THE EFFECTS OF MATRIX GLASS TRANSITION TEMPERATURE AND POLARITY, AND IONIC GROUP SPACERS ON ION AGGREGATION IN STYRENE IONOMERS

by

Mario Gauthier

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Department of Chemistry,
McGill University,
Montreal, Quebec,
Canada.

January 1989

The effects of matrix glass transition temperature and polarity, and ionic group spacers on ion aggregation in styrene ionomers

Abstract

Matrix glass transition temperature depression through internal plasticization of a styrene-sodium methacrylate ionomer resulted in enhanced clustering at low plasticization levels (up to ca. 20 mole%). At higher plasticization levels, ion aggregation was strongly disrupted. Matrix polarity effects were studied by nitrating the styrene units of the same ionomer. A sample with a relaxed dielectric constant comparable to acrylate polymers showed no decrease in clustering. Similarly, plasticization with nitrobenzene resulted in typical nonpolar diluent behavior. Polarity was, therefore, not a significant parameter affecting ion aggregation. New styrene copolymers with substituents $R = -(CH_2)_nCOOMe$ ($n = 1, 5, 10$) or $R = -O(CH_2)_nCOOMe$ ($n = 1, 4, 10$) in the para- position were synthesized, to form a systematic investigation of ionic group spacing effects on the dynamic mechanical properties of ionomers. The results were rationalized in terms of bulkiness and rigidity of the units supporting the ionic groups, and polymer backbone immobilization efficiency. Ion solvation effects were also suggested for the ether derivatives.

Influence de la température de transition vitreuse et de la polarité de la matrice, et d'espaceurs pour les fonctions ioniques sur l'aggrégation dans des ionomères de styrène

Résumé

L'abaissement de la température de transition vitreuse de la matrice par plastification interne d'un ionomère de styrène-méthacrylate de sodium favorisa l'aggrégation ionique à faible niveaux de plastification (jusqu'à ca. 20 mole%). A de plus haut niveaux, la formation de gros aggrégats ioniques (clusters) fut fortement perturbée. L'influence de la polarité de la matrice fut étudiée par nitration des unités styrène du même ionomère. Un échantillon de constante diélectrique comparable aux polymères d'acrylate ne démontra aucune diminution de l'aggrégation. Pareillement, la plastification avec du nitrobenzène montra des caractéristiques propres aux plastifiants non-polaires. Conséquemment, la polarité ne semble pas un facteur prédominant contrôlant l'aggrégation. De nouveaux copolymères de styrène avec des substituants R = $-(CH_2)_nCOOMe$ (n = 1, 5, 10) ou R = $-O(CH_2)_nCOOMe$ (n = 1, 4, 10) en position para- furent synthétisés, pour permettre une étude systématique de l'influence de l'espacement des fonctions ioniques sur les propriétés mécaniques dynamiques des ionomères. Les résultats furent interprétés en termes de grosseur et de rigidité des unités supportant les fonctions ioniques, et d'efficacité à immobiliser la chaîne du polymère. Des effets de solvatation furent également suggérés pour les dérivés d'éthers.

Foreword

In accordance with guideline 7 of the "Guidelines Concerning Thesis Preparation" (Faculty of Graduate Studies and Research, McGill University), the following text is cited:

> "The candidate has the option, subject to the approval of the Department, of including as part of the thesis the text, or duplicated published text, of an original paper, or papers. In this case the thesis must still conform to all other requirements explained in Guidelines Concerning Thesis Preparation. Additional material (procedural and design data as well as descriptions of equipment) must be provided in sufficient detail (e.g. in appendices) to allow a clear and precise judgement to be made of the importance and originality of the research reported. The thesis should be more than a mere collection of manuscripts published or to be published. *It must include a general abstract, a full introduction and literature review and a final overall conclusion.* Connecting texts which provide logical bridges between different manuscripts are usually desirable in the interests of cohesion.
>
> It is acceptable for theses to include as chapters authentic copies of papers already published, provided these are duplicated clearly on regulation thesis stationery and bound as an integral part of the thesis. Photographs or other materials which do not duplicate well must be included in their original form. *In such instances, connecting texts are mandatory and supplementary explanatory material is almost always necessary.*
>
> The inclusion of manuscripts co-authored by the candidate and others is acceptable but the candidate is required to make an explicit statement on who contributed to such work and to what extent, and supervisors must attest to the accuracy of the claims, e.g. before the Oral Committee. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to make the responsibilities of authors perfectly clear. Candidates following this option must inform the Department before it submits the thesis for review."

This thesis is written in the form of four papers, as yet unpublished, which are preceded by a general introduction, and followed by general conclusions.

Following the normal procedure, all the papers have been or will be submitted shortly for publication in scientific journals, with the research director, Professor Adi Eisenberg, as a co-author. However, it is clear that all work has been done by the author of this thesis, except for the normal supervision and advice given by the research director.

Acknowledgements

The contributions of the following persons are most sincerely appreciated and recognized:

Dr. Adi Eisenberg for his guidance and enlightening discussions;

Drs. J. T. Edward, G. Just, J. Chin and A. S. Hay, for their most helpful suggestions and discussions relating to the synthetic aspects of this work;

Susan Williams for her love, patience, encouragement, as well as the typing, proofreading, and many helpful suggestions concerning this thesis;

Daphne Wollmann, Bryn Hird, Jean-Pierre Gouin and all the other fellow graduate students and summer students who created a pleasant and workable environment;

The technical support staff, and particularly Mr. George Kopp (glass blowing), Fred Kluck (machine shop) and Roland Gaulin (electronics shop) for maintaining the equipment in good working condition and producing custom items needed for this work;

The Natural Sciences and Engineering Research Council (Canada), Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (Québec), and McGill University for financial support;

The Natural Sciences and Engineering Research Council (Canada) and the U. S. Army Research Office for financial support of laboratory supplies and equipment.

Table of contents

List of tables

List of figures

Chapter 1. General introduction

1.1. Historical aspects and scope

The incorporation of ions into polymers has led to new materials with greatly modified properties[1-6]. Ionomers[7] are generally defined as organic copolymers containing a minor fraction (up to ca. 15 mole%) of pendant ionic groups. These substances offer challenging areas of interest from the point of view of theoretical considerations, as well as that of possible applications. To the chemist, ionomers provide the opportunity to explore the complex balance of factors involved in the aggregation of ionic compounds in low to medium polarity environments, which are responsible for the sometimes drastic modifications observed in the physical properties of these polymers. To the engineer, ionomers offer materials with a wide range of properties, with characteristics common both to thermoplastics and to cross-linked systems. Their current uses encompass such various domains of application as packagings and coatings, permselective membranes in electrolytic and fuel cells, high-strength elastomers, and reversible gels.

Even though a number of patents were obtained for carboxylated rubber materials starting in the early 1930's, it was not until 1949 that B.F. Goodrich introduced a butadiene-styrene-acrylic acid terpolymer under the name Hycar[8]. At that time, however, the inclusion of carboxyl groups in elastomers was strictly oriented towards the improvement of their hydrocarbon solvent resistance characteristics[9]. The idea of neutralizing the acrylic acid units in the Hycar copolymer is due to Brown[10], as a means to provide sulfurless curing for elastomers. In 1965, duPont introduced the Surlyn[11] ionomers, which are partly neutralized salts of ethylene-methacrylic acid copolymers. Ever since then, the field of ionomers has shown a rapid growth leading to the emergence of a multitude of new products. In parallel to the development of new materials, the study of the morphology of these compounds in relation to their physical properties has also received considerable attention.

Because of the rapid expansion of the field of ion-containing polymers, it seems appropriate to restrict the scope of this introductory review. It was mentioned that, by definition, ionomers are organic polymers with only a minor fraction of ionic groups. They form a subclass of ion-containing polymers which exclude, among others, the polyelectrolytes. For the sake of simplicity, only the synthesis and properties of ionomers based on random copolymers will be discussed. Special cases of ionic group distribution, such as telechelic and block structures (including polyurethanes), as well as ampholytic and zwitterionomeric systems, will be excluded. Detailed descriptions of experimental synthetic procedures will be avoided, and only a summary of the main features of the preparations will be given. The reader should refer to the original literature for more information. Finally, the overview will focus primarily on the nonpatent literature, since it provides more detail and is more easily accessible.

Some representative techniques used to probe the morphology of ionomers will then be presented, together with the experimental evidence they provide for ion aggregation. Finally, a discussion of some structure-properties relations in ionomers, relevant to the present work, will be included prior to the consideration of the structural parameters of interest to this study.

1.2. Synthesis

A multitude of techniques have been reported for the synthesis of ionomeric materials. The ionic groups most commonly introduced in organic polymers are carboxylate and sulfonate moieties. It may seem tempting to divide the various syntheses according to the type of scheme involved. Using this approach, two main types of synthetic techniques can be distinguished. Copolymerization of the main ("inert") monomer with an easily ionizable minor component (e.g. unsaturated carboxylic acid) is the most direct route to the preparation of ionomers. Unfortunately, this method is of limited usefulness because of the often unfavorable copolymerization reactivity ratios

(r_1, r_2) of the monomers. The other technique involves the postpolymerization modification of a homopolymer to introduce the desired functionality. Alternately, copolymerization of the main monomer with a minor fraction of a reactive comonomer, which can subsequently undergo further chemical modifications, may also be of use.

Even though this type of classification handles the majority of the cases encountered in the synthetic literature of ionomers, it can lead to inconsistencies, since some ionomers may be prepared using a few different approaches. Another disadvantage of this classification system is that the division according to the type of functionalization technique is rather artificial as such, and tends to neglect reactivity features common to families of closely related compounds.

To avoid these problems, the approach preferred here is a more natural division of the various syntheses according to the type of the parent (nonfunctionalized) polymer (e.g. diene elastomers, polyolefins, etc.) from which the ionomers are derived. It should also be noted that the procedures given here correspond to the preparation of easily ionizable functionalized polymers (containing e.g. carboxylate, ester or amine moieties). The subsequent conversion to the ionomers (via neutralization, hydrolysis, quaternization, etc.) is, in general, assumed.

1.2.1. Diene elastomers

It was mentioned earlier that carboxylated elastomers were the first commercially available products which could be used to prepare ionomers by simple neutralization. The patent literature for carboxylated elastomers up to 1957 was reviewed by Brown[9]. These materials are generally prepared in the emulsion co- or terpolymerization of dienes (typically butadiene alone, or with styrene or acrylonitrile) with acrylic or methacrylic acid in the presence of potassium persulfate as a free-radical initiator[12]. A number of ionomeric elastomer studies were based on the commercially available materials, but the preparation of copolymers of butadiene with methacrylic acid or methyl acrylate[13], and terpolymers of butadiene, styrene and 4-vinylpyridine[14,15] was also described in the nonpatent literature. Sulfonated diene elastomeric ionomers have also been obtained in the emulsion copolymerization of butadiene or isoprene with sodium 4-styrenesulfonate[16,17], although the products were heterogeneous in composition in the first case. Ionomer precursors were similarly prepared in the emulsion copolymerization of isoprene with the sec-butyl ester of 4-styrenesulfonic acid[18].

Apart from the synthetic materials described so far, natural rubber could also be modified through addition across the double bonds. An example of this is the technique suggested in 1960 by Cunneen et al.[19] to carboxylate natural rubber by the addition of thioglycolic acid, using hydroperoxide initiators. Polyisoprene was sulfonated in a postpolymerization reaction with acetyl sulfate, but resulted in a cyclized product[20]. Newer classes of ionomeric elastomers based on a terpolymer of ethylene, propylene and a diene monomer such as 5-ethylidene-2-norbornene (EPDM), and another one based on polypentenamer, were also studied. As in the case of natural rubber, the functionalization of these elastomers relies on the reactivity of the residual double bonds. Modified EPDM elastomers with carboxylate groups[21] were thus obtained by metalation of the polymer with an n-butyllithium-potassium t-butoxide complex, followed by the addition of an excess of carbon dioxide. Sulfonated polymers resulted from the action of acetyl sulfate[22]. The preparation of polypentenamers containing thioglycolate[23], phosphonate[24], carboxylate[25] and sulfonate[26] moieties has also been described. The free-radical addition of ethyl thioglycolate[23] and dimethylphosphite[24] to the double bonds yielded the corresponding functionalized polymers. The carbene addition of ethyl diazoacetate to polypentenamer resulted in a carboxylated three-membered ring derivative[25]. A sulfur trioxide/triethylphosphate complex was used to introduce sulfonate groups in the same polymer[26]. All the polypentenamer ionomers prepared were also hydrogenated with p-toluenesulfonyl hydrazide[23-26], to provide materials analogous to the polyethylene-based materials.

1.2.2. Polyolefins

The term "ionomer" was initially suggested by Rees and Vaughan[7], referring to the now commercially important Surlyn$^{(R)}$ resins. The commercial samples are ethylene-methacrylic acid copolymers obtained in a high pressure free-radical process, and partially neutralized with zinc or sodium ions. The salts are easily displaced by refluxing the polymer in tetrahydrofuran in the presence of dilute hydrochloric acid[27], in the event that the free acid or other counterions are required. Ethylene-acrylic acid copolymers are commercially available from a few different sources. The synthesis of copolymers of undecenoic acid with propylene[28] and terpolymers also including ethylene units[29] was described in the literature.

The low reactivity of polyolefins makes them generally unsuitable for postpolymerization modification reactions. Significant polymer degradation often results from the vigourous reaction conditions needed for the functionalization of these polymers. Irradiation grafting was used to obtain polyethylene membranes containing styrene units, which were subsequently sulfonated[30]. Acrylic acid was grafted onto polypropylene[31] and ethylene-propylene copolymers[32] in the presence of free-radical initiators. Chlorophosphonated polyethylene[33] and ethylene-propylene copolymers[34] were obtained by bubbling oxygen through a solution of the polymers in phosphorus trichloride. Free phosphonic acid groups resulted from the hydrolysis of the chlorophosphonated derivatives.

1.2.3. Polystyrene

Styrene ionomers obtained with the commonly used free-radical initiation techniques are atactic, which make them particularly well-suited for ion aggregation studies. The inherent advantage of these materials resides in their amorphous character, which eliminates interferences due to crystallinity. Crystallinity is known to have profound effects on the mechanical properties of polymers, and may, on occasion, mask the effects due to ion aggregation. It is, therefore, not surprising that a large number of physical properties studies have been based on styrene ionomers.

The aromatic character of this material makes its functionalization possible via electrophilic substitution reactions on the pendant benzene rings. Sulfonated polystyrene, specifically, is undoubtedly among the most thoroughly characterized systems. The commonly used procedure for the preparation of the sulfonated derivatives involves the direct sulfonation of the styrene homopolymer with acetyl sulfate in dichloromethane, according to a patent by Makowski et al.[35] Other sulfonation procedures described make use of a triethylphosphate-sulfur trioxide complex[36], and lauryl or stearyl sulfate[37] as sulfonating agents. An emulsion technique involving the copolymerization of styrene with sodium styrenesulfonate was also reported[38], although a "blocky" structure was apparently obtained in that case[39].

Among the other styrene ionomers prepared via copolymerization, copolymers with methacrylic acid[40], acrylic acid[41], metal acrylates[42], butyl methacrylate[43] or vinylpyridine[44] can be mentioned. Ionomers with 4-carboxystyrene units were prepared either by lithiation of 4-bromostyrene copolymers with n-butyllithium at low temperature[45] or by the direct metalation of a styrene homopolymer with a TMEDA-n-butyllithium complex[46], followed by the addition of a large excess of carbon dioxide. The synthesis of sodium ionomers derived from styrene-4-hydroxystyrene[47] and styrene-4-hydroxymethylstyrene[48] copolymers was also reported. In the first case, free phenol functionalities were obtained in the low temperature demethylation of a styrene-4-methoxystyrene copolymer with boron tribromide. The hydroxymethyl derivatives involved chloromethylation of polystyrene, followed by esterification with potassium acetate, and saponification of the ester. The sodium salts of both systems were generated in the titration of the alcohols with a sodium naphthalenide solution.

1.2.4. Polytetrafluoroethylene and other membrane materials

Because of their high thermal and chemical stability, as well as their permselectivity, a number of perfluorinated ionomers have found commercial use as membrane materials for applications in strongly oxidizing environments such as those found in the chlor-alkali electrolytic process and in fuel cells. There are currently a few types of materials commercially available, which are essentially copolymers of tetrafluoroethylene and perfluorovinyl ether compounds with a side chain of variable length terminated by sulfonate or carboxylate groups. Examples of the different products are shown in Figure 1.1. They can be differentiated, among others, by the structure of the ionic units. Some of the materials are available both as sulfonated and carboxylated derivatives. Another type of perfluorinated ionomer, not shown in Figure 1.1, is a mixed material containing both carboxylate and sulfonate pendant groups, and commercialized under the trade name Neosepta-F[49].

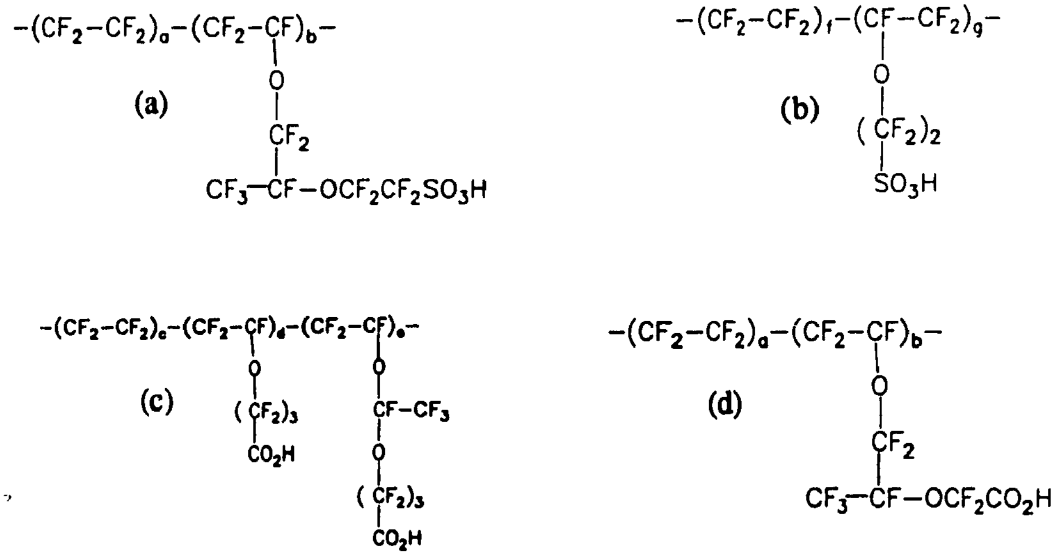


Figure 1.1. Examples of some commonly available perfluorinated membrane materials: (a) a sulfonated Nafion[50], (b) Dow Chemical product[51], (c) a carboxylated Flemion[52], (d) Asahi Chemical product[53].

The sulfonated Nafions are obtained by the copolymerization of tetrafluoroethylene with unsaturated sulfonyl chloride precursors, which yield the ionomers upon hydrolysis with a base. The Asahi Chemical materials are derived from the Nafions by oxidative clipping of the terminal sulfonate groups[53]. The synthesis of the perfluorinated materials is rather involved, and relies on techniques more relevant to industry than to the chemical laboratory.

Other membrane materials developed for electrolytic processes were based on carboxylated phenylated polyphenylene copolymers[54].

1.2.5. Poly(acrylates) and poly(methacrylates)

A number of acrylate-metal acrylate and methacrylate-metal methacrylate ionomers have been prepared by partial hydrolysis of the homopolymers with a base under reflux conditions. Among the materials prepared via base hydrolysis are poly(ethyl acrylate-co-metal acrylate)[55], poly(methyl methacrylate-co-metal methacrylate)[56] and poly(n-butyl methacrylate-metal methacrylate)[57]. Alternatively, the acid form of the polymers was obtained in the solution polymerization of methacrylic or acrylic acid with ethyl acrylate[58], n-butyl acrylate[41] or isopropyl acrylate[59]. Copolymers of 4-vinylpyridine and 2-methyl-5-vinylpyridine with ethyl acrylate and n-butyl acrylate were also studied[60].

1.2.6. Poly(alkylene oxides)

Ionomers derived from copolymers of trioxane and epichlorohydrin were synthesized by Wissbrun[61]. Reaction of the epichlorohydrin copolymer with an excess of disodium thioglycolate yielded the corresponding carboxylated ionomer. The preparation of analogous families of ionomeric polymers based on alkylene oxide backbones was described by Vogl and coworkers in a series of papers[62-67]. These included, among others, copolymers of trioxane with ethyl glycidate[62], terpolymers of these two monomers with 1,3-dioxolane[63], and homopolymers of methyl ω-epoxyalkanoates of variable spacer length, as well as copolymers with some cyclic ethers[64-67]. Unfortunately, very few of the polymers prepared were studied as ionomers.

