subsequent elimination of HBr, followed by tautomerization of the enamine formed to the imine (Schiff base), or by the less likely reaction of amine with **B**, **C** or **D**, followed by tautomerization to the imine. Cyclic functionalities, including the aziridine **H**, may also have been present.

8.3.3.2 Raman spectroscopy

The Raman spectral peak assignments for XAD-4 have been determined, and are presented elsewhere [7]. The Raman spectrum of brominated XAD-4 has also been presented elsewhere [5]. The Raman spectra of brominated XAD-4 and the amine-modified resins were compared and found to be very similar to each other and of not much use in structure elucidation.

The main difference was that the peak due to C-Br at 691 and 574 cm^{-1} [5] were less in the spectra of the modified resins.

8.3.3.3 ^{13}C NMR spectroscopy

The solid-phase ^{13}C CP-MAS NMR and ^{13}C CP-MAS-DD NMR spectra for XAD-4-Br and the amine-modified resins were taken and compared to each other, that of unmodified XAD-4, and model compounds.

The ^{13}C NMR peak assignments for unmodified XAD-4 are presented elsewhere [7]. Dipolar dephasing eliminates the peaks due to the vinyl carbons and the polymer backbone (CH_2, CH, at 41 ppm, and phenyl CH at 129 ppm). The peak at 144 ppm corresponds to the (non-hydrogen) substituted phenyl carbons, the peak at 137 ppm is due to both the vinyl CH and the phenyl **C** attached to the vinyl group, and the peak at 15-16 ppm corresponds to the methyl carbon of the pendant ethylbenzene groups.

For the spectrum of brominated XAD-4, there are no peaks corresponding to the vinyl groups (137 ppm and 114 ppm) (as seen in [5]). The dipolar-dephased spectra show none of the (1,2-dibromoethyl) carbon peaks since they are not mobile enough [5]. This phenomenon was previously seen for resins modified with thiols and disulfides: the dimethylene spacers were not detected in the dipolar dephased spectra [2, 3].

The spectra of the amine-modified XAD-4-Br showed minor differences in comparison to the spectrum of XAD-4-Br, especially in the dipolar dephased spectra, and these peaks are noted in table 8.8. Table 8.8 also compares the peak assignments of analogous model compounds with the modified resins [34].

No or small peaks were seen in the spectra of the amine-modified resins which would indicate the presence of vinylbenzene groups (i.e. at 137 or 114 ppm). All the ^{13}C CP-MAS spectra had peaks due to the polymer backbone (144, 129, 41, 30, and 16 ppm), and some of these were in the dipolar-dephased spectra (144, 16 ppm). These peaks are excluded in the peak assignments of the amine-modified resins. Some of the peaks were visible in the CP-MAS but not the CP-MAS-DD spectra, and others were only seen in the CP-MAS-DD (indicated in table 8.8 by DD) spectra since they were overlapped by peaks due to the backbone in the CP-MAS spectra. It should be noted that the baselines of these spectra were not smooth, and most of the peaks listed were small in comparison to those due to the backbone. Of all the techniques used for characterization of these resins, infrared spectroscopy was the most useful.

Table 8.8. ^{13}C NMR peak assignments for modified XAD-4

Resin	^{13}C NMR peak assignments of model compounds (a)	Peaks (ppm)	Assignment	Notes
XAD-4-Br	138.53, 129.07*, 128.76*, 127.57*, 50.85*, 34.99* (b)	144 (DD)	phenyl C	^{13}C CP-MAS-DD NMR spectra
		15 (DD)	CH_3 of pendant ethyl	
Model	137.07*, 135.84, 128.68*, 128.16*, 126.01*, 106.44* (d)			
1a	52.61, 44.07, 42.00, 15.44* (e)	132, 128, 122 (all DD)		Peaks at 132, 128, 122, 105 ppm possibly due to aromatic vinyl bromide
		117	$CH=CH_2$	
		105		
		45-35 (DD)	CH_2 of amine	
2a	52.56, 41.96 (f)	137	phenyl C and $CH=CH_2$	Peaks at 132, 128, 122, 105 ppm possibly due to aromatic vinyl bromide
		132, 128, 122 (all DD)		
		117	$CH=CH_2$	
		105		
		67 (g)	C-O (h)	
		45-35 (DD)	CH_2 of amine	
3a		132 (DD)		
		121 (DD)		
		~ 45-30 (DD)	CH_2 of amine	
4a	52.65, 49.46, 41.92 (i)	137	phenyl C and $CH=CH_2$	Peaks at 132, 121, 105 ppm possibly due to aromatic vinyl bromide
		132, 121 (both DD)		
		117	$CH=CH_2$	
		105		
		~ 45-30 (DD)	CH_2 of amine	
5a	169.48, 151.38, 133.59*, 131.07*, 116.22*, 114.48*, 109.54 (j)	132 (DD)		Peaks very small, none seen due to amine (**5**)
		121 (DD)		
6a	161.93, 149.17*, 136.43*, 121.69*, 121.09*, 47.81 (k)	160 (g)	pyridine (**6**)	Peaks at 132, 128, 122, ppm possibly due to aromatic vinyl bromide
		137 (g)	phenyl C and $CH=CH_2$	
		132, 128, 121 (all DD)		
		115	$CH=CH_2$	

(a) Data from [34], * means odd parity (i.e. CH, CH_3).
(b) (1,2-dibromoethyl)benzene, [34, Vol. 2, p. 65].
(c) Peak assignments of XAD-4 in reference [7].
(d) β-Bromostyrene (mixture of isomers), [34, Vol. 2, p. 136].
(e) *N*-Ethylethylenediamine, [34, Vol. 1, p. 488].
(f) Diethylenetriamine, [34, Vol. 1, p. 499].
(g) Seen in both CP-MAS and CP-MAS-DD spectra.
(h) May be due to presence of dioxane, [33 , p. 261].
(i) Triethylenetetramine, [34, Vol. 1, p. 501].
(j) Anthranilic acid, [34, Vol. 2, p. 1066].
(k) 2-(Aminomethyl)pyridine, [34, Vol. 3, p. 288].

8.3.4 Potential applications of modified resins and suggestions for further work

Since the modification of brominated XAD-4 has led to an indeterminate mixture of functionalities, further work to determine these functionalities is recommended. These same preparations could be done using the model compound (1,2-dibromoethyl)benzene with simple amines (i.e. methylamine), as well as with the amines used in this study. The product ratio and structure could then be elucidated using traditional organic synthetic methodologies, including ^{1}H NMR spectroscopy. Further amine-modification of XAD-4 could be done to Markovnikov and anti-Markovnikov hydrobrominated XAD-4, using established preparation techniques [17]. This could be done to compare functionalities of modified resins, as well as yields.

XAD-4 was previously epoxidized using dimethyldioxirane [4]. The epoxy groups could act as sites for modification by ring-opening reactions with amines. This has been done similarly by the addition of amines, including 2-aminothiophenol and 2-(aminomethyl)pyridine, to the epoxy groups of a cross-linked methacrylate resin [35].

Modification can change properties of the resins, such as hydrophilicity, which may change behaviour in separation applications such as chromatography [6]. XAD-4 was previously modified for this application using traditional methodologies [36], including by the modification of chloromethylated XAD-4 with ethylenediamine, diethylenetriamine, triethylenetetramine and other amines. No one has previously modified the vinylbenzene groups of XAD-4 to prepare sorbents.

The amines used in this study have been used to modify chloromethylated polystyrene resins to prepare functional polymers [20, 21, 25, 26]. These resins have been used for metal uptake [20, 21], and to prepare solid-phase palladium (II) or rhodium (I) hydrogenation catalysts [25, 26]. We have also studied these and other amines with respect to their metal-complexing ability by pH titration [37], and want to find suitable methods to modify solid-supports with them for applications in water, wastewater, and sludge treatment, with particular attention to the mining industry.

8.4. Conclusions

Several functional polymers were prepared from brominated XAD-4, by modification of its (1,2-dibromoethyl)benzene groups with amines. The presence of peaks in the infrared spectra of the amine-modified resins indicates that many undesired functionalities are present, and further studies with model compounds are warranted. Modification of XAD-4 with amines to create coordinating resins is desired for various applications, and further methods of modification should be explored.

8.5 Acknowledgements

We wish to thank Rohm and Haas Company for donation of 5 kg of Amberlite XAD-4, and for providing information used in this paper. ^{13}C NMR spectra were taken by Dr. F.G. Morin of the Department of Chemistry, McGill University. Elemental analyses were performed in part by M. Soon, Department of Oceanography, University of British Columbia. Some of the infrared spectra were taken by M. Ruzicka. Thanks also go to Dr. R.B. Lennox, Dr. D.N. Harpp, and Dr. D.S. Argyropoulos for helpful discussion. Funding for this project was provided by a Natural Sciences and Engineering Research Council of Canada Strategic Grant.

8.6 References

[1] J.P. Gao, F.G. Morin and G.D. Darling, Macromolecules, 26 (1993), 1196.

[2] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted May 1997. Chapter 4 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[3] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted May 1997. Chapter 5 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[4] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., to be submitted June 1997. Chapter 6 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[5] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted May 1997. Chapter 7 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[6] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted April 1997. Chapter 2 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[7] K.L. Hubbard, J.A. Finch and G.D. Darling, React. Funct. Polym., submitted April 1997. Chapter 3 of the doctoral thesis of K.L. Hubbard, McGill University, June 1997.

[8] R. Kunin, Amberhilites (produced by Rohm and Haas Co.), Number 161 (spring 1979).

[9] R. Kunin, Amberhilites (produced by Rohm and Haas Co.), Number 163 (winter 1980).

[10] E.F. Meitzner and J.A. Oline, U.S. Patent 4,382,124, issued May 3, 1983.

[11] Food and Drug Administration, U.S. Government, 173.65, page 100 in "Code of Federal Regulations", 21, Food and Drugs. Parts 170 to 199, revised April 1, 1994.

[12] R.L. Albright, React. Polym., 4 (1986), 155.

[13] Supelco Product Catalogue, 1995, page 264.

[14] N.A. de Munck, M.W. Verbruggen and J.J.F. Scholten, J. Mol. Catal., 10 (1981), 313.

[15] J.P.C. Bootsma, B. Eling and G. Challa, React. Polym., 3 (1984), 17.

[16] M Periyasamy, W.T. Ford and F.J. McEnroe, J. Polym. Sci., Polym. Chem. Ed., 27 (1989), 2357.

[17] M.C. Faber, H.J. van den Berg, G. Challa and U.K. Pandit, React. Polym., 11 (1989), 117.

[18] Z. Zhengpu, P. Hodge and P.W. Stratford, React. Polym., 15 (1991), 71.

[19] G. Zuo and M. Muhammed, React. Polym., 24 (1995), 165.

[20] M.B. Shambu, M.C. Theodorakis and G.A. Digenis, J. Polym. Sci., Polym. Chem. Ed., 15 (1977), 525.

[21] M. Nishizawa, T. Yokoyama, T. Kimura amd T.M. Suzuki, Polyhedron, 5 (1986), 2047.

[22] T.M. Suzuki and T. Yokoyama, Polyhedron, 2 (1983), 127.

[23] T.M. Suzuki and T. Yokoyama, Polyhedron, 3 (1984), 939.

[24] N.L. Holy, Tetrahedron Lett., 42 (1977), 3703.

[25] N.L. Holy, J. Org. Chem., 43 (1978), 4686.

[26] N.L. Holy, J. Org. Chem., 44 (1979), 239.

[27] T. Saegusa, S. Kobayashi, K. Hayashi and A. Yamada, Polymer J., 10 (1978), 403.

[28] Rohm and Haas Company, "Amberlite XAD-4. Polymeric Adsorbent." product literature, June 1993.

[29] W.M. Coleman and L.T. Taylor, Inorg. Chem., 10 (1971), 2195.

[30] M. Bartholin, G. Boissier and J. Dubois, Makromol. Chem., 182 (1981), 2075.

[31] C.J. Pouchert (Editor), The Aldrich Library of FT-IR Spectra, Edition 1. Aldrich Chemical Company, Inc., Milwaukee, 1985. Volume 1, pages 289, 303, 308, 310, 950, 974, 1017; and Volume 2, pages 189,764.

[32] J.B. Lambert, H.F. Shurvell, D.A. Lightner and R.G. Cooks, Introduction to Organic Spectroscopy, MacMillan Publishing Co., New York, 1987. pages 171, 174-177.

[33] R.M. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric Identification of Organic Compounds, 5th Edition, John Wiley and Sons, Inc., New York, 1991. pages 124, 127, 164, 261.

[34] C.J. Pouchert and J. Behnke (Editors), The Aldrich Library of ^{13}C and ^{1}H FT-NMR Spectra, Edition 1. Aldrich Chemical Company, Inc., Milwaukee, 1993. Volume 1, pages 488, 499, 501; Volume 2, pages 65, 136, 1066; and Volume 3, page 288.

[35] D. Lindsay and D.C. Sherrington, React. Polym., 3 (1985), 327.

[36] T.A. Armer, Ph.D. Thesis, Tulane University, Diss. Abstr. Int. B 43 (6) (1982), 1910; Chem. Abstr. 98 (1983), 35435w.

[37] K.L. Hubbard, G.D. Darling and J.A. Finch, Minerals Eng., 10 (1997), 41.

Chapter 9

Conclusions

9.1. Modifications of the pendant vinylbenzene groups of commercial poly(divinylbenzene-*co*-ethylvinylbenzene)

Commercial poly(divinylbenzene-*co*-ethylvinylbenzene) resins are ideal substrates for the preparation of functional polymers based on their high surface areas, porosities, and accessible sites for grafting. It has been demonstrated that the pendant vinylbenzene groups can be used as sites for modification with as much as 100% conversion of the vinylbenzene groups to functional groups. Many of the modifications performed were one-step with straightforward reaction conditions. One-step reactions were successfully used to introduce a diverse group of functionalities onto the resin including thiol, amine, sulfonate, diol, carboxylic acid, bromine, bromohydrin, and epoxide groups. Some of these resins were functional precursors to other resins; for example, brominated poly(divinylbenzene-*co*-ethylvinylbenzene) was converted to a resin with vicinal dithiol groups.

9.2. Contributions to knowledge

XAD-4 can be used in simple one or multi-step modifications to prepare resins with a variety of functionalities. Many of these modifications had not been previously done on polymer substrates, and none had been previously done using commercial poly(divinylbenzene-*co*-ethylvinylbenzene) resins by reaction with the pendant vinylbenzene groups. These modification methods can be used as alternatives to traditional methodologies, and are generally simple reactions. Highlights of the contributions to knowledge are listed by chapter.

Chapter 2. A Review of the Preparation, Characteristics and Modifications of Polymers with Pendant Vinyl Groups Including poly(Divinylbenzene-*co*-Ethylvinylbenzene) and Related Resins

and

Chapter 3. The Preparation and Characteristics of poly(Divinylbenzene-*co*-Ethylvinylbenzene), including Amberlite XAD-4. Styrenic Resins with Pendant Vinylbenzene Groups

- comprehensive literature survey of the field of polymers with pendant vinyl groups including poly(divinylbenzene-*co*-ethyl styrene) and related resins
- investigated the commercial Amberlite XAD resin series with regard to comparison of vinyl content (XAD-2, XAD-4, XAD-16 and XAD-1180)
- compiled information on Amberlite XAD-4 which reveals its composition, structural characteristics, and presence of vinylbenzene groups
- comparison of commercial resins to lab-made resins of similar composition showed higher surface areas and porosities for commercial resins
- determined the distribution of vinyl groups in XAD-4 beads
- found that XAD-4 is superior with regard to structural features for modification of vinylbenzene groups than the lab-made resins of similar composition

Chapter 4. Thiol Addition to the Pendant Vinylbenzene Groups of poly(Divinylbenzene-*co*-Ethylvinylbenzene), including Amberlite XAD-4. Modification in Organic and Aqueous Solvents.

- first to add thiols to vinylbenzene groups of commercial poly(divinylbenzene-*co*-ethylvinylbenzene) (XAD-4)
- used water and water-soluble initiator for modifications with water-soluble thiols
- introduction of variety of functional groups by one-step modification: thiol, amine, sulfonate, diol, carboxylic acid, aniline, alkyl or aryl groups, all attached by a thioether linkage
- compared use of various solvents: solubility of thiol more important than ability of solvent to swell resin
- compared modification of lab-made versus commercial resin, higher conversions with commercial resin due to higher surface areas and porosities
- distribution of functional groups within bead found to be uniform

Chapter 5. Disulfide Addition to the Pendant Vinylbenzene Groups of Commercial poly(Divinylbenzene-*co*-Ethylvinylbenzene). Modification with Alkyl and Aryl Disulfides.

- one-step disulfide addition a simple, under-utilized synthetic methodology
- first to modify vinyl groups of any polymer with disulfides
- compared use of various solvents
- compared modification methods and disulfides used
- compared disulfide-modified resins to resins modified with analagous thiols

Chapter 6. Epoxidation of the Pendant Vinylbenzene Groups of Commercial poly(Divinylbenzene-*co*-Ethylvinylbenzene).

- first to epoxidize vinylbenzene groups of commercial poly(divinylbenzene-*co*-ethylvinylbenzene) (XAD-4)
- compared various one-step epoxidation methods to find dimethyldioxirane epoxidized resin with no side-reactions
- first to used method which attempted to convert epoxide to thiirane with polymer system
- first to use some epoxidation methods (i.e. hydrogen peroxide with nitriles or ethyl chloroformate) with polymer system
- expanded on previous use of dimethyldioxirane to epoxidize polymers
- some methods produced vicinal diol group as side-functionality

Chapter 7. Bromohydration and Bromination of the Pendant Vinylbenzene Groups of Commercial poly(Divinylbenzene-*co*-Ethylvinylbenzene) Resins. Further Reactions of the (1,2-Dibromoethyl)benzene Groups with Thiourea, and with *N,N*-Dimethylthioformamide with Subsequent Methanolysis to Produce Thiol-Containing Styrenic Resins.