1.2.7. Other polymers

Apart from the alkylene oxide materials mentioned above, a number of aromatic ionomers with ether linkages in the backbone have been prepared, either as sulfonated or carboxylated derivatives. Sulfonated polysulfones were obtained by the action of a sulfur trioxide-triethyl phosphate complex on a solution of the homopolymer in 1,2-dichloroethane[68]. Sulfonation of the poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene) homopolymer, more commonly referred to as poly(aryl-ether-ether-ketone) or PEEK, was also described[69] using sulfuric acid as the sulfonating agent. Poly(2,5-dimethylphenylene oxide) (PPO) was sulfonated with chlorosulfonic acid[70], but also carboxylated via a metalation-carbon dioxide reaction procedure[71]. Ionomers based on condensation polymers, aside from those derived from polyurethanes, have received less attention than vinyl polymers. This is due in part to their greater susceptibility to side reactions, such as hydrolysis, during functionalization procedures. Polyethylene terephthalate ionomer precursors were thus prepared by the irradiation grafting of acrylic acid on films of the polymer[72]. Aromatic polyamides containing sulfonate moieties were obtained in the condensation polymerization of 1,4-bis(trichloromethyl)benzene with p-phenylenediamine sulfate in sulfur trioxide[73].

1.3. Ion aggregation phenomena

It was briefly mentioned earlier that ionic groups introduced in a low polarity organic polymer matrix tend to aggregate. This aggregation is responsible for the sometimes drastic changes observed in the physical properties of ionomers. One example of such an effect is the increase in melt viscosity at 220 °C by about 100 times, obtained by the incorporation of 2 mole% of sodium carboxylate units in polystyrene[46].

It is a well-known fact that ions tend to aggregate in solvents of low to medium polarity[74]. The attachment of these ionic groups to a polymer backbone, however, should intuitively make the situation somewhat more complex, since the extent of ionic aggregation is necessarily more limited because of spatial and steric restrictions. The first theoretical treatment of ion aggregation in ionomers is due to Eisenberg[75]. According to this mathematical model, contact ion pairs are expected to associate into small aggregates (of up to 8 ion pairs), termed multiplets. The association is spontaneous because the energy released upon association to form the multiplets is much larger than the work done in stretching the polymer chains. Because of the exclusion of organic material from these aggregates, multiplets are coated with nonionic backbone material, which forms an insulating layer at their surface. Weaker dipole-dipole interactions can cause the multiplets to further associate into cluster superstructures. The energy released in this process is, however, less considerable and comparable in magnitude to the work done in stretching the polymer chains to form them. It was therefore postulated that there exists a critical temperature T_c at which the thermal energy counterbalances the association energy and the clusters fall apart.

Even though the mathematical model presented by Eisenberg was conceptually simple, it formed the basis for further mathematical refinements suggested subsequently. These are summarized in a recent review by Mauritz[76].

1.4. Experimental evidence for ion aggregation

A number of experimental techniques have been used to obtain direct or indirect hints on the morphology of ionomers. The main results of the different techniques are generally in good agreement, and point to the presence of two distinct phases, attributed to the ion-poor matrix containing some multiplets, and to the ion-rich cluster structures, respectively.

1.4.1. Scattering techniques

Two scattering techniques, namely small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) have supplied direct evidence of the composite nature of ionomers. The SAXS technique, in particular, has been used extensively in developing the different models suggested for the morphology of the cluster superstructures.

Small-angle X-ray scattering is sensitive to electron density differences, which make it a most useful tool to characterize the state of aggregation of counterions in ionomers. Even though significantly better results were obtained for the heavier metals (Rb, Cs), the lighter metals have also been used, as for example lithium salts of poly(ethylene-co-methacrylic acid)[77]. Some of the ionomers studied by this technique were based on copolymers of ethylene[77-81], butadiene[79,82] or styrene[83] with methacrylic acid, sulfonated polystyrene[84-86], and perfluorinated[87-89] ionomers. The appearance of a low-angle peak ($2\theta < 10°$), absent in the nonionized materials, was observed in the salt form of the various ionomers, sometimes above a certain minimum ion concentration which depended on the polymer. The low-angle scattering peak has been detected independently of the type of counterion, although it did influence the magnitude and position of the peak[77]. The ion-related peak was also found to be enhanced in intensity by low levels of humidity, but was destroyed by saturation with water[77,79,86]. This last effect was attributed to the destruction of the outer layer of the cluster structures by solvation of the ions (see below). The ionic peak was also found to be quite insensitive to temperature, persisting beyond 300 °C for a poly(ethylene-co-methacrylic acid) ionomer[78]. Since the interpretation of SAXS is strongly model dependent, the low-angle peak, although unquestionably attributed to the cluster structures, has been viewed as originating from two distinct possible features of these aggregates. Two of the models commonly used to explain SAXS data are the core-shell model, suggested by MacKnight et al.[77] [Figure 1.2(a)], and the hard-sphere model suggested by Yarusso and Cooper[85] [Figure 1.2(b)]. In the first case, the low-angle peak is due to intraparticle scattering, the angle position being characteristic of Bragg spacings of the order of 1-3 nm, assigned to the core-shell spacing[77]. Specific examples of Bragg spacings reported are 2-3.5 nm for polyethylene-based ionomers[77-79], and 5-6 nm in styrene-sodium methacrylate ionomers[83].

A study by Roche et al.[81] on scattering from ionomer samples subjected to deformation (stretching) has prompted the suggestion of a model with a lamellar structure [Figure 1.2(c)]. The lamellar aggregates are constituted of a double layer of amorphous material (presumably the organic polymer backbone) sandwiched between three layers of ionic material. This model was found to be best suited to explain the angular variations observed in the scattered intensity from stretched ionomer samples. This was not the case for the core-shell model, which failed in that instance.

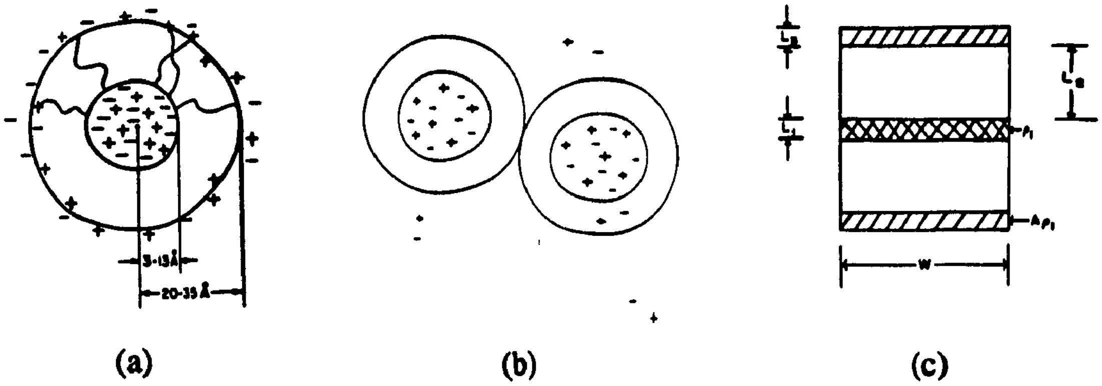


Figure 1.2. Comparison of the core-shell (a), the hard-sphere (b), and the lamellar (c) models for clusters from small-angle scattering experiments.

The interparticle interference model suggested by Yarusso and Cooper[85] has led to cluster dimensions of the order of 2 nm in diameter. This particular model has allowed the quantitative modeling of scattering data of ionomers, although it has been argued[77,90] that some of the properties of the ionic scattering peak generally favor the core-shell model.

The small-angle neutron scattering (SANS) technique[91-94] has played a complementary role in morphology studies, in that it is associated with the type of nuclei causing the scattering, rather than simply with electron density differences[94]. The results thus obtained give structural dimensions in good agreement with the SAXS method.

1.4.2. Spectroscopic techniques

Of the wealth of spectroscopic techniques available, many have provided useful information related to the extent of ion aggregation and to the microstructure of the different ionic aggregates. These include the Raman[95-98], infrared (IR)[99-105], Mössbauer[91,106,107], fluorescence[108,109], nuclear magnetic resonance (NMR)[110], electron spin resonance (ESR)[111,112], and extended X-ray absorption fine structure (EXAFS)[107,113,114] techniques. Of these, only the first three will be reviewed here.

Raman spectroscopy of ionomers has provided quantitative information about the relative distribution of ions into the multiplet and cluster domains, respectively, because the intensity of Raman absorption bands are known to be proportional to the concentration of species causing the absorption[115]. The appearance of two new bands was observed at ca. 250 and 160 cm^{-1} (40 and 62.5 μm) in the sodium salts of copolymers of styrene with methacrylic acid[95] or p-carboxystyrene[97], as well as for poly(ethyl acrylate-co-sodium acrylate)[96]. From mass considerations, the upper and lower frequency bands were attributed to multiplet and cluster structures, respectively. The information obtained on the relative distribution of ions in multiplets and clusters suggested the existence of a "solubility limit" for multiplets in the matrix of the order of

1-2 mole% in the styrene-sodium methacrylate and styrene-sodium p-carboxylate systems. The ethyl acrylate-sodium acrylate ionomers exhibited a significantly higher multiplet solubility limit (ca. 10 mole%), but also the existence of a cluster solubility saturation at around 30-35 mole% ions. It was suggested[96] that the difference in the dielectric constants of the two materials (polystyrene: $\varepsilon = 2.5$, poly(ethyl acrylate): $\varepsilon = 4.0$) may have caused the different responses, due to the presumably greater ion solvating ability of polyacrylates compared to polystyrene. The intensity of the multiplet- and cluster-related bands of the sodium methacrylate and sodium acrylate derivatives was also found to vary with temperature; the intensity of the 250 cm^{-1} (40 μm) (multiplet) band increased at the expense of the 160 cm^{-1} (62.5 μm) (cluster) band with increasing temperature, the total intensity of the two bands remaining constant.

The interpretation of the results of a Raman study on ethylene-methacrylate ionomers[98] was more ambiguous since the variations in the three absorption bands observed could also have been attributed to the lamellar structure and conformational defects of the polyethylene backbone.

Infrared spectroscopy has also shown the appearance of absorption bands which are not present in the nonionic materials, and correspond to differing environments believed to be multiplet and cluster structures. Far IR[99-101] was more useful in this respect than near IR[102-105] spectroscopy, because of severe overlapping problems with the bands of interest in the latter case. In particular, it has been pointed out[105] that near IR may be unsuitable to differentiate between multiplet and cluster aggregates, because some of the effects observed could also be attributed to the absorption of water by the samples.

Mössbauer spectroscopy was used together with magnetization experiments on ^{57}Fe-containing ionomers, to probe the structure of ionic aggregates in some ionomers[91,106,107]. The polymers studied in this way include a butadiene-styrene-vinylpyridine terpolymer complexed with Fe^{3+} ions[91], and perfluorinated polymers[106,107]. The existence of three distinct types of iron species was thus determined in the first case. A large proportion of the metal (40-60%) detected in the butadiene terpolymer was contained in large aggregates, of the order of 3 nm in radius. Of the remaining iron, approximately equal proportions were present as dimers, the rest being in what could be either somewhat larger aggregates, or else located in proximity to larger aggregates[91].

1.4.3. Mechanical properties measurements

Of the different mechanical characterization techniques available, dynamic mechanical and stress relaxation measurements, and melt rheology have been used most extensively to examine ion aggregation effects in ionomers.

Dynamic mechanical measurements, in particular, yield very characteristic results for carboxylated and sulfonated ionomers. Considering the large volume of literature dealing with the dynamic mechanical properties of ionomers, only a couple of specific examples will be given here, namely for ionomers based on styrene-methacrylic acid copolymers[83] and on sulfonated polystyrene[116]. As the concentration of pendant ionic groups is increased, a few distinctive features appear in plots of the storage modulus (G' or E') or loss tangent (tan δ) versus temperature. An approximately linear increase in the matrix glass transition temperature (T_g) is noticeable, its rate of increase with the ion content of the materials (dT_g/dC) ranging from 2 to 10 °C/mole%[117]. This phenomenon has been attributed to a decrease in segmental mobility of the polymer backbone, due to aggregation of the ions[1]. The appearance of a second rubbery plateau in the storage modulus curve can be observed, its magnitude and position being shifted to higher values with increasing ion contents; the width of the primary transition region also broadens at the same time. The presence of a second loss maximum in the loss tangent-temperature curve is also noticeable, the amplitude of the low-temperature peak decreasing in favor of the high-temperature loss maximum. The low-temperature peak was attributed[83] to the ion-poor matrix containing dispersed multiplets acting as thermolabile cross-links. The high-temperature peak, however, was linked to the presence of the larger, ion-rich cluster structures acting as filler particles, providing strong reinforcement above the matrix T_g of the material.

Aggregation phenomena in ionomers also manifest themselves in stress relaxation experiments. As in the case of dynamic mechanical measurements, the appearance of an extended rubbery plateau associated with ion aggregation has been reported in styrene-sodium methacrylate[40] and ethyl acrylate-sodium acrylate[118] ionomers. An additional feature is of interest, however, namely the occurrence of a breakdown of the time-temperature superposition principle[119] above a certain ion concentration. This phenomenon was observed at ion contents above 6 mole% in styrene-methacrylic acid ionomers, and between 12 and 14% in the acrylate system, and was attributed to the presence of a second relaxation mechanism, related to clustering.

It should be noted that the observations given above for dynamic mechanical and stress relaxation experiments of ionomers provide strong support, as in the previous cases, to the concept of a phase-separated morphology, as would be the case for mixed systems like incompatible blends, block copolymers or filled polymers.

Melt rheology studies of ionomers[31,46,120,121] point to the persistent nature of ionic aggregation in these materials. It was mentioned earlier that the introduction of a minor fraction (ca. 2 mole%) of sodium carboxylate groups raised the constant shear viscosity of styrene by a factor of about 100 times at 220 °C. The effect was even more dramatic for the sulfonated analogue with an increase in viscosity by a factor of about 100 000 times[46].

1.4.4. Other techniques

Dielectric measurements of ionomers based on polyethylene[122,123], polystyrene[124,125] and polypentenamers[126] have provided results analogous to the dynamic mechanical methods. Dielectric relaxation maxima were detected at temperatures comparable to those found in the dynamic mechanical analysis, and were attributed to the same effects, namely matrix- and cluster-related transitions[124]. One disadvantage of the dielectric technique is that the high temperature dc conductivity of ionomers tends to be rather large. It was nevertheless possible, after subtraction of the dc component, to establish quantitative relations for the distribution of ions in the styrene-sodium methacrylate system[124]. The total area under the two dielectric relaxation peaks of a loss tangent vs. 1/T plot was found to be proportional to the ion content of the samples (correlation coefficient of 0.976). The area under the low temperature (matrix-related) peak initially increased with ion content, to become approximately constant around 5 mole% ions. The area under the high temperature (cluster-related) peak, on the contrary, started increasing very rapidly at ion concentrations above 5 mole%. The results were interpreted as corresponding to the predominant formation of cluster structures at the higher ion contents (above approximately 5 mole%), in good agreement with the clustering effects observed in the dynamic mechanical and stress relaxation techniques.

Finally, electron microscopy has also provided results in support of a phase-separated model for aggregation in ionomers. Some of the materials studied were based on polyethylene[127,128] and butadiene[14,129]. Micrographs of the ionized samples revealed a grainy structure, not observed in the nonionic materials. Ionic domain sizes varying from 10 to 80 nm were reported in the majority of the studies. It seems that the results obtained by electron microscopy should, however, be considered with much caution, since it was shown[130] that many artifacts can arise from sample preparation methods.

1.5. Structure-properties relations in ionomers

It was shown in the previous section that many techniques have been successfully applied to obtain information about the presence of ionic aggregates in ionomers and, in some cases, about the morphology of those aggregates. The experimental results summarized above are representative of a large number of ionomeric systems. However, the extent to which these phenomena may be observable varies significantly from system to system, leading to the concept of structure-properties relations. Some structural changes may result in rather subtle changes in the physical properties of these materials, but can also cause more dramatic and unexpected effects.

One obvious example of a molecular parameter variation which was already mentioned is the ion content of the samples. It was shown that, in many cases, the behavior of ionomers became dominated by the presence of the larger (cluster) aggregates above a certain ion concentration. It was also pointed out that this "critical" ion content for cluster-dominated behavior varied with the material investigated. This illustrates one of the problems encountered in structure-properties relations investigations. Different materials may often display clearly distinct properties, but can hardly be compared directly, because their structure is very different. In order to obtain meaningful results from structure-properties relations studies, it becomes necessary to compare systems which are as closely related as possible, so that strictly a single parameter is varied at a time. This approach will be stressed in the present work, as will be shown later.

The systematic variation of some structural parameters of interest has been reported in the literature of ionomers. One example is the variation of the type of counterion used[58,77,131-133]. Different alkali and alkaline earth metal counterions yielded only minor variations, at equal ion concentration, in the ion-related rubberlike modulus detected in stress relaxation or dynamic mechanical experiments of ethyl acrylate[58] or EPDM[133] ionomers. The variation in the matrix T_g could, however, be related to the concentration (c), charge (q) and size (a) of the ions: a plot of T_g vs. cq/a could be represented by a single sigmoidal curve for the ethyl acrylate ionomers[58]. The effect of the degree of neutralization (as opposed to the variation of the ion content of the samples) was also explored[125,134]. Dielectric measurements on poly(styrene-co-sodium methacrylate)[125] showed that the solvation of sodium ions in the partially neutralized salts was more important than in the completely neutralized system, owing to the free carboxylic acid units (multiplet solubility limits of ca. 6 and 2 mole% ions, respectively).

More spectacular effects were observed when different types of plasticizers[135,136] were added to ionomers. Dioctyl phthalate, when added (40 wt%) as a backbone plasticizer in a sulfonated styrene ionomer (1.78 mole% ions), caused a decrease in the melt viscosity at 220 °C from 3.2×10^8 poise (3.2×10^7 $kg{\cdot}m^{-1}{\cdot}s^{-1}$) to about 4×10^5 poise (4×10^4 $kg{\cdot}m^{-1}{\cdot}s^{-1}$). In contrast, the same result could be achieved with only 3.5 wt% of glycerol[135].

One last example of the effects of a parameter variation which is not directly related to this work concerns the type of pendant ionic group used. It was mentioned earlier that the melt viscosity of sodium ionomers (2 mole% ions) of polystyrene is about 1000 times smaller for the p-carboxylate than for the p-sulfonate derivative[46]. The glass transition temperatures associated with the cluster structures, as determined by dynamic mechanical measurements, were also higher for the sulfonated[116] than the carboxylated[137] derivatives, suggesting once more that the ionic interactions are stronger in the first case. More importantly, analogous styrene ionomers in which the backbone bore positively charged groups in the form of N-methyl-4-vinylpyridinium iodide units[44] did not show the characteristics of clustered systems when studied by dynamic mechanical techniques.

1.6. Aims of the present work

Some of the parameters affecting ion aggregation in ionomers have been presented. The trends observed in these studies were generally relatively clear-cut, and could be directly related to the parameter of interest. This is not always the case, however, since as was mentioned, it is often difficult to vary strictly one parameter at a time. One example of such a problem is illustrated in relating the clustering behaviors of ethylene, styrene, and acrylate-based ionomers on the basis of their dielectric constants[2]. The decrease in clustering tendencies along the series polyethylene > polystyrene > polyacrylates was linked to the increase in the dielectric constant of those materials in the same order. This was presumably due to the greater ion solvating ability of the more polar compounds. There are, however, a number of problems involved in comparing the different ionomers directly. The structural units involved in each case are very different and possess very distinct characteristics:

1) Polyethylene ionomers ($\varepsilon \approx 2.3$) are partly crystalline. The T_g of the homopolymer, however, is very low (-120 °C)[138].

2) The polystyrene ionomers ($\varepsilon \approx 2.5$) studied are atactic, and therefore noncrystalline materials. The homopolymer can be distinguished from polyethylene by the presence of a bulky benzene ring and a much higher T_g (100 °C)[138].

3) The polyacrylates (typically ethyl acrylate, $\varepsilon \approx 4$), apart from their significantly higher polarity, have a relatively low T_g (PEA: -22 °C)[138], and are also amorphous materials.

It seems from the information given above that a comparison of the three ionomer systems, even though appropriate on a first approximation level, needs further refinement.

Also adding to the confusion concerning the respective effects of matrix glass transition temperature and the polarity of the parent polymers are a series of related studies: It was found that although poly(styrene-co-N-methyl-4-vinylpyridinium iodide) did not display characteristics of clustered systems[44], the same pyridinium units, when incorporated in a low T_g, but also more polar polymer [poly(n-butyl acrylate), $T_g = -56$ °C[138]], a second, cluster-related loss tangent peak appeared in the dynamic mechanical analysis[60]. Furthermore, this effect could be induced in the nonclustered poly(ethyl acrylate-co-N-methyl-4-vinylpyridinium iodide) ionomers by adding dimethyl malonate as an external plasticizer[60]. These studies, even though suggesting that the matrix T_g of the material may play an important role in determining the aggregation behavior of ionomers, left the question of the importance of the matrix polarity unanswered.