- new modifications to XAD-4 by reactions with vinylbenzene groups
- bromination with subsequent addition of thiourea
- bromohydration not previously done on polymers
- prepared polymer-bound vicinal dithiols by bromination, reaction with *N,N*-dimethylthioformamide followed by methanolysis using an underutilized method

Chapter 8. Modifications to the Pendant (1,2-Dibromoethyl)benzene Groups of Brominated Commercial poly(Divinylbenzene-*co*-Ethylvinylbenzene). Reaction with Amines.

- preparation of amine-containing resins by 2-step modification
- attempted introduction of amines to 1,2-dibromo groups for potential applications for ion exchange and use in metallurgy
- side-reactions included elimination

Appendix 1. Screening Ligands for Metallurgical Applications by the Determination of pH of Complexation with Metals

- use of titration to screen ligands for metallurgical applications
- quick screening procedure using constant background matrix
- compiled and organized data for 45 ligands with 3 metals

9.3. Suggestions for further work

Discussed in the previous chapters were suggestions for future research using methodologies studied in this work. Some highlights of these ideas are mentioned below.

- use of other vinyl group-containing substrates such as rubbers
- linear poly(divinylbenzene) could be modified to further aid in structure elucidation
- potential applications of some modified resins as adsorbents, ion exchange or coordinating resins should be investigated
- further improvements to modification yields by variation of reaction conditions
- further studies on modifications with a larger range of thiols using water as the solvent
- modification of epoxide-containing resin by nucleophilic ring-opening reactions, preparation of thiirane
- expansion of choice of disulfides, for example: thiocyanogen, isopropylxanthogen disulfide, benzothiazoyl disulfide, cystine, cyclic disulfides such as lipoic acid and its derivatives, dithioglycolic acid and its derivatives, and other alkyl and aryl disulfides with various functionalities including halogen, alcohol, ester, etc.
- use other solvents in disulfide addition reactions including carbon disulfide and acetic acid, vary amounts of iodine used
- react allyl disulfide with iodine under various conditions, may produce polymer
- use of (1,2-dibromoethyl)benzene as a model compound to study reactions with amines, thiourea, and *N,N*-dimethylthioformamide
- modification of vinylbenzene groups to prepare resins with aziridine groups

Appendix 1

Screening Ligands for Metallurgical Applications by the Determination of pH of Complexation with Metals

Forward to Appendix 1

The content of the following section is comprised of a previously published paper from Minerals Engineering, Volume 10, K.L. Hubbard, G.D. Darling and J.A. Finch, Screening Ligands for Metallurgical Applications by the Determination of pH of Complexation with Metals, pages 41-54, copyright 1997, reprinted with permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK.

This work was done to develop a screening methodology which would aid in the choice of ligands to attach to a solid support. Some of these ligands were attached to poly(divinylbenzene-*co*-ethylvinylbenzene) by thiol addition, and addition of amines to brominated poly(divinylbenzene-*co*-ethylvinylbenzene), as outlined in chapters 4 and 8, respectively. The resin was modified to contain other related functionalities, such as 2-mercaptoethanol and 1,2-dithiol groups (chapters 6 and 7, respectively), which were also studied for their metal-ligand interactions in this paper.

Abstract

Ligands containing thiol and/or amine groups were screened for their metal-complexing ability with various metal chlorides (Fe^{+2}, Fe^{+3}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, and Pb^{+2}) in aqueous solution by pH titration. Use of a consistent background matrix (0.1 M NaCl) and methodology overcame the difficulty of comparison of stability constants available from different sources in the literature. This fast, simple screening technique allows the comparison of many ligands with regard to the pH of complexation of metal ions without the difficult or time-consuming task of calculating stability constants.

Keywords: Hydrometallurgy, ion exchange, solvent extraction, extractive metallurgy, environmental

A1.1. Introduction

The use of complexing agents has a long history in the metals extraction industry. They have been employed for leaching, solvent extraction, design of coordinating resins, and flotation [1]. We are working on the use of various ligands to selectively extract metals from waste sludges [2], and to attach to solid supports such as polystyrene resins or magnetic particles; these can selectively absorb metals from dilute streams [3].

To save time and resources, a primary screening step has been developed involving the pH titration of ligands in the presence of individual metal ions. From this information, appropriate ligands can be chosen for a more detailed exploration of the application in mind.

In the case of the development of coordinating resins, the titration of the "free" ligand (not attached to the solid support) can be used to aid in the choice of which ligands to attach to the resin (solid support). This will minimize the work needed to be done as titrations with the free ligand can be done more quickly and easily than ion-exchange studies on the coordinating resin. The free ligand's behaviour should be similar to its behaviour once attached to a resin. It should be noted that model compounds which emulate how the ligand is attached to the support may also need to be studied if the mode of attachment changes the functionality of the ligand; for example, the conversion of a thiol to a thioether will diminish the binding ability of the sulfur in aqueous solutions. In that case, a suitable model compound would be a thioether of the original free ligand.

Ligands in the presence of individual metals were titrated with base from pH 2 to 11 to determine the pH of complexation. A consistent matrix (0.1 M sodium chloride solution) has been used. This is advantageous because, although the literature includes stability constants for many ligands with different metals, the problem is the use of differing experimental conditions [4-14]. This makes it difficult to compare stability constants since they vary with the matrix and method used. It is also time-consuming and arduous to calculate stability constants from titration data. The literature is also not complete in comparison of the stability constants of the ligands with the metals that we are interested in. In metallurgy, knowledge of the pH of complexation is more important than the actual stability constants. We present here a summary of some of our work which will prove useful for choosing ligands to complex metals at given pH's.

A1.2. Experimental work

A1.2.1 Materials

All ligands and metal chlorides were purchased from Aldrich Chemical Co. Lead nitrate was used instead of lead chloride due to solubility reasons. A list of the ligands studied follows in tables 1 and 2. Standard 0.1000 M sodium hydroxide solution was purchased from VWR Scientific. Doubly distilled water was used for all work. 1 M hydrochloric acid and 1 M sodium hydroxide solutions were used for pH adjustments. The metals studied were Fe^{+2}, Fe^{+3}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, and Pb^{+2}. Titrations involving Fe^{+2} were done under nitrogen to minimize oxidation. Chlorides were used instead of sulfates to minimize consumption of base around pH 2 to 3 (pKa of sulfate).

A1.2.2 Equipment

A Mettler autotitrator (model DL 21) interfaced with a personal computer was used. The data collection software used was TS1 Titration Software, version 3.1, available from McIntosh Analytical Systems, Inc. XY data were converted to overlaid titration curves using Microsoft Excel on a Macintosh computer.

A1.2.3 Method

0.1 M solutions of ligands were prepared immediately before use. To aid in solubilizing ligands, the pH of each solution was adjusted accordingly. 0.1 M solutions of individual metal chlorides were prepared by dissolving the metal salt in pH 2 hydrochloric acid. All titrations were performed from pH 2 to 11, by the addition of standardized base (0.1000 M NaOH) to the hydrochloric acid solution.

Each solution for titration was prepared by adding the metal and/or ligand solutions to 40 mL of pH 2, 0.1 M sodium chloride solution (the background matrix). For each ligand, one equivalent (1 mL of 0.1 M solution, 0.1 mmol) was titrated first to determine its pKa('s) and concentration. Then one equivalent of each metal was titrated individually (1 mL of 0.1 M solution, 0.1 mmol). From this, the pH of metal hydroxide formation was determined, as well as the concentration of the metal. The metal solution previously titrated was then re-acidified to pH 2, and one equivalent of ligand was added. Further pH adjustment to pH 2 was made as needed. Titration was then repeated from pH 2 to pH 11 with observation of changes such as colour or precipitation. The mixture was again re-acidified and a second equivalent of ligand was added and the titration repeated. This procedure was again repeated for a third equivalent of ligand.

Table A1.1. Thiol-Containing Ligands Studied

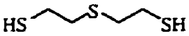
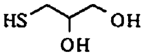
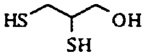
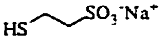
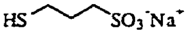
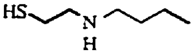
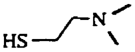
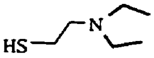
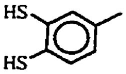
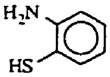
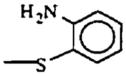
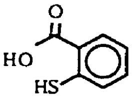
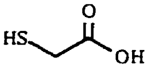
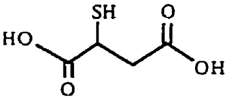
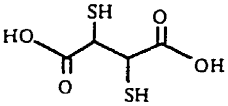
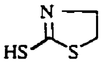
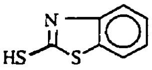
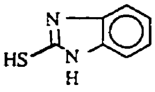
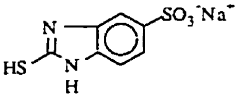
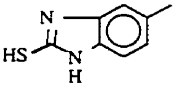
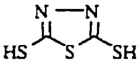
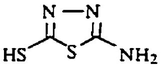
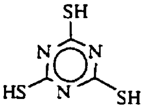
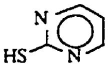
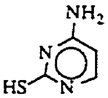
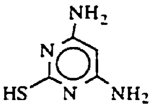
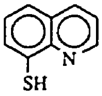
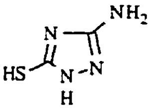
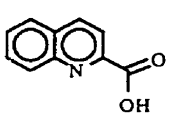
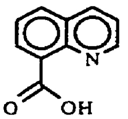
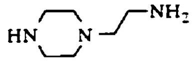
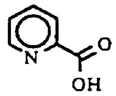
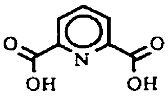
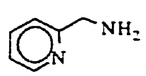
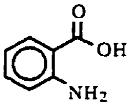
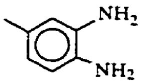
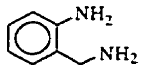
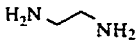
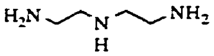
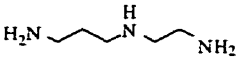
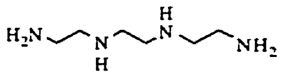
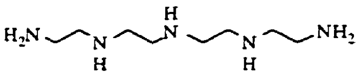
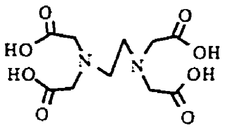
Structure IUPAC Name, [CAS number]	Structure IUPAC Name, [CAS number]	Structure IUPAC Name, [CAS number]
 1,2-ethanedithiol [540-63-6]	 2-mercaptoethyl sulfide [3570-55-6]	
 2-mercaptoethanol [60-24-2]	 3-mercapto-1,2-propanediol [96-27-5]	 2,3-dimercapto-1-propanol [59-52-9]
 2-mercaptoethanesulfonic acid (sodium salt) [19767-45-4]	 3-mercapto-1-propanesulfonic acid (sodium salt) [17636-10-1]	 2,3-dimercapto-1-propanesulfonic acid (sodium salt) (DMPS)
 2-aminoethanethiol hydrochloride (cysteamine) [156-57-0]	 2-(ethylthio)ethylamine hydrochloride [54303-30-9]	 2-(butylamino)ethanethiol [5842-00-2]
 2-dimethylaminoethanethiol hydrochloride [13242-44-9]	 2-diethylaminoethanethiol hydrochloride [1942-52-5]	 3,4-dimercaptotoluene [496-74-2]
 2-aminothiophenol [137-07-5]	 2-(methylmercapto)aniline [2987-53-3]	 2-mercaptobenzoic acid [147-93-3]
 mercaptoacetic acid [68-11-1]	 mercaptosuccinic acid [70-49-5]	 meso-2,3-dimercaptosuccinic acid [304-55-2]
 2-mercaptothiazoline [96-53-7]	 2-mercaptobenzothiazole [149-30-4]	
 2-mercaptobenzimidazole [583-39-1]	 2-mercapto-5-benzimidazolesulfonic acid, sodium salt dihydrate	 2-mercapto-5-methylbenzimidazole [27231-36-3]
 2,5-dimercapto-1,3,4-thiadiazole [1072-71-5]	 5-amino-1,3,4-thiadiazole-2-thiol [2349-67-9]	 trithiocyanuric acid [638-16-4]
 2-mercaptopyrimidine [1450-85-7]	 4-amino-2-mercaptopyrimidine (thiocytosine) [333-49-3]	 4,6-diamino-2-mercaptopyrimidine hemihydrate [1004-39-3]
 8-quinolinethiol hydrochloride [34006-16-1]	 3-amino-5-mercapto-1,2,4-triazole [16691-43-3]	

Table A1.2. Amine-Containing Ligands Studied

Structure IUPAC Name, [CAS number]	Structure IUPAC Name, [CAS number]	Structure IUPAC Name, [CAS number]
 quinaldic acid (2-quinolinecarboxylic acid) [93-10-7]	 8-quinolinecarboxylic acid [86-59-9]	 1-(2-aminoethyl)piperazine [140-31-8]
 picolinic acid [98-98-6]	 2,6-pyridinedicarboxylic acid (dipicolinic acid) [499-83-2]	 2-(aminomethyl)pyridine (2-picolylamine) [3731-51-9]
 anthranilic acid (2-aminobenzoic acid) [118-92-3]	 3,4-diaminotoluene [496-72-0]	 2-aminobenzylamine [4403-69-4]
 ethylenediamine [107-15-3]	 diethylenetriamine [111-40-0]	 N-(2-aminoethyl)-1,3-propanediamine [13531-52-7]
 triethylenetetramine [112-24-3]	 tetraethylenepentamine [112-57-2]	 ethylenediaminetetraacetic acid (EDTA) [60-00-4]

A1.3. Results and Discussion

The simplest way to present the results of the titrations for each metal with all of the ligands studied was to prepare a summary chart showing the pH of complexation for an individual metal by positioning the ligand at the approximate pH that complexation was observed. The results of the titration of the thiol-containing ligands and of the amine ligands in the presence of nickel, copper and zinc ions are summarized in tables A1.3, A1.5, A1.7, A1.9, A1.11, and A1.13. For ligands complexing below pH 4, they are all approximately equivalent based on the titration data; ligand positions in this pH range on the tables are not relative to each other. For some of the ligands, it was difficult to discern where complexation was occurring; both pH values are given in these cases. For many of the titrations, precipitation occurred. Tables A1.4, A1.6, A1.8, A1.10, A1.12, and A1.14 compare the stability constants (pK_1's only) obtained from the cited literature (references 4 to 14) for the three metals. As can be seen, the literature did not contain stability constants for all the ligands studied; as well, they were evaluated using different techniques and experimental conditions.

The stability constants are related to the pH of complexation. The lower the pH of complexation, the more stable the complex, and the higher the stability constant. This trend should be evident in comparison of the pH of complexation to the cited stability constants. As we have simplified the technique, some discrepancies may occur, but our method gives a good first approximation of a ligand's behaviour.

The average time it took to screen one ligand with seven metals, including preparation time, was approximately six hours.

Figure A1.1 shows the titration curves of one equivalent of nickel(II) ion (curve A, 1 Ni(II)), two equivalents of one thiol ligand (L), 2-aminoethanethiol (curve B, 2 L), and one equivalent of nickel ion in the presence of one (curve C, 1 Ni(II) : 1L) and two equivalents of ligand (curve D, 1 Ni(II) : 2 L). Changes in the curves can be seen when comparing these four titrations. The plateaus in the curves indicate changes in speciation, such as the formation of nickel hydroxide, deprotonation of the ligand, or formation of the complex. As can be seen, nickel hydroxide forms around pH 8.25 to 8.5 (curve A), the ligand is converted to the free amine at pH 8.25 (coincidentally), (curve B), while the complex forms at a much lower pH (6), (curves C and D). When only one equivalent of ligand is used, the remaining ligands on nickel are two water molecules, one of which gets deprotonated to form a hydroxide ligand, as can be seen on titration curve C (pH 8.75). With two or more equivalents of ligand (curve D), the second plateau disappears, as only the two equivalents of aminoethanethiol complexes the nickel.

The stoichiometry of the changes in speciation can be observed from the titration data. The width of each plateau, taken from both inflection points, gives the amount of hydroxide added. The titration solution had 0.1 mmol of metal present (1 mL of 0.1 M solution used) (with the exception of the titration of ligand alone). Likewise, the quantities of ligand added were 0.1, 0.2, or 0.3 mmol (1, 2, or 3 mL of 0.1 M solution). Since the concentration of titrant added was 0.1 M, 0.1 mmol (1 mL) hydroxide added was equal to one equivalent (of hydroxide).

In the plateau region of curve A, the nickel precipitated as $Ni(OH)_2$, two equivalents (0.2 mmol) of hydroxide being consumed for each equivalent of nickel ion (0.1 mmol). In curve B, two equivalents (0.2 mmol) of ligand were titrated, and each consumed one equivalent (0.1 mmol) of base to form the free amine from the hydrochloride. Since there were two equivalents of ligand present, the total base consumption was two equivalents (0.2 mmol), as can be seen. For the titration of the solution of one equivalent nickel to one equivalent ligand (curve C), the stoichiometry for the first plateau (pH 6) was two equivalents of base. This was due to the simultaneous deprotonation of the thiol and the amine hydrochloride to enable complexation with the metal. The second, smaller plateau on curve C (pH 8.75) was due to the conversion of one bound water molecule to a bound hydroxide, consuming one equivalent of base. For curve D, the thiol and amine groups were both deprotonated for the two equivalents of ligand, consuming four equivalents of base. Since the nickel was complexed by the two ligands, no water acted as a ligand, so there was only the first plateau.

This is typical behaviour of a system with complexing agents in solution. From the titration curves, we generated the summary tables of the pH of complexation of the many ligands with each of nickel, copper, and zinc. This way, a fast comparison can be made which will aid in the choice of ligands for different applications.

When copper(II) ion and 2-aminoethanethiol hydrochloride were titrated, an indigo-coloured precipitate formed. This was observed for some of the thiol-containing ligands studied with copper. A cupric-cuprous redox couple occurs with thiols, yielding a mixture of Cu(II), Cu(I), thiol and disulfide [15, 16, 17].