The problems of evaluating the relative importance of matrix T_g and polarity effects on the aggregation behavior of ionomers will be addressed in Chapters 2 and 3 of the present work. In the first case, the effects of decreasing the matrix T_g of a styrene-sodium methacrylate ionomer on aggregation will be examined. In contrast to a previous study[136], however, the T_g decrease is achieved, in this case, via internal plasticization rather than through added diluents. A reaction was developed to graft 1-decene on the styrene rings, to examine the effects of the plasticizer in the 0-100% substitution range. In this case, as in the subsequent studies, dynamic mechanical analysis was selected as a sensitive technique to detect clustering effects in the ionomers. Chapter 3 deals with the investigation of the effects of the systematic variation of the matrix polarity of the same styrene-methacrylic acid polymer. This variation was achieved by the controlled nitration of the pendant styrene rings. Nitration levels varying from 0 to 30 mole% were used for this study, and resulted in a relaxed dielectric constant which was comparable, at the higher degree of substitution, to those found in the polyacrylates.

Another problem which was examined to some extent in a previous study[137] is the effects of the position of the pendant ionic groups on aggregation. In this case, the dynamic mechanical properties of styrene ionomers containing sodium p-carboxylate units were compared to those observed for ionomers of sodium methacrylate. This problem is addressed again in Chapters 4 and 5 of this work, but in a much more systematic manner.

Styrene ionomers were prepared containing ω-carboxylated alkyl chains in the para- position of the styrene rings. Two distinct families of derivatives were thus prepared, and could be distinguished by the mode of attachment of the alkyl chain to the ring. In the first case ("alkyl" derivatives), the alkyl chain was attached directly to the ring. Ionomer precursors containing ca. 10 mole% of methyl esters with spacer lengths of 2, 6, and 11 carbon atoms from the styrene rings were prepared. In the second family ("ether" derivatives), the alkyl chain was attached to the ring through an alkyl aryl ether linkage, rather than directly as in the first case. Analogous derivatives with ca. 15 mole% of alkyl units and spacer lengths of 2, 5 and 11 carbon atoms were also synthesized. The synthesis of these two families of compounds is described in Chapter 4. The results of the systematic study, using dynamic mechanical techniques, are reported in Chapter 5.

1.7. References

(1) *Ionic Polymers*; Holliday, L., Ed.; Applied Science: London, 1973.

(2) Eisenberg, A.; King, M. *Ion-Containing Polymers*; Academic: New York, 1977.

(3) Longworth, R. In *Developments in ionic polymers, Vol. 2*; Wilson, A.D.; Prosser, H.J., Eds.; Elsevier: New York, 1983.

(4) MacKnight, W.J.; Earnest, T.R., Jr. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.

(5) Bazuin, C.G.; Eisenberg, A. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 271.

(6) Fitzgerald, J.J.; Weiss, R.A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 99.

(7) Rees, R.W.; Vaughan, D.J. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1965**, *6(1)*, 287.

(8) Hycar is a registered trade mark of the B.F. Goodrich Co.

(9) Brown, H.P. *Rubber Chem. Technol.* **1957**, *30*, 1347.

(10) Brown, H.P.; Duke, N.G. *Rubber world* **1954**, 784.

(11) Surlyn is a registered trade mark of the E.I. duPont de Nemours Co.

(12) Jenkins, D.K.; Duck. E.W. In Reference 1, Chapter 3.

(13) Cooper, W. *J. Polym. Sci.* **1958**, *28*, 195.

(14) Pineri, M.; Meyer, C.; Bourret, A. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1881.

(15) Meyer, C.T.; Pineri, M. *Polymer* **1976**, *17*, 382.

(16) Weiss, R.A.; Lundberg, R.D.; Werner, A. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3427.

(17) Siadat, B.; Oster, B.; Lenz, R.W. *J. Appl. Polym. Sci.* **1981**, *26*, 1027.

(18) Siadat, B.; Lenz, R.W. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3273.

(19) Cunneen, J.I.; Moore, C.G.; Shephard, B.R. *J. Appl. Polym. Sci.* **1960**, *3*, 11.

(20) Zhou, Z.-L.; Eisenberg, A. *J. Appl. Polym. Sci.* **1982**, *27*, 657.

(21) Amass, A.J.; Duck, E.W.; Hawkins, J.R.; Locke, J.M. *Eur. Polym. J.* **1972**, *8*, 781.

(22) Makowski, H.S.; Lundberg, R.D.; Westerman, L.; Bock, J. In *Ions in polymers*; Eisenberg, A., Ed.; Advances in Chemistry 187; American Chemical Society: Washington, DC, 1980; pp 3-19.

(23) Sanui, K.; Lenz, R.W.; MacKnight, W.J. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1965.

(24) Azuma, C.; MacKnight, W.J. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 547.

(25) Tanaka, H.; MacKnight, W.J. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2975.

(26) Rahrig, D.; MacKnight, W.J.; Lenz, R.W. *Macromolecules* **1979**, *12*, 195.

(27) MacKnight, W.J.; McKenna, L.W.; Read, B.E. *J. Appl. Phys.* **1967**, *38*, 4208.

(28) Landoll, L.M.; Breslow, D.S. *Polym. Prepr.* **1987**, *28(1)*, 256.

(29) Purgett, M.D.; Vogl, O. *J. Macromol. Sci., Chem.* **1987**, *A24*, 1465.

(30) Szentirmay, M.N.; Prieto, N.E.; Martin, C.E. *Talanta* **1985**, *32*, 745.

(31) Weiss, R.A.; Agarwal, P.K. *J. Appl. Polym. Sci.* **1981**, *26*, 449.

(32) Crugnola, A.; Pegoraro, M.; Severini, F. *J. Polym. Sci., Pt. C* **1972**, *16*, 4547.

(33) Phillips, P.J.; MacKnight, W.J. *J. Polym. Sci., Polym. Lett. Ed.* **1970**, *8*, 87.

(34) Leonard, E.C., Jr.; Loeb, W.E.; Mason, J.H.; Wheelwright, W.L. *J. Appl. Polym. Sci.* **1961**, *5*, 157.

(35) Makowski, H.S.; Lundberg, R.D.; Singhal, G.H. U.S. Patent 3 870 841 (1975).

(36) Turbak, A.F. *Ind. Eng. Chem. Prod. Res. Dev.* **1962**, *1*, 275.

(37) Thaler, W.A. *Macromolecules* **1983**, *16*, 623.

(38) Weiss, R.A.; Turner, S.R.; Lundberg, R.D. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 525.

(39) Weiss, R.A.; Lundberg, R.D.; Turner, S.R. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 549.

(40) Eisenberg, A.; Navratil, M. *Macromolecules* **1973**, *6*, 604.

(41) Vollmert, B.; Schoene, W. *Angew. Makromol. Chem.* **1971**, *19*, 157.

(42) Wojtczak, Z.; Gronowski, A. *Makromol. Chem.* **1985**, *186*, 139.

(43) Williams, M.W. *J. Polym. Sci., Polym. Symp. Ed.* **1974**, *45*, 129.

(44) Gauthier, S.; Duchesne, D.; Eisenberg, A. *Macromolecules* **1987**, *20*, 753.

(45) Brockman, N.L.; Eisenberg, A. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 3563.

(46) Lundberg, R.D.; Makowski, H.S. In *Ions in polymers*; Eisenberg, A., Ed.; Advances in Chemistry 187; American Chemical Society: Washington, DC, 1980; pp 21-36.

(47) Clas, S.-D.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 2743.

(48) Clas, S.-D.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 2757.

(49) Neosepta-F is a registered trade mark of the Tokuyama Soda Co.

(50) Nafion is a registered trade mark of E.I. du Pont de Nemours Co.

(51) Eisman, G.A. *Proc. Electrochem. Soc.* **1986**, *86-13*, 156.

(52) Flemion is a registered trade mark of Asahi Glass Co.

(53) *Perfluorinated ionomer membranes*; Eisenberg, A.; Yeager, H.L., Eds.; ACS Symposium Series 180; American Chemical Society: Washington, D.C., 1982.

(54) Eisenberg, A.; Besso, E.; Harris, F.W.; Gupta, R.K.; Yeager, H.L.; Steck, A. *Contemp. Top. Polym. Sci.* **1984**, *5*, 375.

(55) Simmons, A.; Natansohn, A.; Eisenberg, A. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 2221.

(56) Kihira, Y. *J. Sci. Hiroshima Univ., Ser. A* **1976**, *40*, 285.

(57) Aras, L.; Vanderschueren, J.; Niezette, J.; Vanderschueren, R. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 799.

(58) Matsuura, H.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1201.

(59) Kihira, Y.; Yamamura, H.; Murakami, I. *J. Macromol. Sci., Phys.* **1987**, *B26*, 201.

(60) Duchesne, D. Ph.D. thesis, McGill University: Montreal, May 1985.

(61) Wissbrun, K.F. *Makromol. Chem.* **1968**, *118*, 211.

(62) DeMejo, L.; MacKnight, W.J.; Vogl, O. *Polymer* **1978**, *19*, 956.

(63) DeMejo, L.; MacKnight, W.J.; Vogl, O. *Polym. J.* **1979**, *11*, 15.

(64) Vogl, O.; Muggee, J.; Bansleben, D. *Polym. J.* **1980**, *12*, 677.

(65) Muggee, J.; Vogl, O. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 2327.

(66) Muggee, J.; Vogl, O. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 649.

(67) Bansleben, D.A.; Janovic, Z.; Vogl, O. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3263.

(68) Noshay, A.; Robeson, L.M. *J. Appl. Polym. Sci.* **1976**, *20*, 1885.

(69) Bailly, C.; Williams, D.J.; Karasz, F.E.; MacKnight, W.J. *Polymer* **1987**, *28*, 1009.

(70) Huang, R.Y.M.; Kim, J.J. *J. Appl. Polym. Sci.* **1984**, *29*, 4017.

(71) Huang, Y.; Cong, G.; MacKnight, W.J. *Macromolecules* **1986**, *19*, 2267.

(72) Huglin, M.B.; Zlatev, V.B. *Eur. Polym. J.* 1974, 10, 199.

(73) Silver, S.M. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1787.

(74) Pettit, L.D.; Bruckenstein, S. *J. Am. Chem. Soc.* **1966**, *88*, 4783.

(75) Eisenberg, A. *Macromolecules* **1970**, *3*, 147.

(76) Mauritz, K. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 65.

(77) MacKnight, W.J.; Taggart, W.P.; Stein, R.S. *J. Polym. Sci., Polym. Symp. Ed.* **1974**, *45*, 113.

(78) Wilson, F.C.; Longworth, R.; Vaughan, D.J. *Polym. Prepr.* **1968**, *9(1)*, 505.

(79) Marx, C.L.; Caulfield, D.F.; Cooper, S.L. *Macromolecules* **1973**, *6*, 344.

(80) Kao, J.; Stein, R.S.; MacKnight, W.J.; Taggart, W.P.; Cargill, G.S., III *Macromolecules* **1974**, *7*, 95.

(81) Roche, E.J.; Stein, R.S.; Russell, T.P.; MacKnight, W.J. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1497.

(82) Pineri, M.; Meyer, C.; Levelut, A.M.; Lambert, M. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 115.

(83) Eisenberg, A.; Navratil, M. *Macromolecules* **1974**, *7*, 90.

(84) Peiffer, D.G.; Weiss. R.A.; Lundberg, R.D. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1503.

(85) Yarusso, D.J.; Cooper, S.L. *Macromolecules* **1983**, *16*, 1871.

(86) Yarusso, D.J.; Cooper, S.L. *Polymer* **1985**, *26*, 371.

(87) Gierke, T.D.; Munn, G.E.; Wilson, F.C. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1687.

(88) Fujimura, M.; Hashimoto, T.; Kawai, H. *Macromolecules* **1982**, *15*, 136.

(89) Kumar, S.; Pineri, M. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1767.

(90) Longworth, R. In Reference 1, Chapter 2.

(91) Meyer, C.T.; Pineri, M. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 569.

(92) Roche, E.J.; Stein, R.S.; MacKnight, W.J. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1035.

(93) Earnest, T.R., Jr.; Higgins, J.S.; Handlin, D.L.; MacKnight, W.J. *Macromolecules* **1981**, *14*, 192.

(94) Pineri, M.; Duplessix, R.; Volino, F. In Reference 53, Chapter 12.

(95) Neppel, A.; Butler, I.S.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 2145.

(96) Neppel, A.; Butler, I.S.; Eisenberg, A. *Macromolecules* **1979**, *12*, 948.

(97) Neppel, A.; Butler, I.S.; Brockman, N.; Eisenberg, A. *J. Macromol. Sci., Phys.* **1981**, *B19*, 61.

(98) Tsujita, Y.; Hsu, S.L.; MacKnight, W.J. *Macromolecules* **1981**, *14*, 1824.

(99) Rouse, G.B.; Risen, W.M., Jr.; Tsatsas, A.T.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 81.

(100) Peiffer, D.G.; Hager, B.L.; Weiss, R.A.; Agarwal, P.K.; Lundberg, R.D. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1869.

(101) Suchocka-Galas, K. *Eur. Polym. J.* **1987**, *23*, 951.

(102) Earnest, T.R., Jr.; MacKnight, W.J. *Macromolecules* **1980**, *13*, 844.

(103) Lowry, S.R.; Mauritz, K.A. *J. Am. Chem. Soc.* **1980**, *102*, 4665.

(104) Painter, P.C.; Brozoski, B.A.; Coleman, M.M. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1069.

(105) Brozoski, B.A.; Painter, P.C.; Coleman, M.M. *Macromolecules* **1984**, *17*, 1591.

(106) Rodmack, B.; Coey, J.M.D.; Pineri, M. In Reference 53, Chapter 9.

(107) Pan, H.K.; Yarusso, D.J.; Knapp, G.S.; Pineri, M.; Meagher, A.; Coey, J.M.D.; Cooper, S.L. *J. Chem. Phys.* **1983**, *79*, 4736.

(108) Okamoto, Y.; Ueba, Y.; Dzhanibekov, N.F.; Banks, E. *Macromolecules* **1981**, *14*, 17.

(109) Szentirmay, M.N.; Prieto, N.E.; Martin, C.R. *J. Phys. Chem.* **1985**, *89*, 3017.

(110) Komoroski, R.A.; Mauritz, K.A. In Reference 53, Chapter 7.

(111) Vasquez, R.; Avalos, J.; Volino, F.; Pineri, M.; Galland, D. *J. Appl. Polym. Sci.* **1983**, *28*, 1093.

(112) Toriumi, H.; Weiss, R.A.; Frank, H.A. *Macromolecules* **1984**, *17*, 2104.

(113) Pan, H.K.; Yarusso, D.J.; Knapp, G.S.; Cooper, S.L. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1389.

(114) Yarusso, D.J.; Ding, Y.S.; Pan, H.K.; Cooper, S.L. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 2073.

(115) Otting, W. *Der Raman-Effekt und seine analytische Anwendung*; Springer: Berlin, 1952.

(116) Rigdahl, M.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1641.

(117) Bazuin. C.G.; Eisenberg, A. *J. Chem. Ed.* **1981**, *58*, 938.

(118) Eisenberg, A.; Matsuura, H.; Tsutsui, T. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 479.

(119) Tobolsky, A.V. *Properties and structure of polymers*; Wiley: New York, 1960.

(120) Sakamoto, K.; MacKnight, W.J.; Porter, R.S. *J. Polym. Sci., Pt. A-2* **1970**, *8*, 277.

(121) Shohamy, E.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1211.

(122) Phillips, P.J.; MacKnight, W.J. *J. Polym. Sci., Pt. A-2* **1970**, *8*, 727.

(123) Phillips, P.J.; Emerson, F.A.; MacKnight, W.J. *Macromolecules* **1970**, *3*, 771.

(124) Hodge, I.M.; Eisenberg, A. *Macromolecules* **1978**, *11*, 283.

(125) Arai, K.; Eisenberg, A. *J. Macromol. Sci., Phys.* **1980**, *B17*, 803.

(126) Rahrig, D.; Azuma, C.; MacKnight, W.J. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 59.

(127) Davis, H.A.; Longworth, R.; Vaughan, D.J. *Polym. Prepr.* **1968**, *9(1)*, 515.

(128) Phillips, P.J. *J. Polym. Sci., Polym. Lett. Ed.* **1972**, *10*, 443.

(129) Marx, C.L.; Koutsky, J.A.; Cooper, S.L. *J. Polym. Sci., Polym. Lett. Ed.* **1971**, *9*, 167.

(130) Handlin, D.L.; MacKnight, W.J.; Thomas, E.L. *Macromolecules* **1981**, *14*, 795.

(131) Bonotto, S.; Bonner, E.F. *Macromolecules* **1968**, *1*, 510.

(132) Navratil, M.; Eisenberg, A. *Macromolecules* **1974**, *7*, 84.

(133) Agarwal, P.K.; Makowski, H.S.; Lundberg, R.D. *Macromolecules* **1980**, *13*, 1679.

(134) MacKnight, W.J.; Kajiyama, T.; McKenna, L. *Polym. Eng. Sci.* **1968**, *8*, 267.

(135) Lundberg, R.D.; Makowski, H.S.; Westerman, L. In *Ions in polymers*; Eisenberg, A., Ed.; Advances in Chemistry 187; American Chemical Society: Washington, DC, 1980; pp 67-76.

(136) Bazuin, C.G.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1137.

(137) Brockman, N.L.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1145.

(138) Nielsen, L.E. *Mechanical properties of polymers*; Reinhold: New York, 1962.

Chapter 2. The effects of internal plasticization on ion aggregation in a styrene ionomer

2.1. Abstract

A copolymer of styrene with 7 mole% methacrylic acid was alkylated with 1-decene in a Friedel-Crafts type reaction. Both glass transition temperatures associated with the matrix and with the clusters were shifted to lower temperatures with increasing alkylation, and the modulus at the rubberlike inflection point dropped by over an order of magnitude. It was shown that ion clustering was enhanced at alkylation levels of up to ca. 20 mol%, compared with the parent ionomer. At higher degrees of alkylation, however, the alkyl chains strongly disrupted the ionic association. Even though some clustering effects were still observed in the loss tangent-temperature curves, the large drop in the rubberlike modulus showed that the influence of the clusters on the rheological properties of the polymer was not significant.

2.2. Introduction

For over two decades, the field of ion-containing polymers has been an area of growing interest. This is demonstrated by a number of books[1,2], reviews[3] and recent symposia[4] on the topic, as well as by the increasing number of ionomers available commercially, with their many current and potential applications[5]. The term ionomer was introduced in 1965 by Rees and Vaughan[6], referring to polymers containing relatively low levels of ionic groups, typically less than about 15 mole percent. The interest in these materials is justified by the sometimes drastic changes observed in the bulk properties of the polymers, as a consequence of the introduction of ions. The investigation of the microstructure of these systems, in particular, is continuing to be an area of great interest[7].

Two broad classes of ion-containing polymers may be considered: anionic and cationic, according to the sign of the charge carried by the backbone. Two of the most common anionic groups introduced in polymers are carboxylic and sulfonic acids, either as part of a copolymerization process, or through a postpolymerization reaction, followed by neutralization with a base. The cationic groups are normally generated by the quaternization of amines with alkyl halides. The modifications in the properties of anionic materials may be explained on the basis of phase separation[7,8], whereby the ions tend to aggregate to form ion-rich regions in the polymer matrix. The existence of two types of aggregates has been proposed[9]. Multiplets, made up of only a few interacting ion pairs, act as thermolabile cross-links. The larger cluster structures, containing more ion pairs, but also a significant amount of organic material from the backbone, act as strong particle reinforcers above the matrix glass transition temperature (T_g). The presence of the larger ionic aggregates leads to the appearance of a second inflection point, and possibly an additional rubbery plateau in the dynamic modulus-temperature curve of the system. The loss tangent curve also shows two maxima, of which the first has been attributed to the polymer matrix containing interspersed multiplets, while the second peak has been related to the presence of the ion-rich cluster structures. Both peaks are shifted to higher temperatures with increasing ion content, the relative amplitudes of the two maxima changing in favor of the cluster peak.

The behavior of the anionic systems is very different from that of cationic materials: previous studies on polystyrene-based N-alkyl-4-vinylpyridinium halide systems have shown no evidence of clustering[10]; however, earlier studies on polybutadiene-based cationomers do show some characteristics of clustered systems at comparable ionic concentrations[11]. Butyl acrylate and plasticized ethyl acrylate cationomers also show similar effects[12].