A comparison was made between two thiols and their model compound thioethers. This was done because one of the methods of resin modification being explored creates a thioether linkage to the resin. As the coordination chemistry of thiols and thioethers is different, it was prudent to study the thioether ligand, once the original thiol ligand was screened. The two thiols chosen were 2-aminoethanethiol hydrochloride and 2-aminothiophenol which both complexed metals (see tables A1.3, A1.5, and A1.7). The corresponding thioethers were 2-(methylmercapto)-aniline and 2-(ethylthio)ethylamine hydrochloride. As expected, the coordinating ability of the thioethers was very low, the only observed complexations were of 2-(ethylthio)ethylamine hydrochloride with Cu^{+2} and Ni^{+2}. The colour of the copper complex was bright blue, similar to that of amine complexes of copper, while the colour of the nickel complex was a yellow-green. Since the screening step showed little complexing ability, it saved much time and resources as no work was needed on resin modification or characterization of the resins for metal-uptake to arrive at the same conclusion.

Results of titrations involving lead, cobalt, ferric and ferrous ions were not as well-defined. Many of the titrations gave precipitated species. Most of the ferric titrations precipitated ferric hydroxide at pH's higher than 4. Likewise, ferrous ion tended to precipitate the hydroxide around pH 8. As lead chloride is insoluble, for many titrations involving lead, the chloride would precipitate out. With these complications, it was decided not to present the results for these metals in this paper.

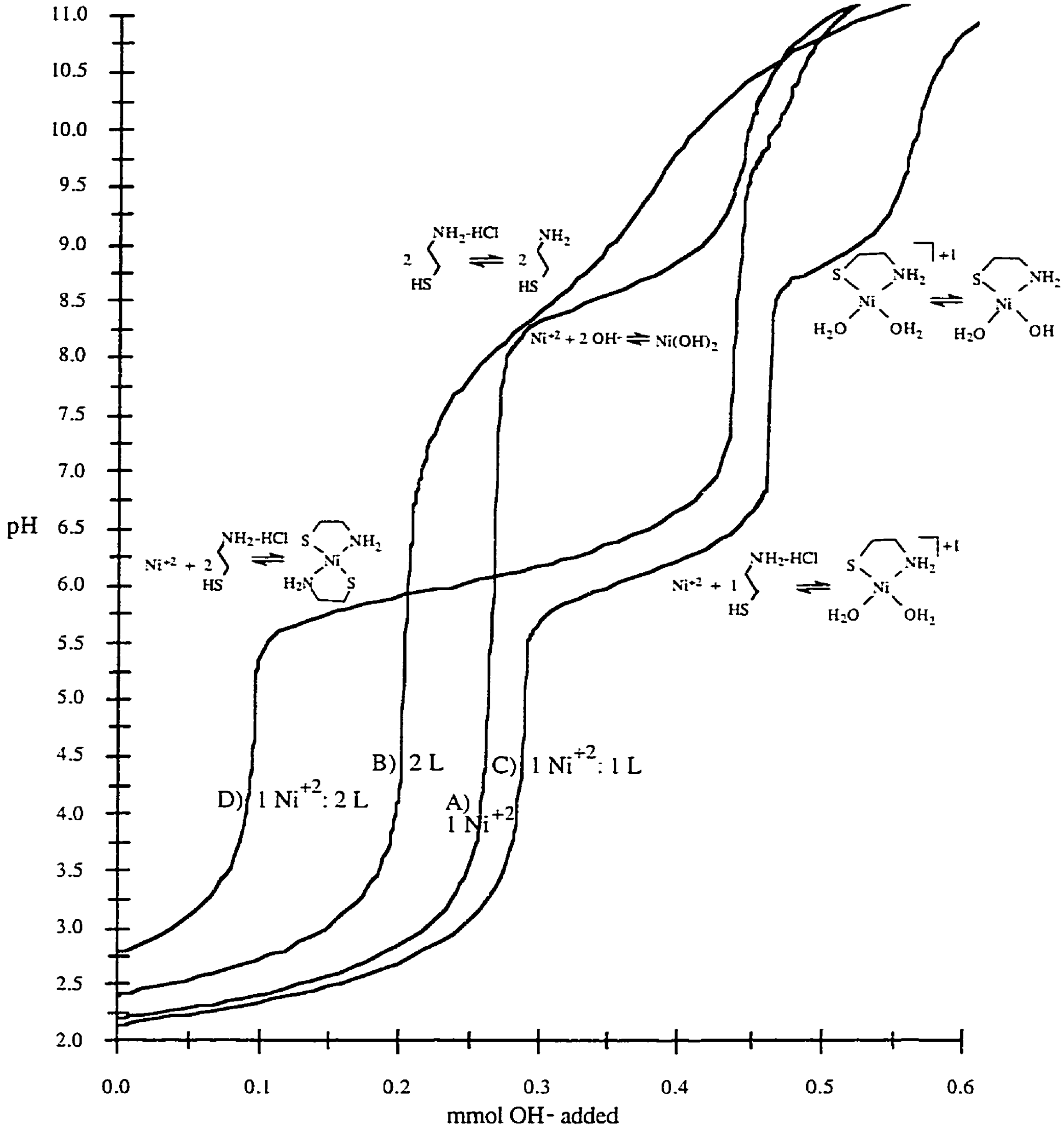
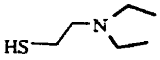
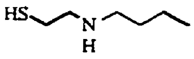
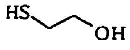
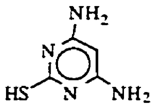
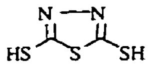
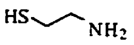
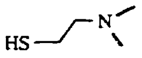
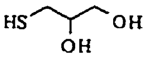
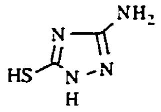
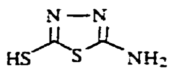
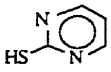
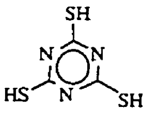
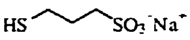
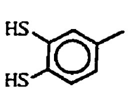
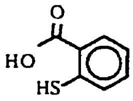
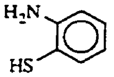
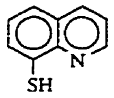
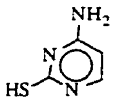
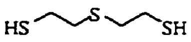
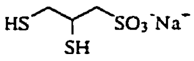
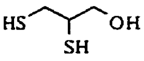
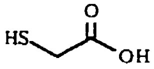
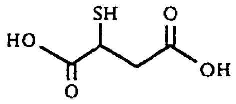
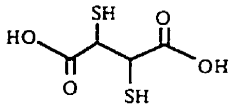
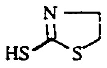
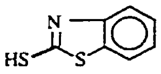
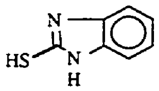
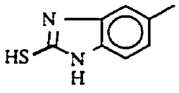
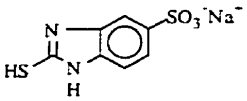


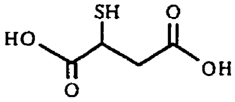
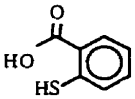
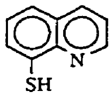
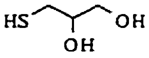
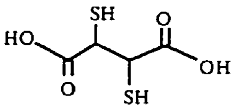
Figure A1.1. Titration curves of Ni^{+2} (A), 2-aminoethanethiol hydrochloride (L, curve B), and Ni^{+2} in the presence of one (C) and two (D) equivalents of 2-aminoethanethiol hydrochloride.

Table A1.3. pH of Complexation of Ni^{+2} with Various Thiol Ligands

pH	Ligands Which Complex Ni^{+2}
≥ 7	 (8 - 9)  (6.5 - 8)  (7 - 8.5)  (6 - 8)  (6 - 8)  (6.5 - 7.25)
6	 (5.5. - 7.5)  (6.25 - 7.25)  (< 7)  (< 3 or 6 - 7.5)  (5 - 7)
5.5	 (> 5.5)  (> 5.5)  (< 6)  (< 6)
4	
≤ 3	                

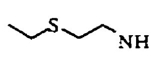
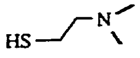
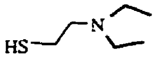
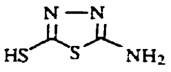
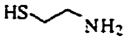
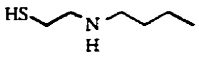
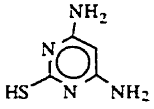
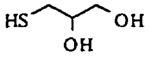
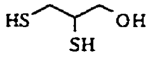
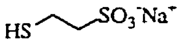
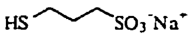
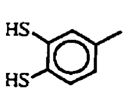
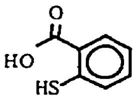
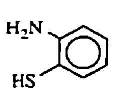
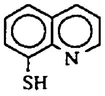
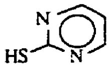
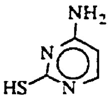
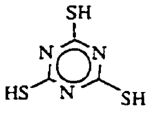
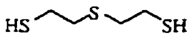
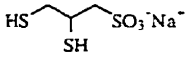
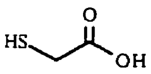
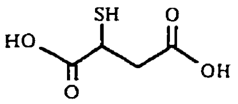
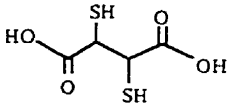
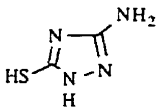
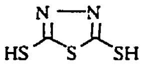
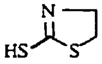
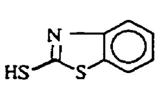
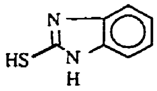
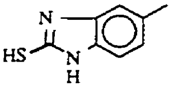
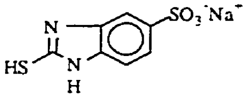
- Conditions: 0.1 M NaCl background, pH adjusted with 1 M HCl, 0.1000 M NaOH titrant

Table A1.4. Cited Stability Constants (pK_1) of Complexation of Ni^{+2} with Various Thiol Ligands

pK_1	Ligands Which Complex Ni^{+2}
3 - 9	 3.23
	 7.97  8.1
9 - 11	 10.05
11 - 12	 11.0  11.25  11.69

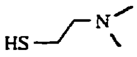
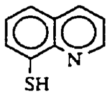
- Note: Stability constants are from different references with different experimental conditions

Table A1.5. pH of Complexation of Cu^{+2} with Various Thiol Ligands

pH	Ligands Which Complex Cu^{+2}
6	 (6)  (5.5 - 7)  (5.5 - 6.5)  (6 - 7 or < 3)  (5 - 7)
5.5	 (5 - 6)  (5.25 - 6)  (> 5)  (< 5.5 - 6.5)  (< 2 - 7)
5	 (< 6)  (< 6)
4	
≤ 3	                   

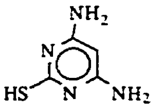
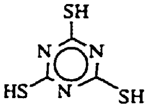
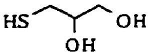
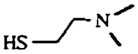
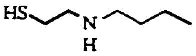
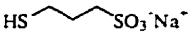
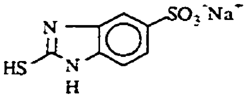
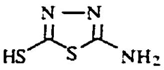
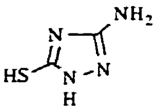
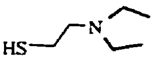
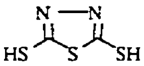
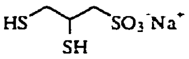
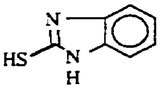
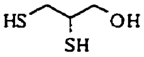
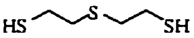
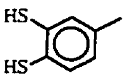
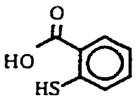
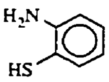
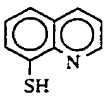
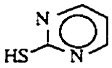
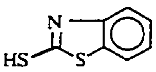
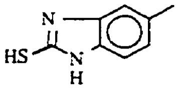
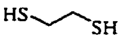
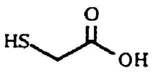
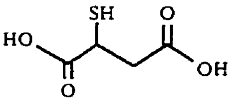
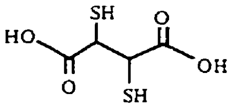
- Conditions: 0.1 M NaCl background, pH adjusted with 1 M HCl, 0.1000 M NaOH titrant

Table A1.6. Cited Stability Constants (pK_I) of Complexation of Cu^{+2} with Various Thiol Ligands

pK_I	Ligands Which Complex Cu^{+2}
5 - 9	 5.58
	 7.31
9 - 12	 9.76
12 - 14	 12 - 14

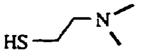
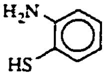
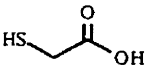
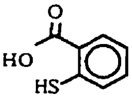
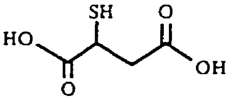
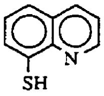
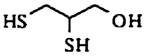
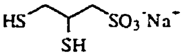
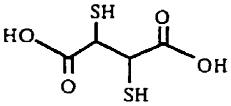
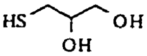
- Note: Stability constants are from different references with different experimental conditions

Table A1.7. pH of Complexation of Zn^{+2} with Various Thiol Ligands

pH	Ligands Which Complex Zn^{+2}
≥ 7	 (7.5 - 9)  (6.5 - 7.5)
6.5	 (6 - 7.5)  (6 - 7)  (5.5 - 7.5)  (5.5 - 7.5)  (5.5 - 7.5)  (5.5 - 7.5)  (6 - 7)  (< 3 or 6 - 7)  (5.5 - 7.5)
6	 (~ 6 - 6.5)  (5.5 - 7.25)  (5 - 6.5)
5	 (4 - 6)  (< 3 or 5 - 6)
4	 (< 3 - 6)  (3.5 - 4.5)
≤ 3	          

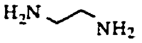
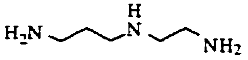
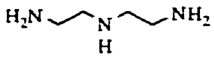
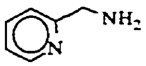
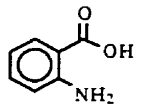
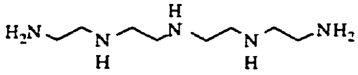
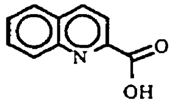
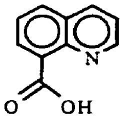
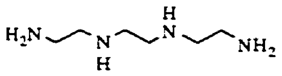
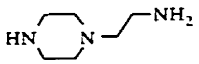
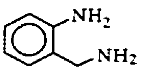
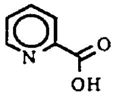
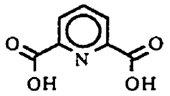
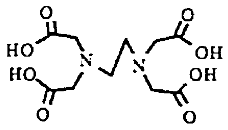
- Conditions: 0.1 M NaCl background, pH adjusted with 1 M HCl, 0.1000 M NaOH titrant

Table A1.8. Cited Stability Constants (pK_I) of Complexation of Zn^{+2} with Various Thiol Ligands

pK_I	Ligands Which Complex Zn^{+2}
6 - 8	 6.92  7.33
8 - 10	 8.36  8.45  8.47
10 - 13	 10.22  11.0
13 - 15	 13.5  14.09
15 - 17	 15.82
17 - 19	 18.00

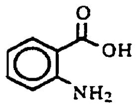
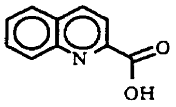
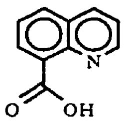
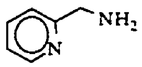
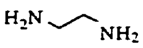
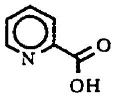
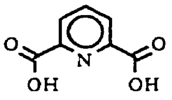
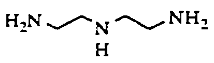
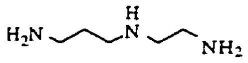
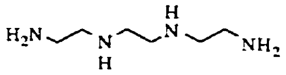
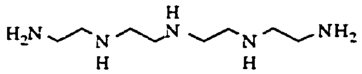
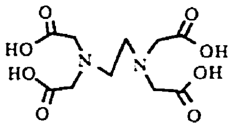
- Note: Stability constants are from different references with different experimental conditions

Table A1.9. pH of Complexation of Ni^{+2} with Various Amine Ligands

pH	Ligands Which Complex Ni^{+2}
6.5	 (6 - 7)  (6 - 7)
6	
5	 (~ 5 or < 3)  (~ 5 or < 3)  (~ 5 or < 3)
4	 (< 3 - 5)  (< 3 -4)  (< 3 - 5)
≤ 3	     

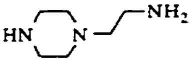
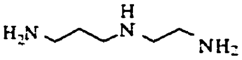
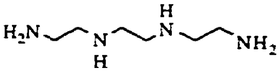
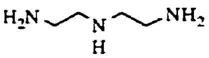
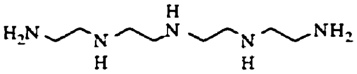
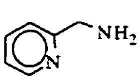
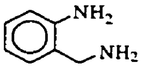
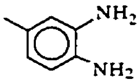
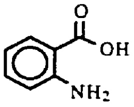
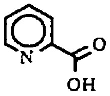
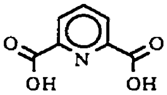
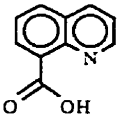
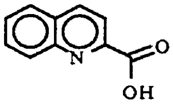
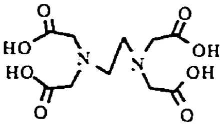
- Conditions: 0.1 M NaCl background, pH adjusted with 1 M HCl, 0.1000 M NaOH titrant

Table A1.10. Cited Stability Constants (pK_1) of Complexation of Ni^{+2} with Various Amine Ligands

pK_1	Ligands Which Complex Ni^{+2}
2 - 5	 2.12  4.6
5 - 8	 4.4 - 6.2  7.32  7.45  6.80
8 - 11	 8  10.7  11.0
14 - 17	 14.5
17 - 20	 17.51  18.56

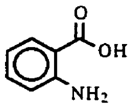
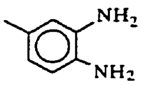
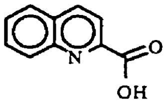
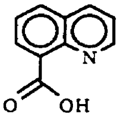
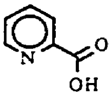
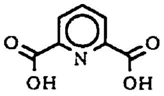
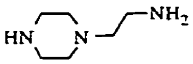
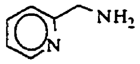
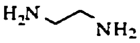
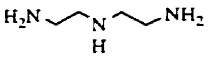
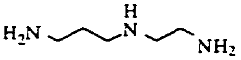
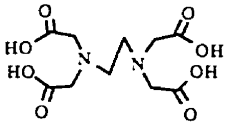
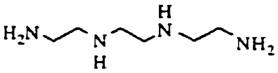
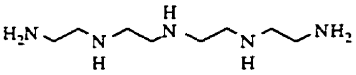
- Note: Stability constants are from different references with different experimental conditions