The differences observed in anionic systems compared with cationics of similar structure illustrate one of the many structural factors known to affect ion aggregation, namely, in this case, the type of ion used. Some of the other factors involved are the placement of the ions relative to the chain[13], the type of counterion used[14], and the degree of neutralization[15]. The polarity of the backbone, which is related to the dielectric constant of the matrix, has also been suggested as a significant parameter affecting ion aggregation[2,12]. More recent results[16] have shown, however, that polarity itself may not be as important as specific interactions in determining the clustering behavior of carboxylated ionomers. One final example of a parameter affecting ion aggregation is the matrix glass transition temperature of the polymer, sometimes related to the stiffness of the chain. Thus, some high temperature polymers do not exhibit clustering[17], while a lowering of the T_g induces cluster formation in other systems[12].

Some effects of low molecular weight diluents in ionomers, which are relevant to this study, have been explored by Bazuin and Eisenberg[18]. In this case, the effects on the mechanical behavior of two diluents, one nonpolar (diethylbenzene, DEB) and the other polar and hydrogen-bonded (glycerol) were observed in a carboxylated and in a sulfonated styrene ionomer. Diethylbenzene was found to act as a conventional nonpolar plasticizer, the Fox equation[19] being followed quite closely. Furthermore, the slope steepness of the modulus-temperature plot in the glass transition region decreased, and both the matrix and the ionic loss tangent peaks broadened and shifted to lower temperatures with increasing DEB content. The modulus of the ion-related rubberlike plateau observed in the bulk material decreased in height and was shifted down on the temperature scale, eventually to disappear at higher DEB contents.

The original aim of this work was to explore the effect of the variation of the glass transition temperature on ionic aggregation in a carboxylated polystyrene-based ionomer. In contrast to previous work, however, this T_g variation was to be accomplished via internal plasticization, in the absence of small molecules. The lowering of the T_g, combined with the low polarity of the product would, intuitively, have been expected to favour clustering. However it was found that, although some clustering enhancement was observed at low levels of substitution, high levels had a strong disruptive effect on large scale ionic aggregation. These phenomena are the subject of the present work. SAXS experiments on the alkylated materials are currently in progress and will be reported subsequently.

2.3. Experimental

A copolymer of styrene-methacrylic acid (PS-0.07MAA of molecular weight ca. 10^5 g/mol) was prepared using a bulk polymerization technique already reported[20].

The methacrylic acid content of the copolymers was determined by titration of 0.4 g samples in 90/10 v/v benzene-methanol as a solvent. The solutions were titrated to the phenolphthalein end point with methanolic 0.05 N NaOH, and a blank correction was included in the calculations.

The following alkylation procedure was developed to graft alkyl chains onto the aromatic rings of styrene. The alkylating agent, 1-decene (Aldrich), was previously purified by distillation under reduced pressure (bp. 63-64 °C/12mm Hg). All other reagents and solvents were reagent grade and used as received from the suppliers. The copolymer (5g, 45.2 mmol of styrene units) was dissolved in 125 mL of a 25/10 v/v carbon disulfide (A&C American Chemicals)/1-nitropropane (Aldrich) mixture contained in a round-bottomed flask fitted with a refluxing condenser. Decene (20 mL, 106 mmol) was added to the flask, and the solution warmed to near its boiling point. A solution of 6 g (45 mmol) of anhydrous aluminum chloride (Anachemia) in 50 mL of the carbon disulfide-nitropropane solvent was then added with vigorous stirring to the polymer solution. The condenser was fitted with a drying tube, to avoid the introduction of excessive amounts of moisture into the system. The reaction mixture was refluxed for variable amounts of time, to produce degrees of alkylation of up to ca. 100 mole% based on the styrene rings.

The volume of solvent in the reaction flask was then reduced to ca. 100 mL on a rotary evaporator, and the polymer precipitated with vigorous stirring in 1 L of methanol. Sample purification was achieved by redissolving the air-dried polymer in a boiling mixture of 500 mL chlorobenzene (Anachemia) and 50 mL iso-propanol (A&C American Chemicals) with stirring, followed by the addition of 25 mL of distilled water, and overnight refluxing. The aqueous phase was then eliminated, and the organic solution washed 5 times with 150 mL portions of distilled water. The amount of solvent was again reduced to about 100 mL, and the polymer precipitated in 1 L of methanol. The samples were finally dried for 2-3 days in a vacuum oven at 150 °C. The degree of substitution evaluated by NMR spectroscopy was used to calculate expected sample weight increases to allow yield calculations. Experimental yields of purified alkylated polymers were typically 80-90% of the theoretical value.

Samples with alkylation levels of up to 103 mol% (based on the styrene rings) were obtained in this manner. Slightly modified reaction conditions were used to produce alkylated ionomers in the 0-30% range with better control on the reaction time. In this case, 250 mL and 100 mL of the CS_2/nitropropane solvent were used for the polymer and aluminum chloride, respectively, yielding approximately halved concentrations for all reagents.

2.3.1. Characterization

The degree of alkylation was determined by two independent methods. The first technique involved the determination of the equivalent weight (EW) of the material by standard acid-base titration. Assuming that none of the carboxylic acid groups of the copolymer were affected in the Friedel-Crafts reaction, the degree of alkylation (x) could be calculated from the equivalent weight (EW) determined by titration of the copolymer as

$$x = \frac{(EW - 1470\ g{\cdot}mol^{-1})}{(3333 - 1470)\ g{\cdot}mol^{-1}} \qquad \text{(Eq. 2.1)}$$

where the constants 1470 g·mol^{-1} and 3333 g·mol^{-1} represent the equivalent weights of nonalkylated and 100%-alkylated PS-0.07MAA, respectively.

The second method used to determine the alkylation level was Fourier Transform ^{1}H NMR spectroscopy. All NMR spectra were recorded on a Varian XL-200 spectrometer at 20°C. A mixture of 90/10 v/v of deuterated benzene and deuterated methanol was used as a solvent for all samples. Series of 32 transients were recorded for each spectrum. The alkylation level was in this case evaluated from the ratio of the integrated areas of the peaks for the aromatic (δ = 6.2-7.6 ppm) and the aliphatic protons (δ = 0.5-2.5 ppm), respectively.

2.3.2. Mechanical measurements

The dynamic mechanical properties of the samples were determined as a function of temperature using an inverted torsional pendulum described elsewhere[21]. The system used a PDP-11/03 microcomputer for signal acquisition and analysis.

The samples used in the instrument had approximate dimensions of 1.7 x 0.6 x 0.2 cm^3, and were molded from 1 g of predried material (1 week in vacuo at 150 °C) by compression at 50-100 °C above matrix T_g. Pressure was maintained at up to 15 MPa for 15-20 minutes. The mold was then left to cool slowly on the press to below T_g, and the sample taken out. The molded sample was stored in a vacuum oven at a temperature close to its matrix T_g, or used immediately in the instrument.

Software was developed for the IBM Personal Computer(TM) model XT by Miss S. M. Williams as a part of another project to evaluate the peak maxima and the inflection points in the modulus-temperature curves, with the help of curve smoothing and baseline subtraction routines. The numerical analysis of the data was performed on the IBM-PC computer, after transfer from the PDP-11 computer via an RS-232C serial interface.

2.4. Results and Discussion

2.4.1. Synthesis

Decene was selected as the alkylating agent because a minimum is observed at that value in a plot of the glass transition temperature versus chain length in the analogous poly(4-alkylstyrene) series, at T_g = -65 °C[22]. It should consequently be possible to achieve a large T_g depression with a C_{10} unit, while avoiding complications due to side chain crystallization, which is apparently significant for side chains longer than about 12-14 carbon atoms. The product obtained in the reaction has the advantage of being reasonably well characterized for the purpose of this study. The reaction conditions used, as well as the steric hindrance caused by the backbone, are expected to favor predominantly the formation of the para- isomer[23]. As is generally the case with Friedel-Crafts reactions, the cationic alkyl species generated in the reaction are likely to rearrange, via hydride migration, thus producing isomers with attachment points at C-2 to C-5 on the alkyl chain. The presence of a few different isomers is considered an advantage here, since this factor should further contribute to the inhibition of side chains crystallization. The absence, within experimental error limits, of further rearrangements such as methyl migrations, is demonstrated by the NMR results. The evaluation of the degree of alkylation from the ratio of the integrated areas of the aromatic protons (δ = 6.2-7.6 ppm) to the area of all the aliphatic protons (δ = 0.5-2.5 ppm), or only the methyl protons (δ = 0.95 ppm) in the spectrum, respectively, gives the same results.

The degrees of alkylation obtained from the equivalent weight determinations, and those from NMR are summarized in Table 2.1. It can be seen that neither technique gives consistently higher or lower results; the variations, therefore, are most likely due only to random errors. It should be noted that since the method involving titrations relies on the difference between the equivalent weight of the alkylated and the nonalkylated materials, its precision is somewhat limited at the lower alkylation levels. An error of ca. 2 drops or 0.05 mL can be assumed in the titrations, due to the relatively diffuse end point observed in titrations in organic solvents. Since titrant (0.05 N NaOH) volumes of typically 3 to 5 mL were used for 0.4 g samples, relative errors of ca. 1-1.7% were obtained on the individual measurements. When the EW of the nonalkylated polymer is subtracted from the EW of the alkylated material, however, the absolute errors add up, yielding rather large relative errors ranging from about 5% (102% alkylated sample) to 15% (10% alkylated). The NMR technique is expected to give more reliable results than the equivalent weight approach at the lower alkyl contents. The accuracy of the values obtained in this manner (considering spectrum phasing errors), is expected to be of the order of about 5 percent of the values determined. Consequently, the alkylation levels used in the calibration curves for the alkylation reaction (Figure 2.1), and reported subsequently, are the average of the two determinations.

Table 2.1. Comparison of the results obtained for the determination of the alkylation level by NMR, and by titration.

Titration (mol%)	NMR (mol%)
10 ± 2	7.5 ± 0.4
18 ± 2	15.0 ± 0.8
36 ± 3	32 ± 2
52 ± 3	53 ± 3
78 ± 4	70 ± 4
102 ± 5	104 ± 5

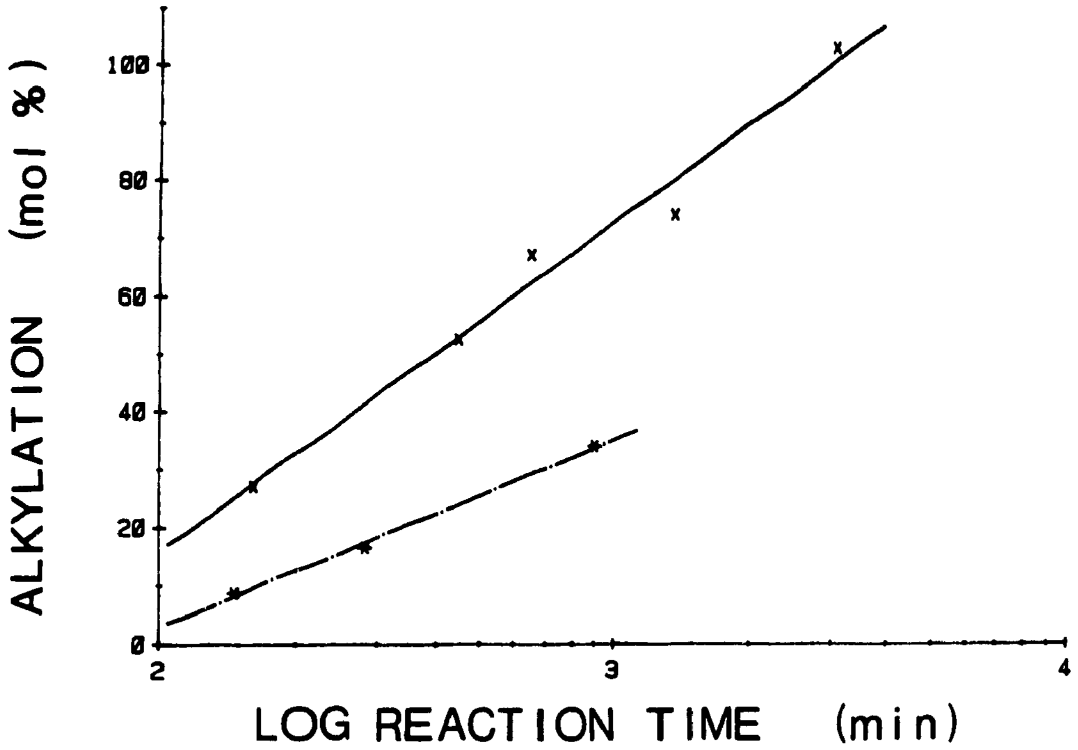


Figure 2.1. Conversion curves for the Friedel-Crafts alkylation of the PS-0.07MAA copolymer with 1-decene in the reaction conditions described above.

Two lines (Figure 2.1) were obtained to relate the degree of alkylation of the copolymers to the reaction time. The curve with the lower slope refers to samples prepared under the more dilute reaction conditions. This modified procedure was preferred for the samples with the lower alkyl contents, to maintain a better control on the reaction times involved.

The fact that the plot of the degree of alkylation against the logarithm of the reactions time displays relatively good linearity (correlation coefficient $r^2 = 0.990$) does not seem to have any theoretical significance. The reaction was found to obey pseudo-first order kinetics in concentration of polymer, for degrees of alkylation of up to 67 mol%. The rate constants were determined as $(7.6 \pm 0.4) \times 10^{-6}$ and $(3.1 \pm 0.1) \times 10^{-5}$ s^{-1} for the dilute and the concentrated solutions, respectively. The values of the uncertainties (from linear regression analysis), however, should be regarded with much caution, because of the very limited number of points available for the analysis (3 in each case).

2.4.2. Mechanical Properties

The storage modulus, loss modulus and loss tangent curves for the sodium-neutralized styrene-methacrylic acid ionomers (PS-0.07MAA-Na) at degrees of alkylation varying from 0 to 103 mol% are displayed in Figures 2.2-2.4. The useful information extracted from these curves with the help of the data analysis program is summarized in Table 2.2. The table lists, for each sample, the matrix tan δ peak position (T_{g1}) and its width at half-height ($W_{1/2}$), the value of the rubberlike inflection modulus (G'_{in}) and temperature (T_{in}), and the cluster peak position (T_{g2}) and width at half-height ($W_{1/2}$). The procedure used to obtain it will be discussed in the next section.

The width of the glassy to rubbery transition zone in the G' curves (Figure 2.2) increases with the alkylation level. This parallels the observation by Bazuin and Eisenberg[18] for ionomers with low molecular weight diluents. The phenomenon is

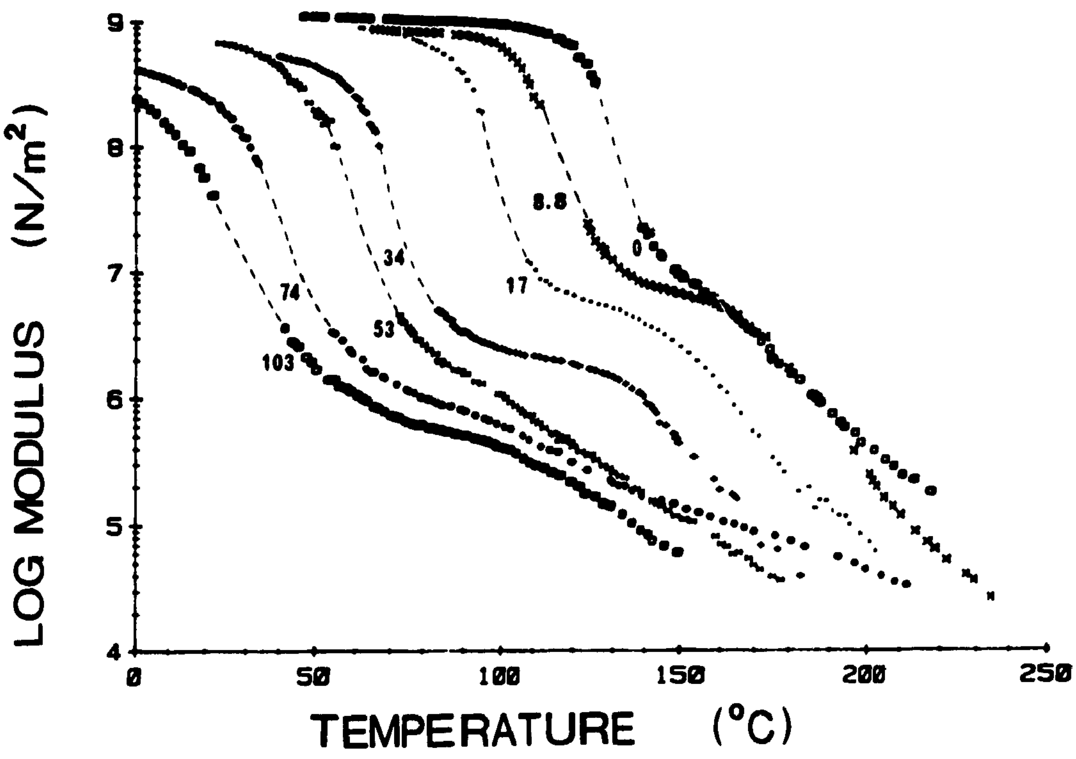


Figure 2.2. Storage modulus curves for the PS-0.07MAA-Na system alkylated with 1-decene. The curves are identified by the mole % of styrene rings with alkyl chains grafted on them.

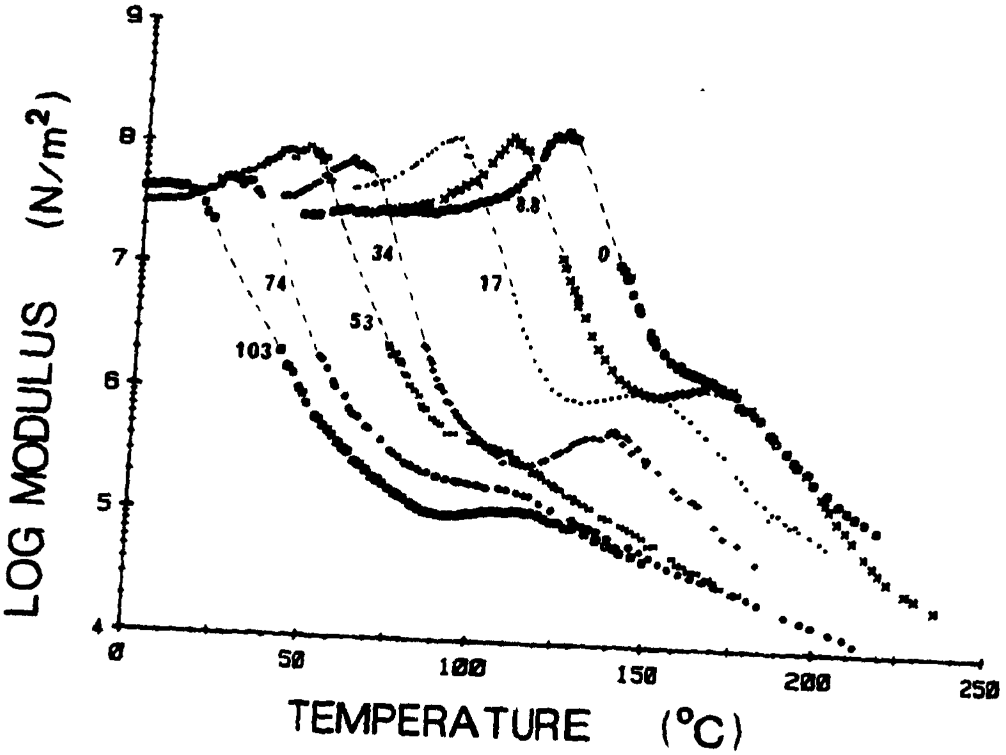


Figure 2.3. Loss modulus curves for the alkylated PS-0.07MAA-Na ionomers.

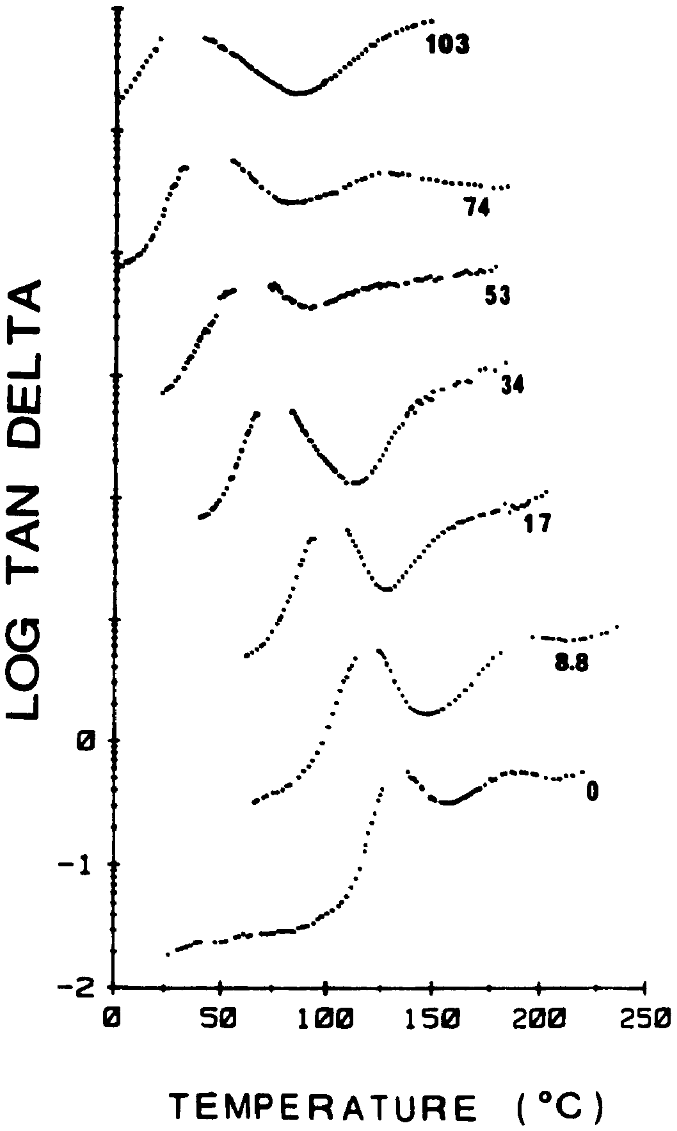


Figure 2.4. Loss tangent curves for the ionomers of Figure 2.2. Each curve is shifted up by an order of magnitude with respect to the previous one, for improved clarity.

quantified by the width at half-height for the matrix peaks (Table 2.2, third column). A three-dimensional damped Debye lattice model was used by Chapoy and Tobolsky[24], and by Aklonis and Rele[25], to explain the widening of the transition region in plasticized samples. In this model, the diluent reduces intermolecular interactions and progressively destroys the three-dimensional torsional oscillator lattice, thereby reducing the steepness of the slope in the transition region.

Table 2.2. Summary of the results obtained from the numerical analysis of the loss tangent and modulus-temperature curves of the alkylated ionomers.

Alkyl-ation	Matrix		"Rubbery" inflec-tion point		Clusters	
	T_{g1}	$W_{1/2}$	T_{in}	G'_{in}	T_{g2}	$W_{1/2}$
(mol%)	(°C)	(°C)	(°C)	(MPa)	(°C)	(°C)
0	133	22	158	6.2	186	30
8.8	119	23	146	7.3	191	38
17	101	22	125	5.8	166	37
34	75	25	107	2.3	148	39
74	44	31	87	0.87	128	45
103	33	42	85	0.57	127	36

The rubberlike plateau in the G'-temperature curves is initially extended as the plasticizer content increases and the T_g of the material goes down; however, it becomes less clearly defined at the higher (74 and 103 mol%) alkylation levels.

The shift in the temperature of the two maxima in the tan delta curves is depicted in Figure 2.5. It can be seen that at low (up to ca. 10 mol%) degrees of alkylation, the behavior of the cluster T_g curve is very different from that of the matrix T_g curve. The

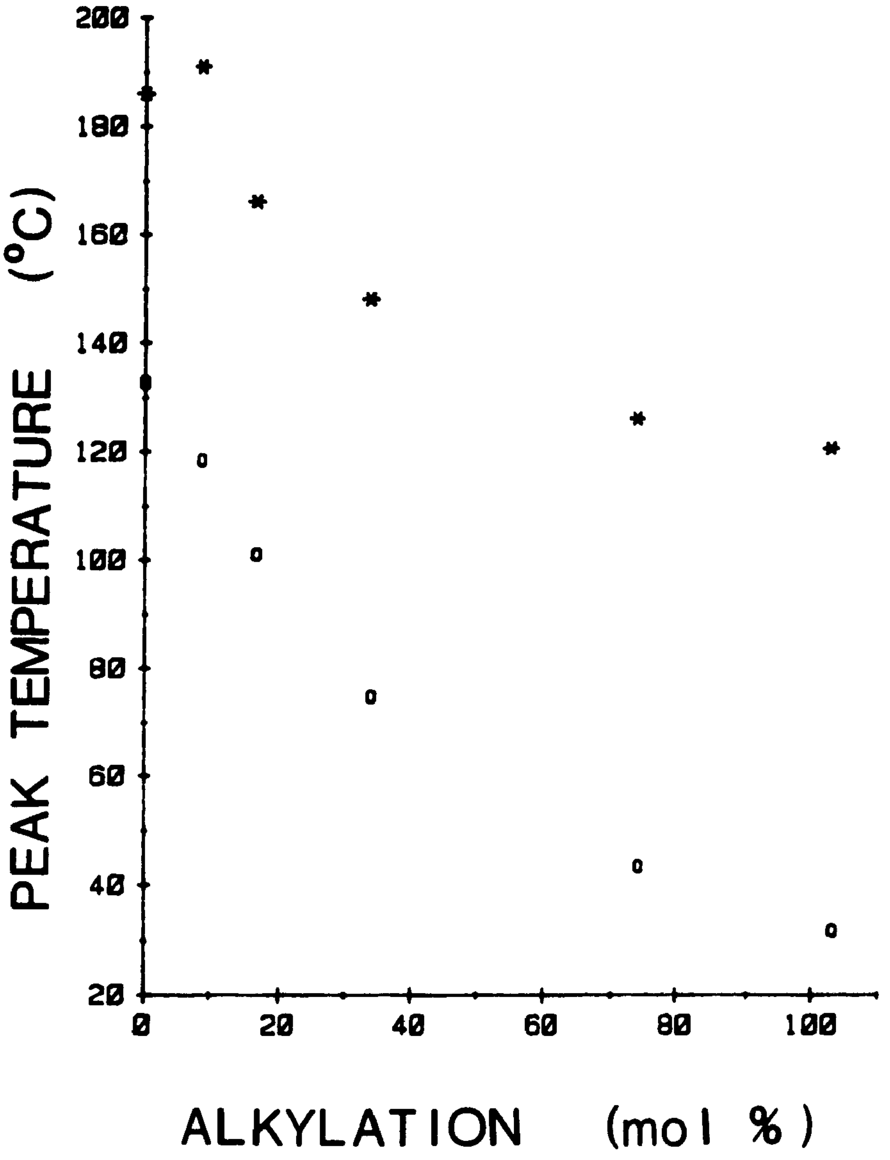


Figure 2.5. Peak positions of the loss tangent maxima associated with the matrix (O) and ion-rich domains (*) for the alkylated PS-0.07MAA-Na ionomers.

matrix curve decreases monotonically with plasticizer content. The cluster T_g, on the contrary, increases initially with respect to the parent ionomer. The point for the cluster T_g of the 8.8% alkylated ionomer is of particular interest here. The errors involved in determining the positions of the maxima with the help of the data fitting and baseline subtraction routines are expected to be of the order of 1°C for the sharp matrix peak, and 2-3°C for the cluster peak, depending on its shape. Therefore, it seems unlikely that this particular point can be attributed to experimental error, but rather represents the manifestation of an enhanced state of clustering. These results are consistent with the observation by Duchesne and Eisenberg[12] that decreasing the matrix T_g from an ethyl acrylate (T_g = -24 °C) to a butyl acrylate matrix (T_g = -54 °C)[22] induced cluster formation in vinylpyridinium ionomers; similar results were obtained when the ethyl acrylate ionomers were plasticized with dimethyl malonate.

The validity of the present findings is further reinforced by the evaluation of the apparent average molecular weight between cross-links from the rubberlike inflection point of the G'-Temperature curve ($G_{in} = \rho R T_{in} / M_c$) for the different samples. A measure of the extent of aggregation can be obtained by comparing the experimentally determined M_c [M_c(exp)] to the M_c calculated for strictly multiplet-type ionic interactions [M_c(cal)], and equal to the equivalent weight of the sample. This is presented graphically in Figure 2.6 as a ratio of the two values. The 8.8% and 17% samples have a M_c ratio clearly higher than the parent ionomer, revealing once again an increased state of clustering. It is believed that the consistency of the data presented in Figures 2.5 and 2.6 points to an enhanced state of large scale ionic aggregation (clusters) at the lower alkylation levels. At alkylation levels above 50-60 mol%, however, the ionic interactions fall below the statistical multiplet-type level [$M_c(cal)/M_c(exp) < 1$], pointing to the highly disruptive nature of the grafted alkyl chains. It seems likely that the bulkiness of the grafted alkyl chains hinders significantly the approach of ion pairs at

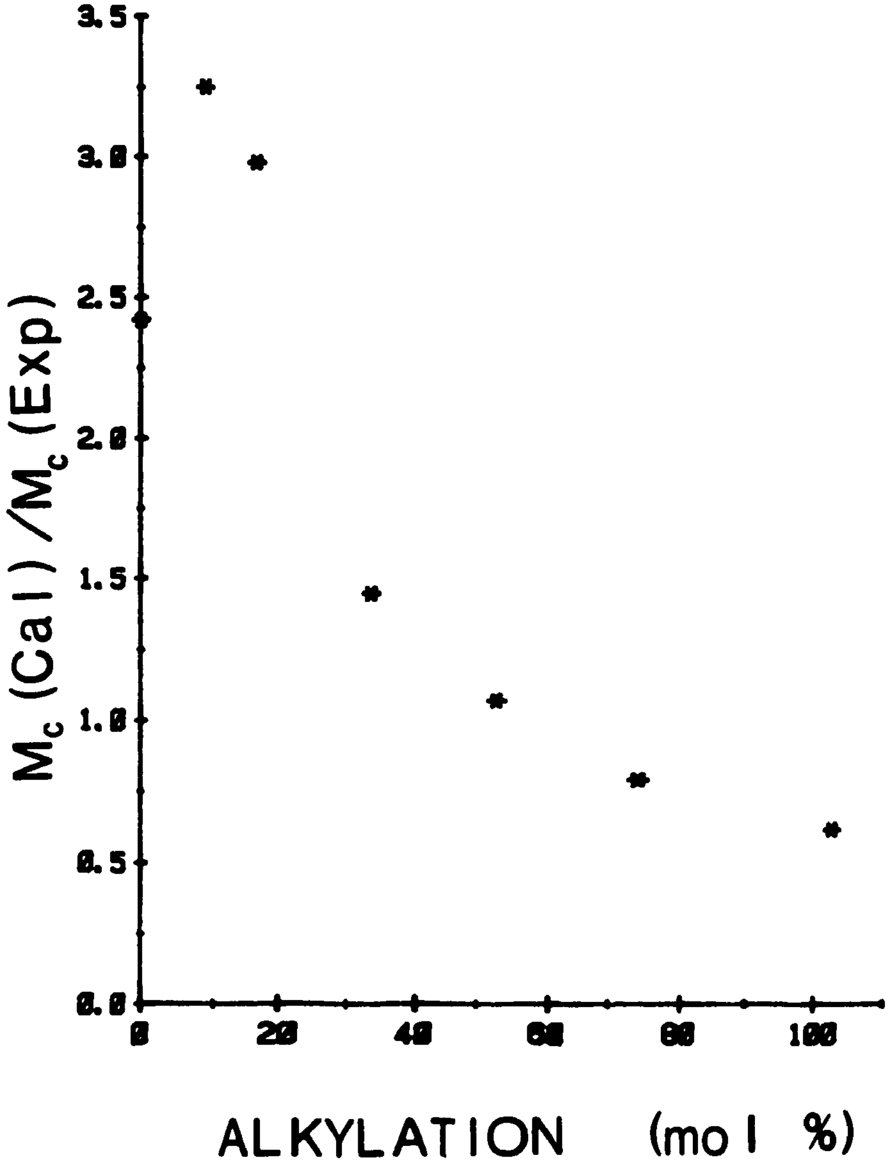


Figure 2.6. Extent of aggregation observed in the alkylated ionomers expressed as the ratio of calculated M_C for multiplet-type interactions to experimental M_C.

high concentrations, thereby reducing the extent of interactions and the driving force for large scale aggregation.

2.4.3. Numerical Analysis

The dynamic mechanical curves of the PS-0.088Dec-0.07MAA-Na sample (with decene grafted on 8.8% of the styrene rings) were selected to illustrate the usage of the curve fitting and baseline subtraction procedures. A numerical analysis approach (curve fitting) is used in the program to find the position and width at half-height of the maxima in the loss tangent-temperature curves, as well as the location of the inflection points (with the corresponding magnitude of the modulus) in the G' modulus-temperature curves. Figure 2.7 displays the set of dynamic curves, as obtained from a torsion pendulum run. A polynomial (solid curve) was fitted to the loss tangent curve of Figure 2.8, by least squares analysis of the raw data. The order of the polynomial, in this case 6, was selected to provide a reasonable degree of smoothing, without introducing artifacts such as ripple, caused by exceedingly high order fits. The baseline, shown as a dotted line on Figure 2.8, was set graphically on the display of the computer, to be subtracted from the curve. The baseline may be either linear or a polynomial; linear baselines were used for this work. Polynomial baselines can be particularly useful to subtract a shoulder from a peak, and are essentially equivalent to deconvoluting the peaks. The equation for the subtracted peak was then scanned by the program to find the two maxima at T = 119°C and 191°C. The width at half-height ($W_{1/2}$) of the subtracted peaks is also easily evaluated from the fitted equation in the data analysis program. The subtracted peaks are also plotted in Figure 2.8. The symmetry of the high temperature peak obtained in this manner is quite remarkable, even in the cases where it is less pronounced than in the example here. It was preferred to fit the two tan delta peaks individually, to take advantage of the data smoothing achieved by selecting low order polynomials. The rubberlike inflection point of the G' curve of Figure 2.7 was obtained by first fitting a polynomial of order 10 to the experimental data for a section of the curve from 120 to 180°C. The second derivative of the fitted curve was then scanned for zeros. In this case, inflection points were found at T = 144.1 °C (G'_{in} = 7.63 x 10^6 N/m^2) and T = 174.9 °C (G'_{in} = 2.46 x 10^6 N/m^2), the former value proving to be the correct one (Figure 2.7). The results obtained by numerical analysis of all the curves are summarized in Table 2.2.

The numerical data analysis technique presented here is believed to represent a most useful tool in the analysis of dynamic mechanical data. This is particularly true in the case of torsion pendulum data, where the signal is lost in the vicinity of the glass transition temperature. It provides an analytical, more reliable approach to the evaluation of the glass transition temperatures and inflection moduli. One word of caution is, however, necessary concerning the use of the baseline subtraction procedure, in particular in the case of the relatively broad cluster T_g. There is, indeed, a certain amount of subjectivity involved in selecting the baseline for a given peak, which can yield some variations in the results obtained. This is why the results obtained for the sharp matrix T_g are expected to be reliable to about ± 1 °C, while the error on the broader cluster T_g, however, is more likely of the order of 2-3 °C, depending on the particular case involved.

2.5. Conclusions

It was shown that the lowering of the matrix T_g of carboxylated ionomeric systems at low levels of internal plasticization leads to increased ionic aggregation. In this particular case, clustering enhancement was observed, with respect to the nonalkylated parent ionomer, for 1-decene contents of up to 15-20 mol%. At much higher alkylation levels, however, the large grafted alkyl chains apparently reduced the aggregation state to mostly multiplet-type interactions.

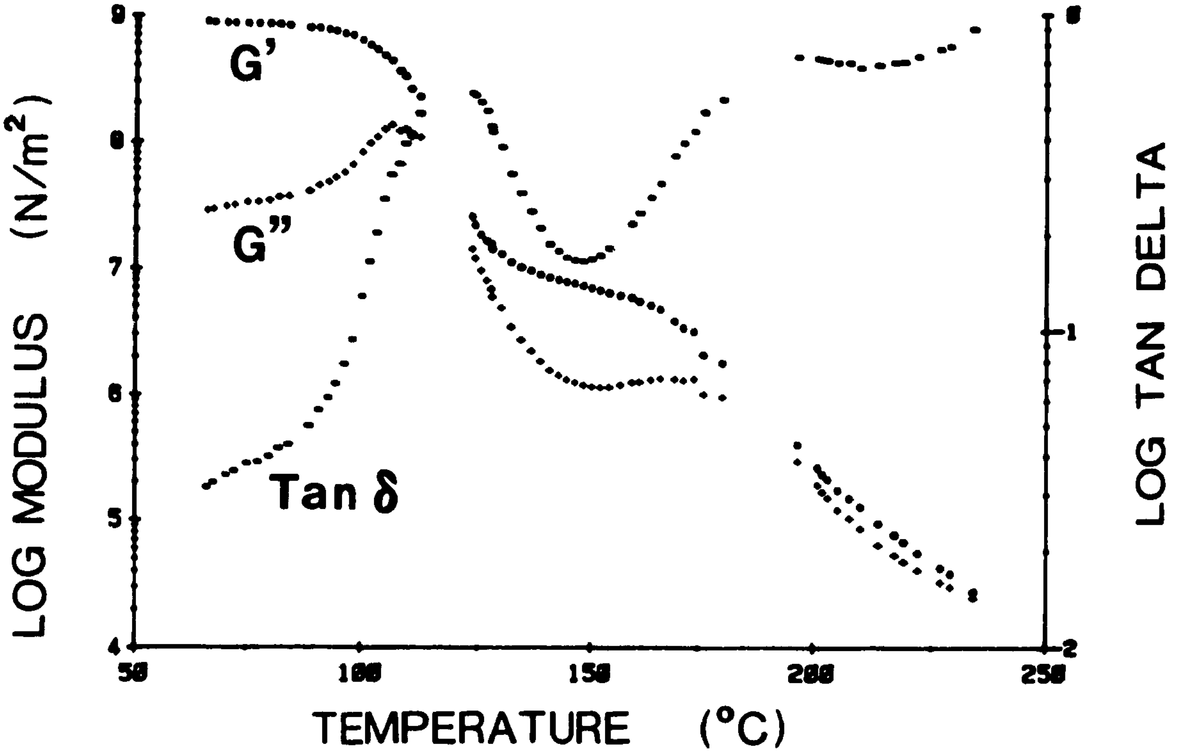


Figure 2.7. Original torsion pendulum curve for the PS-0.088Dec-0.07MAA-Na sample used as an example for the numerical data analysis.

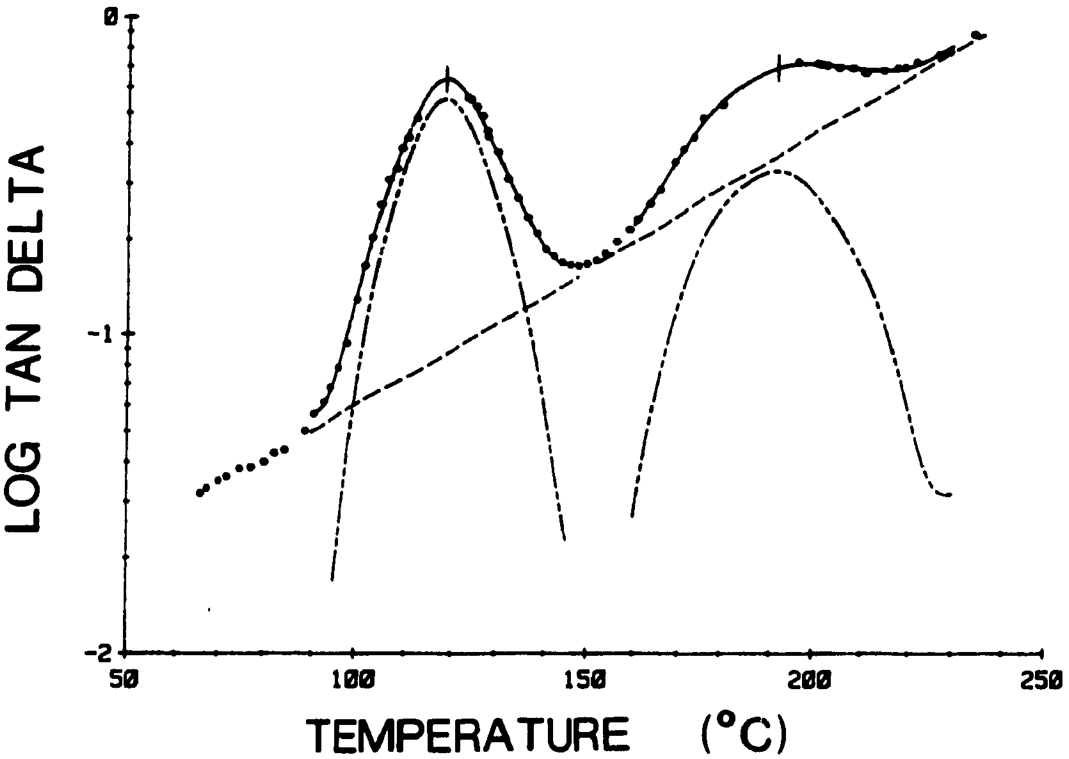


Figure 2.8. Curve fitting and baseline subtraction for the tan δ curve of Figure 2.7.

A reaction was suggested to graft 1-decene onto the rings of aromatic homopolymers and carboxylated copolymers in a Friedel-Crafts type reaction, in order to lower the T_g of the samples. The kinetics of the reaction were briefly examined.