Table A1.11. pH of Complexation of Cu^{+2} with Various Amine Ligands

pH	Ligands Which Complex Cu^{+2}
6	 (~ 6)
5	 (4 - 6)
4	 (< 4)
≤ 3	           

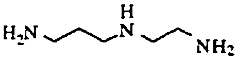
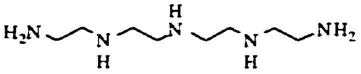
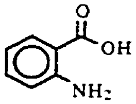
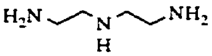
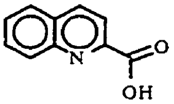
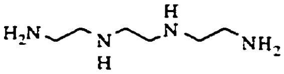
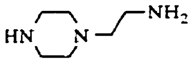
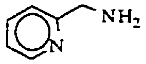
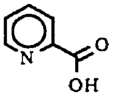
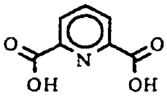
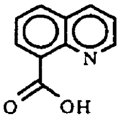
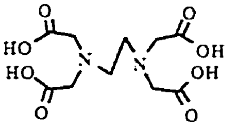
- Conditions: 0.1 M NaCl background, pH adjusted with 1 M HCl, 0.1000 M NaOH titrant

Table A1.12. Cited Stability Constants (pK_I) of Complexation of Cu^{+2} with Various Amine Ligands

pK_I	Ligands Which Complex Cu^{+2}
4 - 8	 4.25  4.74  5.91  7.8  7.96
8 - 10	 8.9  9.3  9.64
10 - 17	 10.44  16.1  16.3
17 - 21	 18.79  20.9
21 - 24	 23.58

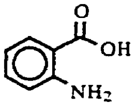
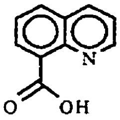
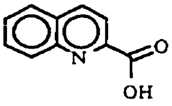
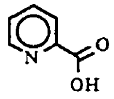
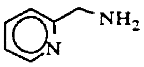
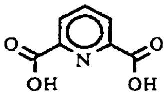
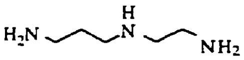
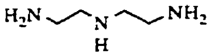
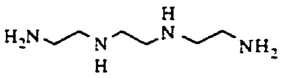
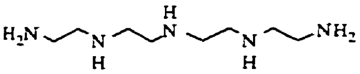
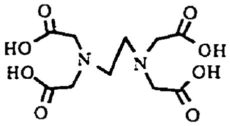
- Note: Stability constants are from different references with different experimental conditions

Table A1.13. pH of Complexation of Zn^{+2} with Various Amine Ligands

pH	Ligands Which Complex Zn^{+2}
7	 (6.5 - 8)
6.5	 (6 - 7)
6	
5	 (4.5 - 5)  (~ 5)
4	 (~ 4 or < 3)  (< 3 - 4)
≤ 3	      

- Conditions: 0.1 M NaCl background, pH adjusted with 1 M HCl, 0.1000 M NaOH titrant

Table A1.14. Cited Stability Constants (pK_I) of Complexation of Zn^{+2} with Various Amine Ligands

pK_I	Ligands Which Complex Zn^{+2}
2 - 5	 2.57  4.9  5.1
5 - 7	 5.3  5.41  5.53
7 - 9	 7.0  8.62  8.9
9 - 13	 12.05
13 - 15	
15 - 17	 15.4  16.26

- Note: Stability constants are from different references with different experimental conditions

A1.4. Conclusions

The screening of ligands by use of pH titration is described. The pH of complexation with metals is in general agreement with the stability constants where available. The results should help in the choice of complexing agents for particular applications.

A1.5. Acknowledgements

This work could not have been completed without the assistance of three undergraduate students: Gaelle Prevost, Ryan Wada, and Kris Schantz. They spent many long hours performing titrations and organizing the resulting information. This research was funded by the Natural Sciences and Engineering Research Council of Canada under the Strategic Grants Program.

A1.6. References

[1] Kauffman, G.B. (ed.) Coordination Chemistry. A Century of Progress. ACS Symposium Series No. 565, American Chemical Society: Washington, 1994.
[2] Rao, S.R., Xu, Z. & Finch, J.A. Waste Processing and Recycling in Mineral and Metallurgical Industries II. (eds., S.R. Rao, L.M. Amaratunga, G.G. Richards & P.D. Kondos), The Metallurgical Society of the Canadian Institute of Mining, Conference Proceedings, Vancouver, B.C. August 20-24, 1995. pages 69-78.
[3] Liu, Q., Xu, Z. & Finch, J.A., Self-assembly of bolaamphiphile on nano-sized magnetic particles. 70th Colloid and Surface Science Symposium. Clarkson University, Potsdam, N.Y., June 1996. (poster #104)
[4] Perrin, D. D. Stability Constants of Metal-Ion Complexes. Part B. IUPAC Chemical Data Series, No. 22. Pergamon Press: Oxford, 1979. pages 60, 62, 63, 78, 146, 148.
[5] Bjerrum, J., Schwarzenbach, G. & Sillén, L. G. Stability Constants of Metal-Ion Complexes, with Solubility Products of Inorganic Substances. 1st ed., Vol. 1, Special Publication No. 6, The Chemical Society: London, 1957. page 73.
[6] Sillén, L. G. & Martell, A. E. Stability Constants of Metal-Ion Complexes. 2nd ed.; Special Publication No. 17, The Chemical Society: London, 1964. pages 369, 403, 424, 482, 505, 546, 576.

[7] Sillén, L. G. & Martell, A. E. Stability Constants of Metal-Ion Complexes. Supplement No. 1. Special Publication No. 25; The Chemical Society: London, 1971. pages 435, 504, 508, 578.

[8] Martell, A. E. & Smith, R. M. Critical Stability Constants. Vol. 1. Plenum Press: New York, 1974. pages 338, 369, 370, 372.

[9] Martell, A. E. & Smith, R. M. Critical Stability Constants. Vol. 2. Plenum Press: New York, 1975. pages 32, 49, 101, 102, 105, 106, 136.

[10] Martell, A. E. & Smith, R. M. Critical Stability Constants. Vol. 3. Plenum Press: New York, 1977. pages 283.

[11] Martell, A. E. & Smith, R. M. Critical Stability Constants. Vol. 5. Plenum Press: New York, 1982. pages 164, 369, 370.

[12] Chaberek, S. & Martell, A. E. Sequestering Agents - A Discussion of the Chemical Behaviour and Applications of Metal Chelate Compounds in Aqueous Systems. Wiley: New York, 1959. pages 516-580.

[13] Dick, J. G. Analytical Chemistry. McGraw-Hill Book Co.: New York, 1973, pages 664, 667-8.

[14] Mittal, M. L., Saxena, R. S. & Pandy, A. V., Metal complexes of 2-dimethylaminoethanethiol hydrochloride. Journal of Inorganic and Nuclear Chemistry, 35 (1975), 1691.

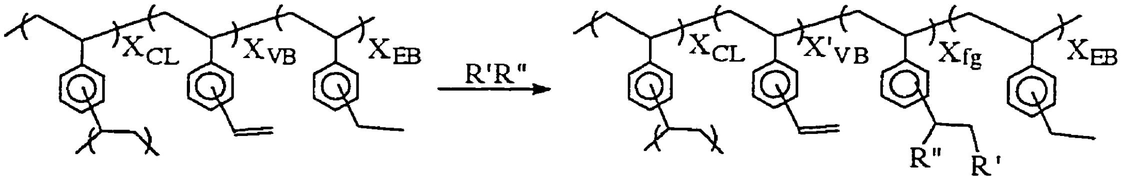
[15] Li, N.C. and Manning, R.A., Some metal complexes of sulfur-containing amino acids. Journal of the American Chemical Society, 77 (1955), 5225.

[16] Musker, W.K. & Neagley, C.H., Experimental complications in studies of the reaction of copper(II) with penicillamine and related thiols. Inorganic Chemistry, 14 (1975), 1728.

[17] Micheloni, M., May, P.M. & Williams, D. R., Metal-ligand complexes involved in rheumatoid arthritis-IV. Journal of Inorganic and Nuclear Chemistry, 40 (1978), 1209.

Appendix 2

Derivation of Degree of Functionalization Equations



Scheme A2.1. Modification of poly(divinylbenzene-*co*-ethylvinylbenzene).