A convenient data analysis technique was also suggested for the dynamic mechanical data of ionomers, leading to a more objective evaluation of the rubberlike inflection modulus and of the glass transition temperatures associated with the matrix and the ion-rich domains, respectively.

2.6. Acknowledgements

Funding for this work was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC). One of the authors (M.G.) would also like to acknowledge the financial support of NSERC and of the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (Quebec). The authors are also very grateful to Ms. S.M. Williams for the development of the software used in the numerical analysis of the dynamic mechanical data.

2.7. References

(1) (a) *Ionic Polymers*; Holliday, L., Ed.; Applied Science: London, 1975. (b) *Ions in polymers*; Eisenberg, A., Ed.; Advances in Chemistry 187; American Chemical Society: Washington, DC, 1980. (c) *Developments in Ionic Polymers Vol. 1*; Wilson, A.D., Prosser, H.J., Eds.; Applied Science: London, 1983. (d) *Ibid. Vol. 2*; Wilson, A.D., Prosser, H.J., Eds.; Applied Science: London, 1986.

(2) Eisenberg, A.; King, M. *Ion-Containing Polymers*; Academic: New York, 1977.

(3) See for example (a) Bazuin, C.G.; Eisenberg, A. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 271. (b) MacKnight, W.J.; Earnest, T.R., Jr. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.

(4) (a) *Coulombic Interactions in Macromolecular Systems*; Eisenberg, A., Bailey, F.E., Eds.; ACS Symposium Series 302; American Chemical Society: Washington,

DC, 1986. (b) *Structure and Properties of Ionomers*; Pineri, M.; Eisenberg, A., Eds.; NATO ASI Series C Vol. 198; Reidel: Dordrecht, Holland, 1987.

(5) (a) Weiss, R.A.; MacKnight, W.J.; Lundberg, R.D.; Mauritz, K.A.; Thies, C.; Brant, D.A. In *Coulombic Interactions in Macromolecular Systems*; Eisenberg, A., Bailey, F.E., Eds.; ACS Symposium Series 302; American Chemical Society: Washington, DC, 1986; pp 2-19. (b) Lundberg, R.D. In *Structure and Properties of Ionomers*; Pineri, M.; Eisenberg, A., Eds.; NATO ASI Series C Vol. 198; Reidel: Dordrecht, Holland, 1987; pp 429-438. (c) Tan, J.S. *Ibid.* pp 439-451.

(6) (a) Rees, R. W.; Vaughan, D. J. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1965**, *6(1)*, 287. (b) Rees, R.W.; Vaughan, D.J. *Ibid.* **1965**, *6(1)*, 296.

(7) (a) MacKnight, W.J.; Taggart, W.P.; Stein, R.S. *J. Polym. Sci., Polym. Symp.* **1974**, *45*, 113. (b) Yarusso, D.J.; Cooper, S.L. *Macromolecules* **1983**, *16*, 1871.

(8) (a) Bonotto, S.; Bonner, C.F. *Macromolecules* **1968**, *1*, 510. (b) Tobolsky, A.V.; Lyons, P.F.; Hata N. *Macromolecules* **1968**, *1*, 515.

(9) Eisenberg, A. *Macromolecules* **1970**, *3*, 147.

(10) Gauthier, S.; Duchesne, D.; Eisenberg, A. *Macromolecules* **1987**, *20*, 753.

(11) (a) Otocka, E.P.; Eirich, F.R. *J. Polym. Sci., Part A-2*, **1968**, *6*, 921. (b) Otocka, E.P.; Eirich, F.R. *Ibid.* **1968**, *6*, 933.

(12) (a) Duchesne, D. Ph.D. Thesis, McGill University: Montreal, May 1985. (b) Duchesne, D.; Eisenberg, A. To be published.

(13) Brockman, N.L.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1145.

(14) (a) Navratil, M.; Eisenberg, A. *Macromolecules* **1974**, *7*, 84. (b) Makowski, H.S.; Lundberg, R.D.; Westerman, L.; Bock, J. In *Ions in polymers*; Eisenberg, A., Ed.; Advances in Chemistry 187; American Chemical Society: Washington, DC, 1980; pp 3-19.

(15) MacKnight, W.J.; McKenna, L.W.; Read, B.E. *J. Appl. Phys.* **1967**, *38*, 4208.

(16) Gauthier, M.; Eisenberg, A. Submitted for publication in *Macromolecules*.

(17) (a) Besso, E.; Legras, R.; Eisenberg, A.; Gupta, R.; Harris, F.W.; Steck, A.E.; Yeager, H.L. *J. Appl. Polym. Sci.* **1985**, *30*, 2821. (b) Drzewinsky, M.; MacKnight, W.J. *Ibid.* **1985**, *30*, 4753.

(18) Bazuin, C. G.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1137.

(19) Fox, T.G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.

(20) Navratil, M.; Eisenberg, A. *Macromolecules* **1973**, *6*, 604.

(21) Cayrol, B. Ph.D. Thesis, McGill University: Montreal, 1972.

(22) Lee, W.A.; Rutherford, R.A. In *Polymer Handbook, 2nd ed.*; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1974; p III-139.

(23) Roberts, R. M.; Khalaf, A. A.; *Friedel-Crafts Alkylation Chemistry: A Century of Discovery*; Dekker: New York, 1984; Chapter 4.

(24) Chapoy, L. L.; Tobolsky, A. V. *Chem. Scrip.* **1972**, *2*, 44.

(25) Aklonis, A. A.; Rele, V. B. *J. Polym. Sci., Polym. Symp.* **1974**, *46*, 127.

Chapter 3. Matrix polarity effects on ionic aggregation in a nitrated styrene ionomer

3.1. Abstract

A styrene-methacrylic acid copolymer (7 mol% acid) was partially nitrated. The relaxed dielectric constant of the sodium-neutralized material was raised from 3.2 (nonnitrated) to 7.3 (32% nitrated). The tan δ peak associated with clusters in the sodium ionomer, as detected by dynamic mechanical measurements, was unaffected. In a parallel study, the styrene-sodium methacrylate ionomer was plasticized with nitrobenzene. Despite its high polarity, the diluent displayed the effects of typical nonpolar plasticizers, affecting the matrix and the ion-rich domains to the same extent. Comparison with previous results and consideration of cohesive energy density data suggests that specific interactions are an important factor in determining the plasticizing behavior of diluents, rather than the dielectric constant alone. A nitration technique is also suggested for polystyrene which allows control of the degree of substitution in the 0-100% range, and yields predominantly the para- isomer.

3.2. Introduction

The addition of small amounts (2-15 mole%) of ions to organic polymers, by such means as copolymerization or postpolymerization modification, has led to new materials with modified properties[1,2] which are of ever growing industrial importance[3]. It is generally accepted that ionomers, as defined by Rees and Vaughan[4], owe their peculiar properties to the aggregation of the ions introduced into the organic matrix. Two distinct types of aggregates are believed to be formed as a result of ionic associations in carboxylate and sulfonate systems[5]. Multiplets consist of small aggregates of ions in the form of quartets, sextets, etc. The ionic interactions make the multiplets behave like thermolabile cross-links, increasing the glass transition temperature (T_g) of the matrix.

Clusters are larger, ion-rich structures which behave like filler particles, providing strong reinforcement above the glass transition temperature of the polymer matrix. There are different ways to probe the structure of clusters, from which a few models have been suggested[6], and some disagreement still persists. Some of the experimental techniques which have provided results in support of the multiplet-cluster view include Small-Angle X-Ray Scattering (SAXS)[7,8], Raman spectroscopy[9], as well as dielectric[10] and mechanical properties measurements[11].

The X-ray technique is most useful in that it gives time-averaged morphological information, but it relies on electron density differences, and is therefore preferentially applicable to large, electron-rich counterions like cesium. Dynamic mechanical measurements, on the other hand, give dynamic information (e.g. glass transitions of different phases), and can be applied to all counterions. The measurements yield information about clustering, provided that the ion-rich structures are large enough to behave as a separate phase. Dynamic mechanical techniques give very characteristic results for carboxylate or sulfonate ionomers. The storage modulus (E' or G') versus temperature curves display an additional rubberlike plateau which, in general, becomes more clearly developed as the ion content of the ionomer increases. Also, the loss tangent curve displays two loss maxima, the low temperature peak being attributed to the T_g of the polymer matrix containing some interspersed multiplets, while the high temperature peak is associated with the T_g of the ion-rich domains[8].

Some structural parameters of polymers are clearly known to affect the properties of ionomers. The effects of the variation of the type of counterion[12], or the placement[13] and nature[14] of pendant ions, for example, have been studied. The effect of the dielectric constant of the polymer matrix has also been explored to some extent. Eisenberg and King[2] pointed out that while the rheological properties of ethylene-based ionomers ($\varepsilon \approx 2.3$) are dominated by clustering even at ionic concentrations as low as 1%, similar styrene-based systems ($\varepsilon \approx 2.5$) only show comparable effects starting at 4-6 mole% of ions. Furthermore, acrylate-based systems ($\varepsilon \approx 4$) display significant clustering effects only at ionic concentrations as high as about 10-15 mole%. Although a comparison of these results apparently suggests a significant effect of the polarity of the polymer matrix on ionic aggregation, one problem is evident. The three systems have pendant groups of a very different nature, possibly leading to different steric effects, as well as differences in specific molecular interactions.

In order to investigate more fully the influence of matrix polarity on ionic aggregation, there is an obvious need for a method which allows one to vary systematically the polarity without changing the nature of the backbone or the pendant ionic groups attached to it.

A tabulation of dielectric constants for organic liquids[15] reveals the high dielectric constant of nitrobenzene ($\varepsilon = 34.8$ at 25 °C). Nitration of aromatic compounds being an easy reaction, the controlled nitration of a styrene-based copolymer should provide the desired system.

Nitration of polystyrene is well-documented in the chemical literature. Unfortunately, little effort has been devoted to the production of polymers with low (0-50 mole%) nitration levels, the general tendency being to aim at high degrees of substitution (100-200%)[16-18]. Even in cases where partial nitration is achieved, the reaction conditions suggested are, in general, not very flexible, leading to solubility problems for the polymer, and yielding nonuniform products and irreproducible results when the proportions of solvent to nitric acid are changed[18]. It would nevertheless appear that one of the techniques suggested[16] might have a limited usefulness in controlling the degree of substitution of the products, although no such attempt was reported in the original paper.

A somewhat more interesting approach is the nitration by *in situ* generation of the nitronium ions from inorganic nitrates and trifluoroacetic anhydride[19]. That procedure, however, uses relatively high salt concentrations, and leads to solubility problems for many inorganic nitrates as well as to sample contamination by salt residues, undesirable in the case of ionomers.

Since no known nitration technique could be applied directly to modify the ionomers in a controlled manner, a new approach was devised. The technique is applicable without modification to degrees of substitution in the 0-100% range, and leaves no nonvolatile residues. The products apparently contain mostly, and possibly exclusively, the para- isomer. The technique was applied equally successfully to polystyrene homopolymer and to the PS-MAA copolymer used in the aggregation study. In this case, a styrene-methacrylic acid copolymer with 7 mole% acid and denoted as PS-0.07MAA, according to the convention suggested by Eisenberg and King[2], was used.

The aim of this study was to examine the effects on ionic aggregation of the systematic variation of the dielectric constant of the polymer matrix, via nitration. The choice of the nitro group is of particular relevance to this work. In spite of its high polarity, it is not significantly subject to specific interactions with ions, because the negative end of its dipole is delocalized on one nitrogen and two oxygen atoms[20]. It therefore becomes possible to separate dipolar and specific interaction effects on ionic aggregation. The results obtained for the dynamic mechanical properties of the nitrated sodium methacrylate ionomers were quite unexpected, and suggested a comparative study of the effects of plasticization with nitrobenzene on the PS-MAA-Na system.

The work of Bazuin and Eisenberg[21] on plasticized PS-MAA-Na ionomers has already highlighted the importance of the nature of diluents on their plasticizer behavior. The effects of a nonpolar and a highly polar and hydrogen-bonded plasticizer were compared. While diethylbenzene affected the matrix and cluster aggregates to the same extent, glycerol, used in the same concentration range, clearly affected the ion-rich domains preferentially. This is discussed in greater detail below.

3.3. Experimental

3.3.1. Materials and Equipment

Styrene monomer (Aldrich, 99%, inhibited with tert-butylcatechol) was washed three times with a 5% aqueous sodium hydroxide solution and twice with distilled water, to remove the inhibitor. The monomer was dried over calcium hydride (Aldrich, 95+%, 40 mesh) overnight with stirring and distilled at reduced pressure (b.p. 47-48 °C/22 mm). Methacrylic acid monomer (Aldrich, 99%) was also distilled at reduced pressure (b.p. 67 °C/6 mm). Both monomers were stored for at most a few days in tightly stoppered flasks in a freezer (-20 °C) before use.

The solvents, nitrobenzene (Aldrich, 99%), and 1,2-dichloroethane (A&C American Chemicals, reagent), as well as the fuming nitric acid (Mallinckrodt, 90%) used in the nitration procedure were utilized without purification. The nitrobenzene used in the plasticization study was dried over phosphorus pentoxide (Anachemia, reagent) for three days, then decanted and distilled at reduced pressure (86 °C/7 mm). It was then transferred to oven-dried 2 mL ampoules which were immediately sealed with a flame for later use. A benzene/methanol solution, 90:10 by volume, used in the neutralization procedure for the styrene-co-methacrylic acid polymer, was prepared from A&C American Chemicals reagent grade solvents. The N,N-dimethylformamide (DMF) used as solvent in the potentiometric titration of the nitrated PS-MAA polymers was also A&C American Chemicals reagent grade.

The ^{1}H nuclear magnetic resonance (NMR) spectra used to characterize the products were recorded on a Varian XL-200 Fourier transform instrument, with at least 64 transients acquired. The spectra of the polymers with degrees of nitration lower than 40% were recorded in deuterated chloroform (MSD Isotopes, 99.8% d) at room temperature. Deuterated dimethyl sulfoxide (MSD Isotopes, 99.9% d) was used at 70 °C for samples with higher degrees of substitution. Infrared (IR) spectra of polymer films were recorded on an Analect AQS-18 Fourier transform spectrometer with a resolution of 2 cm^{-1} in the 400 to 4400 cm^{-1} range; 64 transients were acquired for both the background and the sample.

Potentiometric titration curves were established using a Corning 245 pH meter equipped with a general purpose combined glass/saturated calomel electrode.

A Perkin-Elmer DSC-2C Differential Scanning Calorimeter (DSC) was used to determine the glass transition temperature of nitrated polystyrene samples as a function of the degree of nitration (as determined by NMR). The relaxed and/or unrelaxed dielectric constants of some of the materials were measured using a General Radio 1621 Precision Capacitance Measurement System. The dynamic mechanical properties of the samples were determined with a Polymer Laboratories Mark II Dynamic Mechanical Thermal Analyzer (DMTA) interfaced with an IBM PC-XT$^{(TM)}$ compatible computer. The instrument was used in the dual cantilever bending mode at a frequency of 1 Hz. Heating rates of 1 °C/minute were used, and the oven of the instrument was continuously purged with a flow of dry nitrogen. The data obtained were analyzed with programs initially developed by Ms. Susan Williams for an automated torsional pendulum (TP) system, and described elsewhere[22].

3.3.2. Synthesis

Styrene homopolymer and the copolymer with methacrylic acid (ca. 7.5% MAA mol/mol content) of molecular weight 10^5 g/mol were prepared via bulk polymerization with benzoyl peroxide (6.66 g/L) at 60 °C[23,24] using a technique already reported[25]. The exact methacrylic acid content of the copolymer was determined by titration of triplicate 0.4g samples in benzene/methanol 90/10 by volume with a standard methanolic 0.05 N sodium hydroxide solution. The sample solution was titrated to the phenolphthalein end point and a blank correction was included in the calculations.

Nitration tests were initially carried out on the styrene homopolymer, and the technique was later employed to nitrate the copolymers used in the ionic aggregation study. Although many different solvent systems were tested for the nitration reaction, a mixture of nitrobenzene with 1,2-dichloroethane, 3:1 by volume, provided the homogeneous solution conditions necessary for the uniform nitration of the polymers in the 0-100+% range. In a typical nitration test, polystyrene, 1.00g, was first dissolved in 17.2 mL of the 3:1 nitrobenzene/1,2-dichloroethane solvent in a 50 mL 3-neck flask. The flask was immersed in a stirred water bath at 20 °C, and fuming (90%) nitric acid, 2.8 mL, was slowly added dropwise with magnetic stirring in ca. 8 minutes, so that the temperature in the flask remained at (20.0 ± 0.5) °C. The resulting solution, 3 M in nitric acid, was stirred for 60 minutes longer at 20 °C after the addition of the acid was completed. Distilled water (10 mL) was finally added to stop the reaction, and the polymer recovered by precipitation of the organic phase in methanol. The light yellow solid was collected and air-dried on a Buchner funnel before drying in a vacuum oven at 60 °C overnight. The yield was 1.05g of polymer with 27% substitution.

3.3.3. Sample preparation and analysis

The ratio of the integrated NMR peaks for the protons α to the nitro group ($\delta = 7.85$ ppm) to those for the rest of the aromatic protons ($\delta = 7.10$ and 6.55 ppm) was used to determine the degree of nitration. It should be noted that all the nitration and plasticization levels reported in this work are molar ratios. They are calculated from the molar ratio of aromatic rings bearing nitro groups to the total amount of rings present. In the case of plasticized samples, however, the weight fraction of plasticizer is also reported (between parentheses) for convenience. A curve relating the concentration of nitric acid to the degree of nitration under the conditions given above was constructed for the 0-44% substitution range from the NMR results.

The technique used for polystyrene was also used to nitrate the styrene-methacrylic acid (PS-MAA) copolymer. The degrees of substitution of those polymers were determined with the same NMR technique used for the styrene homopolymer. Nitration levels were also confirmed in this case from the equivalent weights determined by titrating 0.4g samples potentiometrically in DMF with the standard 0.05 N sodium hydroxide solution. A more accurate estimate of the end point was obtained by fitting a sixth order polynomial to the data obtained in the transition region using a computer, and scanning the second derivative of the curve for the inflection point where $y''(x)=0$.

The glass transition temperature (T_g) of the nitrated polystyrene samples was measured as a function of the degree of nitration on the Perkin-Elmer differential scanning calorimeter. The values reported were obtained in the second run, after leaving the samples at (T_g + 15) °C for a few minutes, followed by quick quenching (320°C/minute or the maximum attained by the instrument).

The polymer films used in IR spectroscopy were obtained by compression molding at ca. 10 MPa of 0.05g of material between two aluminum plates covered with aluminum foil. The temperature was maintained for at least 5 minutes at (200 ± 10) °C. Infrared spectra were recorded for 103% nitrated polystyrene, 100% nitrated PS-MAA copolymer (based on the benzene rings), and 32% nitrated PS-MAA.

The nitrated PS-MAA samples used for dynamic mechanical measurements were prepared by weighing precisely 1.5g batches of material in 250 mL round-bottomed flasks, dissolving them in 100 mL 90/10 benzene/methanol, and adding a proper amount of 0.05 N methanolic NaOH solution for complete neutralization, according to the predetermined equivalent weights of the materials. The samples were then freeze-dried, and sample drying completed by putting 1.30g of the freeze-dried materials in a vacuum oven at 100 °C for at least 14 days prior to molding. Each sample was compression molded in a preheated mold at 220 °C. The temperature was maintained at (220 ± 5) °C and the pressure at 20 MPa for 10 minutes. The pressure was then very slowly released, and the mold was allowed to cool on the press to 5-10 °C below the matrix glass transition temperature of the polymer (as estimated from the DSC results) before it was taken out of the mold. Typical DMTA sample dimensions were 36 mm length x 12 mm width x 2.5 mm thickness. The exact dimensions were measured to ±0.01 mm with a micrometer immediately before mounting on the DMTA for dynamic mechanical measurements.

The PS-MAA samples containing nitrobenzene as an external plasticizer were prepared by drying appropriate amounts of freeze-dried PS-MAA, fully neutralized with sodium hydroxide, in vacuo at 100 °C for at least 14 days, as before. The sample weights were calculated so that the total weight, after removal of excess nitrobenzene, would be 1.30g. The dry samples were then impregnated with 4 mL of dry nitrobenzene and transferred quantitatively to small boats made from teflon sheets. Each sample was left to soak for one hour in a desiccator at room temperature, and then transferred to a drying pistol at 100 °C (water), purged with dry nitrogen, for one hour longer. The temperature was decreased to 56 °C (boiling acetone), and the excess nitrobenzene slowly pumped out until proper sample weight was reached. Molding of the plasticized samples was done as in the case of the nitrated samples, except that the temperature was kept at 200 °C while the pressure was applied, so as not to lose significant amounts of nitrobenzene (b.p. 214°C/760 mm).

Two samples, containing about 10% and 30% nitrobenzene mol/mol, respectively, were prepared with the technique described above. The molded 30% sample was weighed precisely (±0.1 mg) before and after the run, to evaluate the amount of plasticizer lost during the run. It was then brought to constant weight in a drying pistol at 150 °C (boiling N,N-dimethylformamide) under vacuum, to evaluate the amount of plasticizer originally present. The effect of temperature on plasticizer loss was explored in a more detailed manner by preparing an extra sample containing about 10% nitrobenzene. The sample was set up in the DMTA for a fake run at 1 °C/minute and taken out for weighing at a temperature of 185 °C, which is of particular interest to this study.

For dielectric measurements, dried nonnitrated and 32% nitrated PS-MAA-Na samples were molded at 210 °C/20 MPa for 10 minutes in a circular mold (ca. 19 mm diameter x 1.5 mm thickness). The mold was lined with aluminum foil at the bottom and on the plunger, to serve as electrical contacts for the measurements. The capacitances of the samples at 100 Hz were measured with the General Radio capacitance bridge to determine both their unrelaxed (room temperature) and relaxed (ca. 200 °C) dielectric constants.

3.4. Results and Discussion

3.4.1. Synthesis and sample analysis

The methacrylic acid content of the copolymer was determined, by titration in benzene/methanol, to be $(7.0 \pm 0.1)\%$ on a mole/mole basis. The uncertainty in the MAA content was evaluated from an error of 2 drops, or 0.05 mL, on the titrant volumes used for both the sample and the blank, arising from the somewhat diffuse end point observed in titrations in organic solvents. Titrant volumes of 6.0 mL were typically used for the samples, yielding a relative error of 1.7%.

The curve relating the degree of nitration obtained (as determined by NMR) to the concentration of fuming nitric acid used is given in Figure 3.1. The solid curve was fitted to the data with a second order polynomial (correlation coefficient $r^2 = 0.995$), and may be used to approximate the degree of substitution X(mol%) as

$$X(\text{mol\%}) = 8.18 \cdot \underline{M}^2 - 20.9 \cdot \underline{M} + 17.0 \qquad \text{(Eq. 3.1)}$$

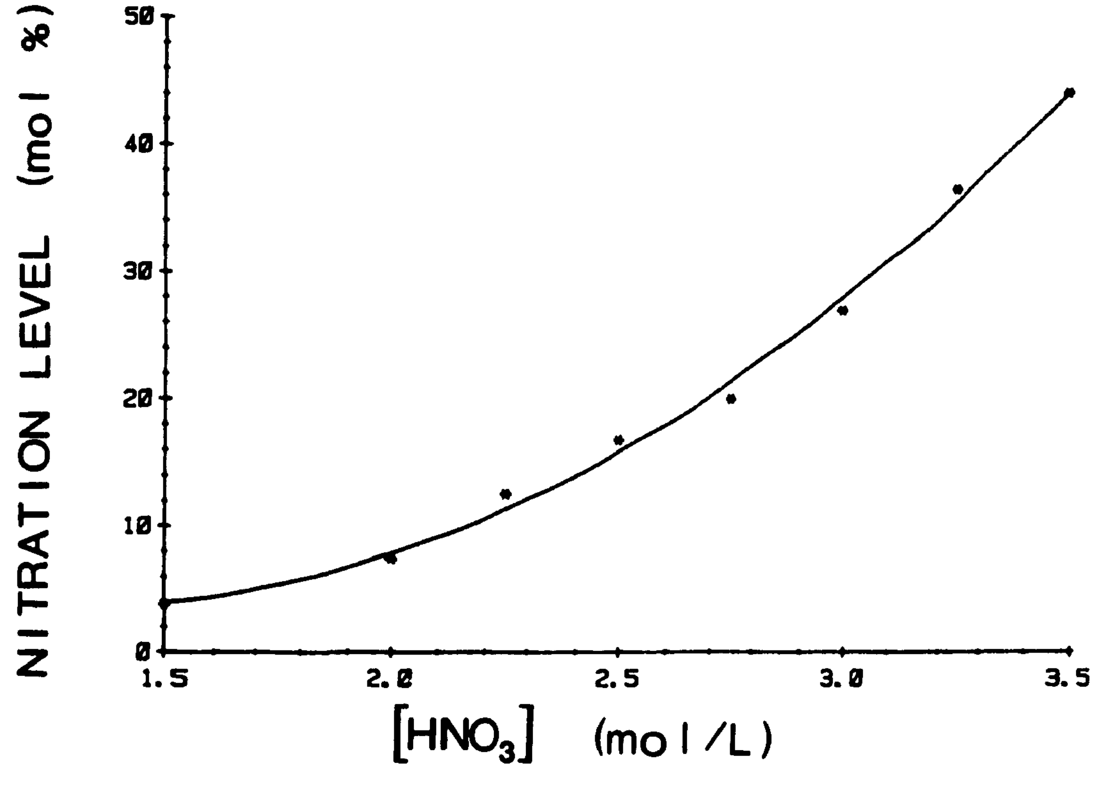


Figure 3.1. Nitration of polystyrene in 3:1 nitrobenzene/ 1,2-dichloroethane with fuming nitric acid at 20 °C after 60 minutes.

where M represents the HNO_3 molarity. The usefulness of this nitration technique lies in the fact that a homogeneous system is obtained in all proportions with nitric acid, making it possible to control smoothly the nitration level in the 0-100+% range. Although the values shown in Figure 3.1 only refer to degrees of substitution of less than about 50%, samples were prepared (in less accurately temperature-controlled conditions) with up to 106% substitution, by increasing the nitric acid concentration and/or temperature.

The infrared spectrum of a 103% nitrated polystyrene sample showed para-substitution on the rings, in the form of a characteristic doublet pattern[26] at 1800 and 1925 cm^{-1} (5.56 and 5.19 μm, overtones), and a strong band appearing at 830 cm^{-1} (12.05 μm, out-of-plane bending). The weaker, but still present bands at 710 and 750 cm^{-1} (14.1 μm and 13.3 μm, out-of-plane bending) for monosubstituted benzene rings also indicate that not all the styrene units may be nitrated. It seems likely, considering the nitration level determined by NMR (103%), that small amounts of the 2,4-dinitro isomer are also present. However, the associated IR bands are apparently too weak to be detected in the 1650-2000 cm^{-1} (5-6.1 μm) region. The comparison of the NMR spectra of the nitrated polymers with model compounds likewise did not reveal the presence of significant amounts of dinitro isomers. The presence of other isomers in the complete nitration of polystyrene with nitric acid has already been confirmed in oxidation studies of the products, the para- isomer being predominant[27].

The infrared spectrum of 30% nitrated polystyrene was, as expected, closer to polystyrene than to the 103% nitrated sample, showing the usual quadruplet structure in the 1650-2000 cm^{-1} region (5-6.1 μm) for monosubstitution of the ring, as well as the features, though less pronounced, already described for the fully nitrated sample. Infrared spectra of 32% and 100% nitrated PS-MAA copolymers were essentially identical to those obtained for the corresponding nitrated styrene polymers, except for an additional carbonyl band at 1740 cm^{-1} (5.75 μm).

It should be noted that the predominant para- nitration observed in the samples supports the assumption, used in the calculations from the NMR integrals, that the nitro group introduced has two neighboring protons on the ring. The assumption would, of course, be invalid if significant amounts of the ortho- isomer, or disubstituted species, were present.

The degree of substitution X(mol%) of the PS-MAA samples was also calculated from the equivalent weights (EW) of the copolymers as determined by titration with the standard 0.05 N NaOH solution, according to the equation

$$X(\text{mol}\%) = \frac{(\text{EW} - 1470) \cdot 100\%}{598} \qquad (\text{Eq.3.2})$$

where 1470 represents the equivalent weight of PS-0.07MAA, and 598 represents the equivalent weight difference between 100% and 0% nitrated polymers. The good agreement between the values determined from the equivalent weight and the NMR results (Table 3.1) provides further support for the assumptions made, and indicates that the methacrylic acid groups were unaffected in the reaction. The accuracy of the NMR

Table 3.1. Comparison of the nitration levels determined by NMR and by titration (recalculated from the EW) of nitrated PS-0.07MAA copolymers.

NMR % NO_2	Titration % NO_2
16.0 ± 0.8	15 ± 9
40 ± 2	38 ± 9
74 ± 4	74 ± 9

technique, resulting from the variations observed in the integrals due to spectrum phasing errors, was estimated to be about 5% of the values determined. The larger errors obtained with the equivalent weights technique arise from the subtraction of the EW of the nitrated material from the EW of PS-0.07MAA, both of similar magnitudes and with relative errors of 1.7%.

3.4.2. Physical properties

The glass transition temperature (T_g) of nitrated polystyrene samples, as determined by DSC, increased monotonically in the 0-100% range (correlation coefficient $r^2 = 0.9994$) with the degree of substitution X(mol%):

$$T_g(^\circ C) = 106.4 + 0.850 \cdot X(\text{mol}\%) \qquad \text{(Eq. 3.3)}$$

Cross-linking problems were first observed on the DSC when samples were left at temperatures of the order of (T_g + 50) °C for about 15 minutes. The T_g of the samples increased by a few degrees, and they became insoluble in DMF. The tendency of nitrated polystyrene samples to cross-link increased with the degree of substitution, as well as with the MAA content, in the case of the copolymers.

The cross-linking problems encountered made it critical to choose the optimum methacrylic acid content for the study. The styrene-sodium methacrylate system is well characterized, with a cluster T_g increasing more rapidly than the matrix T_g, particularly at ion contents greater than 5 mole%[8]. Nitration, on the other hand, shifts the matrix T_g of the materials to higher temperatures, eventually causing the two loss maxima in the tan δ vs. temperature curve to merge when the degree of nitration is increased. It would therefore seem preferable to use a PS-MAA sample with a higher ion content for the study, e.g. 10%, with a matrix T_g of 145 °C and a cluster T_g of 220 °C, according to torsional pendulum measurements[8]. Preliminary work, however, showed that 50% nitrated PS-0.10MAA-Na samples cross-linked when heated to 80 °C for a few hours.

The particular choice of 7% MAA content, with a matrix T_g of ca. 135 °C, and a cluster T_g of ca. 185 °C[8], therefore, represents a compromise between the better spacing of the loss maxima observed at higher ion contents, and the cross-linking tendency of the samples. A range of 0-32% nitration was used in this work, but extended drying periods (2 weeks) at relatively low temperature (100 °C) were needed in order to prevent cross-linking. The equivalence of the extended sample drying periods at a lower temperature with shorter periods at higher temperature (4 days at 150 °C) was demonstrated by comparison of two DMTA runs for the nonnitrated ionomer, which yielded identical results.

A nitration level of 32% raised the relaxed dielectric constant of the PS-0.07MAA-Na ionomer (measured at 200 °C) from 3.2 to 7.3. The corresponding unrelaxed dielectric constants (at room temperature) were 2.9 and 3.7 for the nonnitrated and 32% nitrated ionomers, respectively. The unrelaxed dielectric constant ($\varepsilon = 2.9$) obtained for the PS-0.07MAA-Na sample is consistent with dielectric data varying from $\varepsilon = 2.7$ to 3.2 reported by Hodge and Eisenberg[10] for the same materials with MAA contents from 2 to 9 mole%. Ishida[28], in his dielectric relaxation study of acrylate polymers, reported relaxed and unrelaxed dielectric constants of 7.1 and 4.7, for poly(methyl acrylate) at 100Hz and temperatures of 46.5 and 14.5 °C, respectively. The added nitro groups therefore increase the polarity of the styrene matrix to raise it to a level comparable to the acrylate polymers.

Stress relaxation studies of ethyl acrylate-based ionomer systems[29] have revealed that time-temperature superposition breaks down at ionic concentrations of the order of 12 to 16%. More recently, dynamic mechanical studies of the same materials[24] have shown that the high-temperature loss tangent maximum becomes predominant at ion concentrations of the order of 10-15%. The higher ion content observed in the acrylate ionomers as the onset of cluster-dominated rheological properties, compared to the styrene systems (4-6%), was attributed to their higher dielectric constant.

It therefore seemed reasonable to expect that, if matrix polarity was an important parameter affecting ion aggregation, an increase caused by partial nitration of the matrix should affect aggregation in a similar manner. The higher polarity of the nitrated materials was expected to decrease the proportion of ionic material included in the clusters in favor of the multiplets, affecting at the same time the relative intensities of the two associated loss maxima.

The dynamic mechanical measurements yielded, on the contrary, surprisingly different results. The matrix T_g of the nitrated PS-MAA-Na samples increased, as expected, with increasing nitro group content (Figure 3.2), but the cluster T_g was essentially unaffected, both in shape and in position, by the highly polar nitro groups, even at the upper nitration level. It therefore seems that the polarity of the polymer matrix is not, in itself, a predominant parameter affecting ionic aggregation.

As noted earlier, Bazuin and Eisenberg, in their plasticization study[21], explored the effects of two diluents of a very different nature on the PS-MAA-Na system. Diethylbenzene (DEB), a nonpolar diluent, affected the tan δ peaks associated with the matrix and with the clusters to a similar extent, as demonstrated by the similar decrease in both T_g's observed with increasing DEB concentration (Figure 3.3). Glycerol, a very polar ($\varepsilon = 42.5$ at 25 °C[15]) and strongly hydrogen-bonded diluent, on the contrary, affected preferentially the cluster peak. Considerations of the different nature of nitrobenzene, compared to glycerol, and the unexpected results obtained for the dynamic mechanical properties of the nitrated polymers, led to a plasticization study with that particular diluent. Nitrobenzene is a substance which, apart from its lack of hydrogen-bonding ability, has a high dielectric constant ($\varepsilon = 34.8$ at 25 °C, and 20.8 at 130 °C[15]),

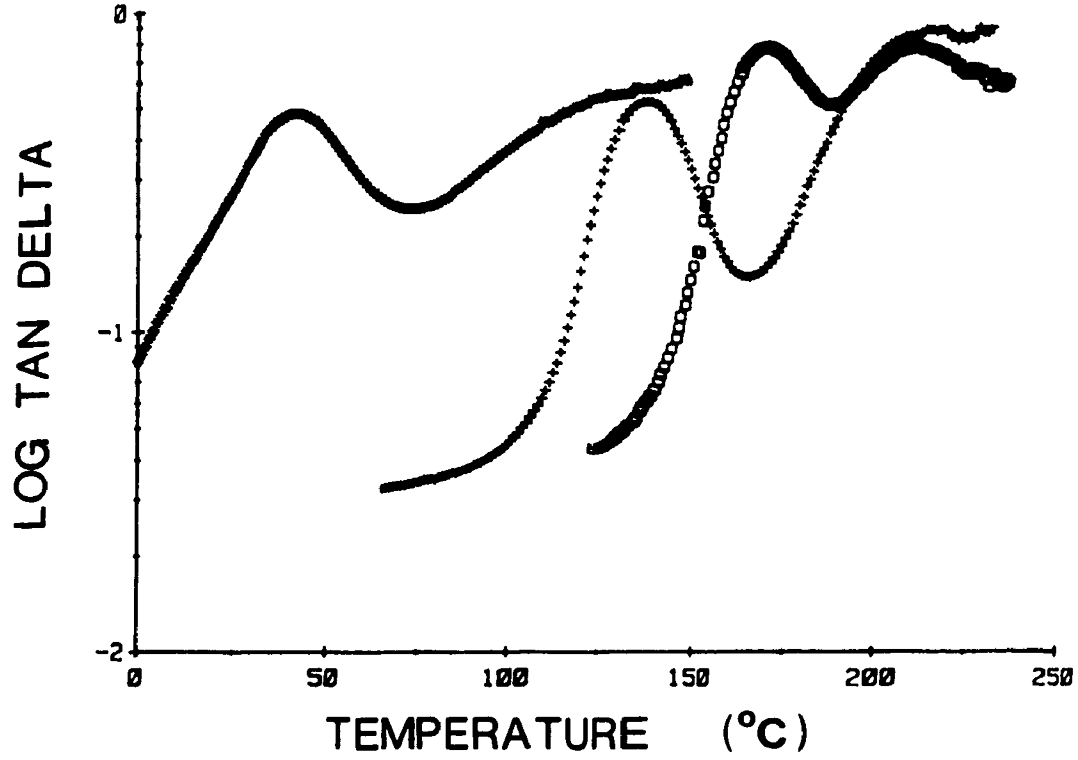


Figure 3.2. Dynamic loss tangent curves of + PS-0.07MAA-Na, O PS-0.07MAA-Na 32% nitrated, * PS-0.07MAA-Na plasticized with 25% mol/mol (30% w/w) nitrobenzene.

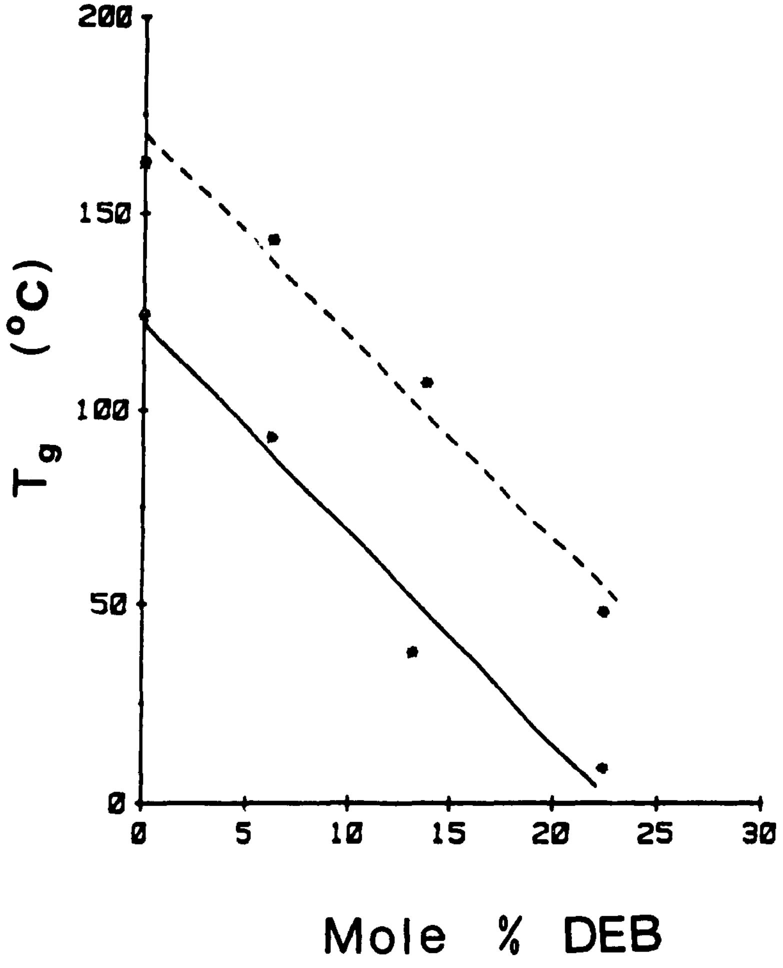


Figure 3.3. Matrix (——) and cluster (----) glass transition temperatures of PS-0.05MAA-Na ionomers plasticized with diethylbenzene, as estimated from Ref. 21.

comparable to glycerol. It is also similar in structure to the nitrated polymer, apart from its additional mobility.

Because cluster structures are known to be highly water-sensitive, the nitrobenzene was carefully dried over phosphorus pentoxide, and sealed immediately afterward in dry ampoules, to avoid absorption of water vapor in the atmosphere. The freeze-dried PS-MAA-Na samples were, like the nitrated ones, further dried at 100 °C for 14 days. One reason to provide the same treatment to the samples is obviously the need for identical sample history. Another reason, less obvious, is that at 100 °C, which is lower than the T_g of the material (ca. 135 °C), the freeze-dried snow does not compact, and therefore absorbs the plasticizer more readily and insures its even distribution.

The effect of nitrobenzene, as compared to nitration, on the glass transition temperatures of the matrix and ion-rich regions, is illustrated in Figure 3.4. Nitrobenzene concentrations of 9.5% and 25% mol/mol were determined from the sample weight difference before the DMTA run, and after drying to constant weight in a drying pistol at 150 °C (DMF) under vacuum. The plasticizer behavior of nitrobenzene is somewhat surprising, when compared to the results of Bazuin and Eisenberg[21]. Nitrobenzene seems to affect the matrix and cluster regions to the same extent, as in the case of diethylbenzene (Figure 3.3). This is particularly interesting, because of the comparable dielectric constants of nitrobenzene and glycerol (ε = 34.8 vs. 42.5, respectively, at 25°C). Thus, nitrobenzene, in spite of its high dielectric constant, acts essentially like a nonpolar plasticizer (diethylbenzene). The plasticizer behavior of nitrobenzene is in marked contrast with glycerol which, apart from depressing the matrix T_g slightly, virtually eliminated the clusters, causing a quick drop in G' above T_g with increasing glycerol concentration.