Terms and Symbols

avg MW	average molecular weight per repeat unit (g/mol)
X_{CL}	degree of functionalization of cross-linked groups (as fraction) (note, for simplification assume it does not change, although it can without changing the outcome of the equations)
X_{VB}	degree of functionalization of vinylbenzene groups (as fraction)
X'_{VB}	degree of functionalization of vinylbenzene groups in modified resin (as fraction)
X_{fg}	degree of functionalization of functional groups (as fraction)
X_{EB}	degree of functionalization of ethylbenzene groups (as fraction)
MW fg	molecular weight of modifying reagent (R'R", i.e. R' + R")
mol fg/g	moles of functional group per gram modified resin (generally found by elemental analysis)

MW of divinylbenzene (DVB): 130.2 g/mol

MW of modified unit: (130.2 + MW fg) g/mol (since it is due to modification of vinylbenzene group)

MW of ethylvinylbenzene (EVB): 132.2 g/mol

General equation for avg MW of modified resin:

(1) $\text{avg MW} = 132.2 \times X_{EB} + 130.2 \times (X_{CL} + X'_{VB}) + (130.2 + \text{MW fg}) \times X_{fg}$

(2) $X_{EB} + X_{CL} + X'_{VB} + X_{fg} = 1.00$ (total of the mole fractions of all units)

For a resin prepared from 80 mol % DVB and 20 mol % EVB (i.e. XAD-4), and since CL, VB and functional (fg) groups were derived from DVB:

$(X_{CL} + X_{VB} + X_{fg}) = 0.80$ and $X_{EB} = 0.20$

When $X_{fg} = 0$ (i.e. unmodified XAD-4), then

(3) $\text{avg MW} = 132.2 \times X_{EB} + 130.2 \times (X_{CL} + X_{VB})$

$\text{avg MW} = 132.2 \times 0.20 + 130.2 \times 0.80$

avg MW = 130.6 g/mol (avg MW per repeat unit of unmodified resin)

For a resin modified with R'R" having MW fg

(1) $\text{avg MW} = 132.2 \times X_{EB} + 130.2 \times (X_{CL} + X'_{VB}) + (130.2 + \text{MW fg}) \times X_{fg}$

rearranging (1) gives:

(4) $\text{avg MW} = \{132.2 \times X_{EB} + 130.2 \times (X_{CL} + X'_{VB} + X_{fg})\} + \text{MW fg} \times X_{fg}$

and

for $X_{EB} = 0.20$ and $(X_{CL} + X'_{VB} + X_{fg}) = 0.80$, substituting into $\{132.2 \times X_{EB} + 130.2 \times (X_{CL} + X'_{VB} + X_{fg})\}$ simplifies to: 130.6 g/mol = avg MW per repeat unit of unmodified resin (having 80:20 DVB:EVB)

Thus, for a resin with 80:20 DVB:EVB composition, (4) becomes:

(5) $\text{avg MW} = 130.6 + (\text{MW fg} \times X_{fg})$

and since

(6) $\text{mol fg/g} = X_{fg} \div \text{avg MW}$

rearranging (6) gives:

(7) $X_{fg} = (\text{mol fg/g}) \times \text{avg MW}$

then substituting (5) into (7) gives:

(8) $X_{fg} = (\text{mol fg/g}) \times \{130.6 + (\text{MW fg} \times X_{fg})\}$

rearranging (8) and multiplying by 100% gives X_{fg} (in %):

$$(9) \qquad X_{fg} = \frac{130.6 \times (\text{mol fg/g})}{1 - (\text{mol fg/g} \times \text{MW fg})} \times 100\%$$

For example, when various RR' groups are used, and substituted into (9), the equation for the degree of functionalization of modified XAD-4 (in %) becomes:

When R'R" = HSR, and n is the number of S atoms per HSR molecule:

$$(10) \qquad X_{2\text{-SR}} = \frac{130.6 \times (\text{mol S/g} \div \text{n})}{1 - ((\text{mol S/g} \div \text{n}) \times \text{MW HSR})} \times 100\%$$

When R'R" = RSSR, and n is the number of S atoms per RSSR molecule:

$$(11) \qquad X_{1,2\text{-SR}} = \frac{130.6 \times (\text{mol S/g} \div \text{n})}{1 - ((\text{mol S/g} \div \text{n}) \times \text{MW RSSR})} \times 100\%$$

When R'R" = Br_2:

$$(12) \qquad X_{1,2\text{-Br}} = \frac{130.6 \text{ g / mol} \times (\text{mol Br/g} \div 2)}{1 - (\text{mol Br/g} \times \text{MW Br})} \times 100\%$$

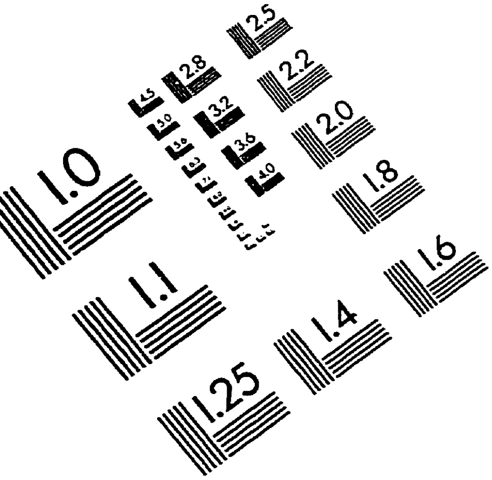
When R" = Br and R' = OH (bromohydrin):

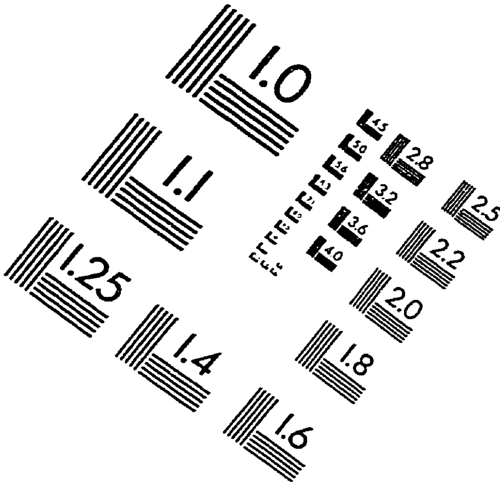
$$(13) \qquad X_{1,2\text{-BrOH}} = \frac{130.6 \text{ g / mol} \times (\text{mol Br/g})}{1 - (\text{mol Br/g} \times \text{MW OHBr})} \times 100\%$$

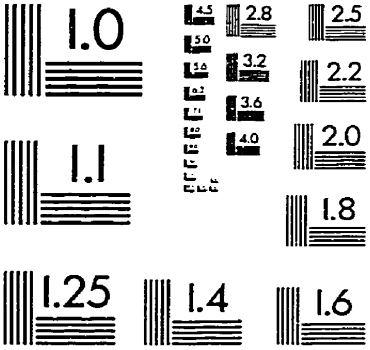
When R'R" = O (epoxide):

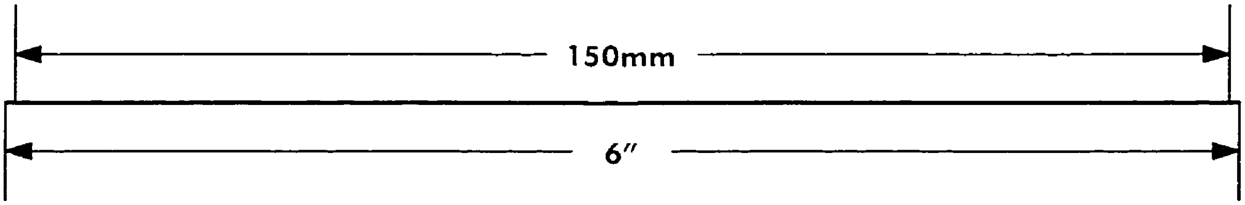
$$(14) \qquad X_{\text{epox}} = \frac{130.6 \times (\text{mol O/g})}{1 - (\text{mol O/g} \times \text{MW O})} \times 100\%$$

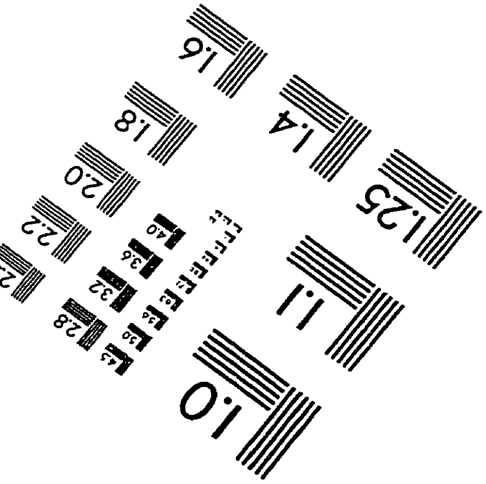
IMAGE EVALUATION
TEST TARGET (QA-3)

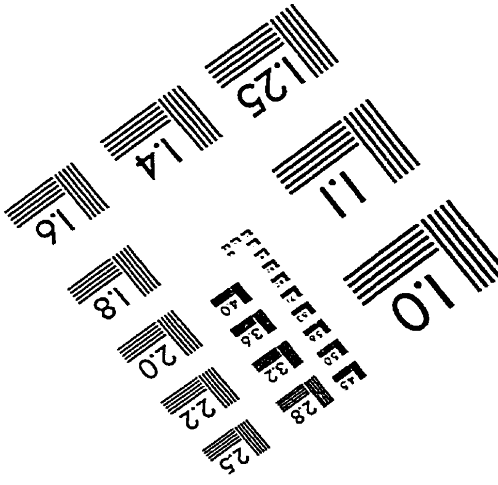












APPLIED IMAGE . Inc
1653 East Main Street
Rochester, NY 14609 USA
Phone: 716/482-0300
Fax: 716/288-5989