The programs used in the data analysis were developed by Ms. Susan Williams to compensate for the apparent baseline shift in the tan δ vs. temperature curves obtained on both the torsional pendulum and the DMTA systems. A graphic approach, described in a

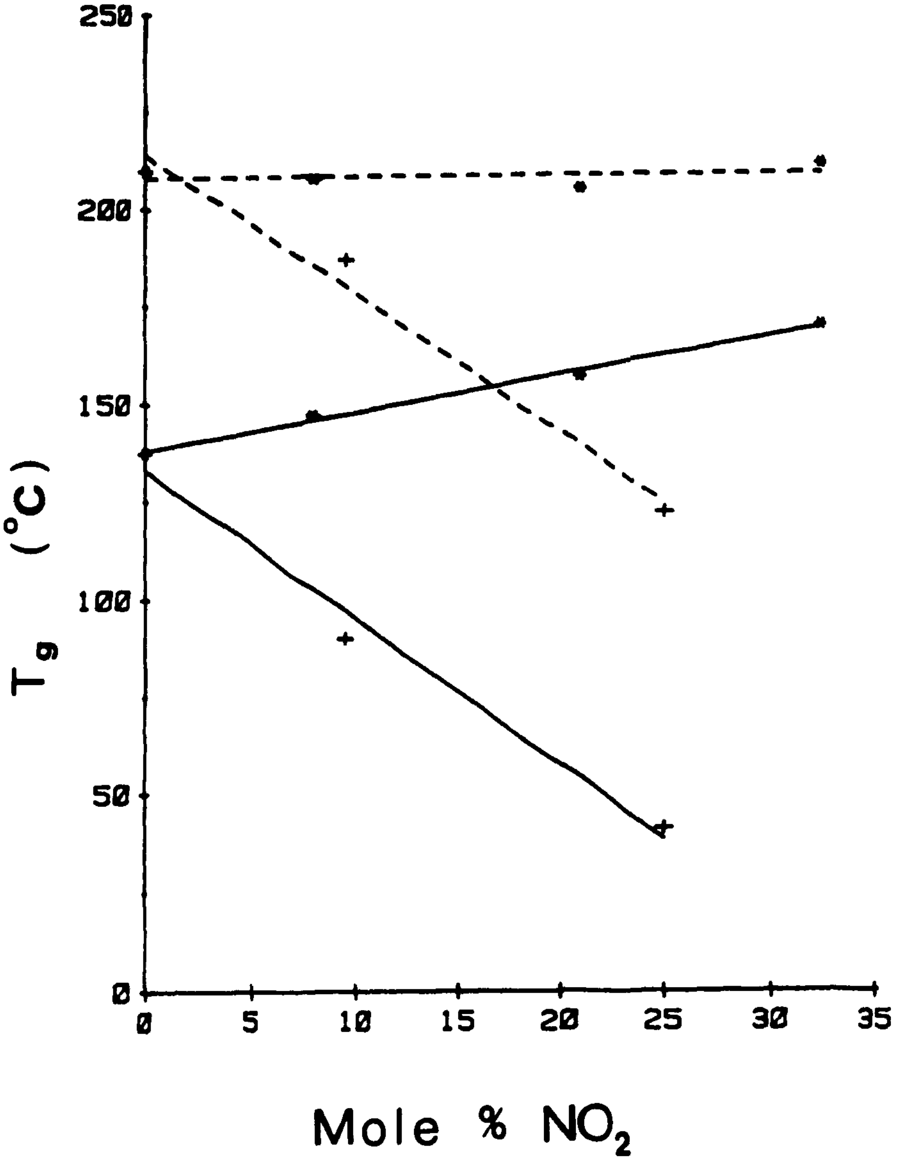


Figure 3.4. Peak positions of the dynamic loss tangent maxima in PS-0.07MAA-Na nitrated (*) and plasticized with nitrobenzene (+) for the matrix (———) and ion-rich domains (-----).

more detailed manner elsewhere[22], is used to subtract a linear or polynomial baseline from a portion of the tan δ curve. Linear baselines were used in this case. The loss maxima generated by the procedure are more symmetrical than the original peaks, and make it easier to locate the maxima and evaluate the width at half height of the peaks.

The value of the storage modulus E'_{in} at the inflection point of the rubberlike plateau was used to calculate the average molecular weight between cross-links according to the equation[30]

$$M_c = \frac{3 \rho R T_{in} v_2^{1/3}}{E'_{in}} \qquad \text{(Eq. 3.4)}$$

as reported in Table 3.2.

Table 3.2. Average molecular weight between cross-links calculated from the storage modulus at the inflection point of the rubberlike plateau for nitrated and plasticized PS-0.07MAA-Na ionomers.

Nitrated		Plasticized	
% NO_2 (mol/mol)	M_c (g/mol)	% NO_2 (mol/mol)	M_c (g/mol)
8.0	460	0	300
21	370	9.5	430
32	490	25	760

The evaluation of E'_{in} was done with the help of another function of the data analysis programs developed. A polynomial curve (typically of order 8) was fitted to a portion of the experimental data points, and the second derivative of the curve scanned for the inflection point. Both the inflection temperature (T_{in}) and modulus (E'_{in}) were thus obtained. The value $\rho = 1.05 \times 10^3$ kg/m^3 for the density of polystyrene[31] was used as an approximation for the ionomers. The correction factor involving v_2 (volume fraction of polymer) was used for the plasticized samples.

The theoretical M_c value calculated for strictly multiplet-type interactions was 1470 g/mol. The experimental values reported in Table 3.2 show no significant trend for the nitrated ionomers. This is consistent with the constant appearance of the cluster peak observed in the loss tangent curves of both the 32% nitrated and the nonnitrated PS-0.07MAA-Na ionomers (Figure 3.2), and reflects a comparable relative distribution of ions in the matrix and ion-rich phases of both samples. The plasticized ionomers, however, show a clearly increasing trend for M_c. This is similar to the observations made by Bazuin and Eisenberg[21] for PS-0.05MAA-Na samples plasticized with diethylbenzene, and attributed to the progressive destruction of the network by dilution with the plasticizer.

The plasticizer loss studies show significant losses of nitrobenzene by the end of the run. The 25% mol/mol (30% w/w) sample, which was tested in the 60 to 250 °C range at a heating rate of 1 °C/minute had lost, by the end of the run (250 °C), 42% of the plasticizer initially present. The more detailed study performed on another 10%-plasticized sample (actually 10.3% mol/mol), however, showed that by the time the sample reached 185 °C, which is the glass transition temperature associated with the ion-rich domains at 1 Hz, only 25% of the plasticizer was lost. The losses should have been even less important by the time the 25%-plasticized PS-MAA-Na sample reached its cluster T_g (122 °C).

The results obtained for both the nitrated and the nitrobenzene-plasticized PS-MAA-Na systems can be rationalized in terms of the relative importance of polarity versus specific interaction effects.

As pointed out earlier, the delocalization of the negative end of the dipole on the nitro group has been suggested to explain the poor ion-solvating ability of compounds like nitrobenzene[20]. In a first attempt to rationalize the present results, classifications of solvents in terms of their solvating power were identified. Although many empirical scales have been suggested[32], there is no general systematic approach to the problem. In particular, most of the suggested scales are derived from the study of very specific systems and have the tendency not to distinguish between polarity and specific interaction contributions to solvation. The relative importance of polarity in affecting the course of chemical reactions -- often including a partly or completely ionic transition state -- was very much disparaged by Dack[33]. His argument is that the polarity felt by polar or ionic species on a microscopic level is very different from the bulk property measured. This phenomenon, referred to as dielectric saturation, occurs when an ion, for example, is solvated by a polar solvent. The dipoles of the solvent molecules align themselves around the ion and partly cancel each other's contribution. Theoretical calculations by Ritson and Hasted[34] based on a few models have shown that while the bulk dielectric constant of water is 78.54, its microscopic dielectric constant within 1.5 Å (0.15 nm) of an ion is about 5. The bulk value is regained at about 4 Å (0.4 nm) from the ion. The same alignment phenomenon may cause solvent molecules as different as methanol ($\varepsilon = 32.6$) and acetone ($\varepsilon = 20.7$) to have very similar microscopic dielectric constants[33].

It seemed therefore preferable to try to separate, as much as possible, polarity effects from specific interactions, which is not achieved with the empirical scales mentioned above. A more quantitative measure of the relative importance of polar versus specific interaction effects may be obtained from cohesive energy density (CED) data for solvents, in the form of three-dimensional solubility parameters[35], of which several relevant examples are given in Table 3.3. The total CED (δ_o) is actually a measure of the energy required to vaporize 1 mL (10^{-6} m^3) of the solvent at zero pressure, i.e. without PV work. It may be decomposed into three components, related to dispersive forces (δ_d), polar (δ_p) and specific interaction or hydrogen-bonding (δ_h) contributions related to δ_o through the equation

$$\mathrm{CED} = \delta_o^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad \text{(Eq. 3.5).}$$

A comparison of the δ_o values reported for hexane, benzene, ethyl acetate, methanol and water show an intuitively expected increase in δ_o, but also points at the considerable variations encountered in the relative magnitudes of the δ_d, δ_p and δ_h parameters. While specific interaction effects account for less than 2% of the total CED (δ_o^2) of benzene, they account for more than 50% of the CED of methanol. Although

Table 3.3. Solubility parameters of solvents and polymers $(\mathrm{J{\cdot}m^{-3}})^{1/2}{\cdot}10^{-3}$ (from Ref. 35).

Substance	δ_o	δ_d	δ_p	δ_h
Hexane	30.3	30.2	0	0
Benzene	38.3	37.4	2.1	4.2
Ethyl acetate	38.1	31.1	10.9	18.8
Nitrobenzene	44.4	36.0	25.1	8.4
Methanol	61.9	31.0	25.1	45.6
Glycerol	88.3	35.4	?	?
Water	98.3	25.1	62.8	69.9
Polyethylene	33.1	--	--	--
Polystyrene	38.1	--	--	--
Poly(ethyl acrylate)	39.1	--	--	--

three-dimensional solubility parameters are not available for polymers, the value of $\delta_o = 39.1$ for poly(ethyl acrylate) is very comparable to $\delta_o = 38.1$ for ethyl acetate. The comparison of ethyl acetate, as a model compound for poly(ethyl acrylate), to nitrobenzene ($\delta_0 = 44.4$) show a similar overall CED. The individual components are, however, quite different. While the two substances have comparable dispersive force components, the balance of the polarity and specific interaction-associated effects are mostly due to polarity in the case of nitrobenzene, and to specific interactions for ethyl acetate.

Further support for the specific interactions concept can be found in the literature. Kay et al.[36] used conductometry to study alkali perchlorate solutions in acetonitrile and compared them with similar measurements in alcohols. They concluded that in the case of small ions (e.g. sodium), the acid/base (or donor/acceptor) character of the solvent was predominant in determining the extent of ion solvation. For larger ions such as cesium, the greater ability of the solvent molecules to approach cations make ion-dipole interactions more important in the solvation process. The donor/acceptor character of solvents was also found important by Mayer et al.[37] in their study of the dissociation of quinuclidinium chloride in different solvents, including nitrobenzene. The exceptionally low dissociation constant observed in nitrobenzene was attributed to its weak donor and acceptor character.

It seems likely, from the data presented above, that the unexpected effects observed in both the nitrated and nitrobenzene-plasticized PS-MAA-Na ionomers are a direct result of the low degree of specific interactions, rather than due to polarity effects. Apart from specific interactions, it seems reasonable to assume that another factor not examined here, namely structural (steric) effects, may have some influence on clustering.

3.5. Conclusions

The results of this work have shown that the dielectric constant of the polymer matrix is not, by itself, a predominant factor controlling ionic aggregation. The nitration of styrene-sodium methacrylate copolymers has no effect on clustering in the 8-32%

range, in spite of the increased dielectric constant of the materials ($\varepsilon = 7.3$ at 200 °C for 32% NO_2).

A parallel plasticization study with nitrobenzene indicated that the ion-rich domains were affected to the same extent as the matrix, as already reported for nonpolar plasticizers. In spite of its high polarity, nitrobenzene behaves very differently from glycerol, also a polar substance which plasticizes the ion-rich domains much more than the matrix. The presence of specific interactions, therefore, seems to be a more important parameter than polarity alone in determining the plasticizer effect of added diluents.

A nitration technique was also suggested which allows control of the degree of nitration in the 0-100% range for polystyrene and styrene-methacrylic acid copolymers. The T_g of nitrated polystyrene increased linearly with the nitration level.

3.6. Acknowledgements

Funding for this work was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC). One of the authors (M.G.) would also like to acknowledge the financial support of NSERC and of the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (Quebec).

3.7. References

(1) (a) *Ionic Polymers*; Holliday, L., Ed.; Applied Science: London, 1975. (b) Bazuin, C.G.; Eisenberg, A. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 271. (c) MacKnight, W.J.; Earnest, T.R., Jr. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.

(2) Eisenberg, A.; King, M. *Ion-Containing Polymers*; Academic: New York, 1977.

(3) (a) Weiss, R.A.; MacKnight, W.J.; Lundberg, R.D.; Mauritz, K.A.; Thies, C.; Brant, D.A. In *Coulombic Interactions in Macromolecular Systems*; Eisenberg, A., Bailey, F.E., Eds.; ACS Symposium Series 302; American Chemical Society: Washington, DC, 1986; pp 2-19. (b) Lundberg, R.D. In *Structure and Properties*

of Ionomers; Pineri, M.; Eisenberg, A., Eds.; NATO ASI Series C Vol. 198; Reidel: Dordrecht, Holland, 1987; pp 429-438. (c) Tan, J.S. *Ibid.* pp 439-451.

(4) (a) Rees, R.W.; Vaughan, D.J. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1965**, *6(1)*, 287. (b) Rees, R.W.; Vaughan, D.J. *Ibid.* **1965**, *6(1)*, 296.

(5) Eisenberg, A. *Macromolecules* **1970**, *3*, 147.

(6) (a) MacKnight, W.J.; Taggart, W.P.; Stein, R.S. *J. Polym. Sci., Polym. Symp.* **1974**, *45*, 113. (b) Yarusso, D.J.; Cooper, S.L. *Macromolecules* **1983**, *16*, 1871.

(7) Pineri, M.; Meyer, C.; Levelut, A.M.; Lambert, M. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 115.

(8) Navratil, M.; Eisenberg, A. *Macromolecules* **1974**, *7*, 90.

(9) (a) Neppel, A.; Butler, I.S.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 2145. (b) Neppel, A.; Butler, I.S.; Eisenberg, A. *Macromolecules* **1979**, *12*, 948.

(10) (a) Phillips, P.J.; MacKnight, W.J. *J. Polym. Sci., Part A-2* **1970**, *8*, 727. (b) Hodge, I.M.; Eisenberg, A. *Macromolecules* **1978**, *11*, 283.

(11) See for example Reference 8 or 1(c).

(12) (a) Navratil, M.; Eisenberg, A. *Macromolecules* **1974**, *7*, 84. (b) Makowski, H.S.; Lundberg, R.D.; Westerman, L.; Bock, J. In *Ions in polymers*; Eisenberg, A., Ed.; Advances in Chemistry 187; American Chemical Society: Washington, DC, 1980; pp 3-19.

(13) Brockman, N.L.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1145.

(14) (a) Lundberg, R.D.; Makowski, H.S. In *Ions in polymers*; Eisenberg, A., Ed.; Advances in Chemistry 187; American Chemical Society: Washington, DC, 1980; pp 21-36. (b) Rigdahl, M.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1641. (c) Fitzgerald, J.J.; Weiss, R.A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 99.

(15) *CRC Handbook of Chemistry and Physics, 61st ed.*; Weast, R.C., Astle, M.J., Eds.; Chemical Rubber Company: Boca Raton, 1981; p E-56.

(16) Seliger, H. *Makromol. Chem.* **1973**, *169*, 83.

(17) (a) Bachman, G.B.; Hellman, H.; Robinson, K.R.; Finholt, R.W.; Kahler, E.J.; Filar, L.J.; Heisey, L.V.; Lewis, L.L.; Micucci, D.D. *J. Org. Chem.* **1947**, *12*, 108. (b) Zenftman, H. *J. Chem. Soc.* **1950**, 982. (c) Blanchette, J.A.; Cotman, J.D., Jr. *J. Org. Chem.* **1958**, *23*, 1117.

(18) Bajaj, I.; Kapoor, S.K.; Chatterjee, S.R. *Def. Sci. J.* **1968**, *18*, 89.

(19) (a) Crivello, J.V. *J. Org. Chem.* **1981**, *46*, 3056. (b) Crivello, J.V. U.S. Patent 3 715 323, 1973; Chem. Abstr. **1973**, *78*, 111976c.

(20) Burgess, J. *Metal ions in solution*; Ellis Horwood: Chichester, 1978; p 30.

(21) Bazuin, C.G.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1137.

(22) Gauthier, M.; Eisenberg, A. To be published.

(23) Flory, P.J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, 1953; p 140.

(24) Simmons, A.H. M.Sc. Thesis, McGill University: Montreal, October 1986.

(25) Navratil, M.; Eisenberg, A. *Macromolecules* **1973**, *6*, 604.

(26) Pasto, D.J.; Johnson, C.R. *Organic Structure Determination*; Prentice-Hall: Englewood Cliffs, 1969; Chapter 4.

(27) (a) Rafikov, S.R.; Ergozhin, E.E. *Dokl. Chem. (Engl. Transl.)* **1968**, *181*, 708; *Dokl. Akad. Nauk SSSR* **1968**, *181*, 899. (b) Rondestvedt, C.S., Jr.; Jeffrey, J.R.; Miller, J.E. *Ind. Eng. Chem. Prod. Res. Dev.* **1977**, *16*, 309.

(28) Ishida, Y. *Kolloid Z.* **1961**, *174*, 124.

(29) Eisenberg, A.; Matsuura, H.; Tsutsui, T. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 479.

(30) Treloar, L.R.G. *The Physics of Rubber Elasticity*; Oxford University: Oxford, 1958; Chapter 9.

(31) Rudd, F.J. In *Polymer Handbook, 2nd ed.*; Brandrup, J., Immergut, E.H., Eds.; Wiley: New York, 1974; p V-59.

(32) Reichardt, C. *Angew. Chem. Internat. Ed.* **1965**, *4*, 29.

(33) Dack, M.R.J. In *Techniques of Chemistry Vol. VIII. Solutions and Solubilities Part II*; Dack, M.R.J., Ed.; Wiley: New York, 1976.

(34) Ritson, D.M.; Hasted, J.B. *J. Chem. Phys.* **1948**, *16*, 11.

(35) Burrell, H. In *Polymer Handbook, 2nd ed.*; Brandrup, J., Immergut, E.H., Eds.; Wiley: New York, 1974; p IV-337.

(36) Kay, R.L.; Hales, B.J.; Cunningham, G.P. *J. Phys. Chem.* **1967**, *71*, 3925.

(37) Mayer, U.; Gutmann, V.; Kösters, K. *Monatsh. Chem.* **1976**, *107*, 845.

Chapter 4. Alkylated styrene ionomers with variable length spacers. I. Synthesis

4.1. Abstract

Two analogous series of ionomer precursors based on 4-substituted styrene copolymers were prepared with substituents R = $-(CH_2)_nCO_2Me$ (n = 1, 5, 10), or R = $-O(CH_2)_nCO_2Me$ (n = 1, 4, 10), and degrees of substitution from 10 to 15 mole%. The synthesis of the alkyl series compounds involved either chloromethylation of polystyrene or bromoalkylation via lithiation of a styrene-4-bromostyrene copolymer, followed by conversion to the nitriles. Methyl esters were then produced by reaction of the nitriles with methanol/HCl gas. The ether series compounds were obtained directly by reacting a styrene-4-hydroxystyrene copolymer with the methyl esters of the corresponding ω-bromoaliphatic carboxylic acids in a Williamson ether-type synthesis.

4.2. Introduction

Functionalized polymers, both soluble and cross-linked, have recently found multiple applications as polymeric reagents, protecting groups and in the field of catalysis[1]. Originally limited to ion-exchange resins[2], their use for polymer-supported polypeptide synthesis, suggested by Merrifield[3], revolutionized the area. The interest in these materials is partly justified by the ease of isolation of the products formed in a polymer-supported reaction, especially in the case of cross-linked resin systems. Likewise the desire to develop reaction schemes analogous to those found in small molecules stimulated research in the field[4].

Polystyrene, among others, has been a substrate of choice in the preparation of functionalized polymers, because of its stable backbone and the ease of electrophilic aromatic substitution on the pendant rings. It appears, however, that insoluble supports (typically polystyrene cross-linked with 1-2 mole% of divinylbenzene) have received far more attention than soluble polymers. This could be explained by their greater ease of recovery, but also by the sometimes less demanding reaction conditions required in the functionalization of cross-linked polymer resins, particularly when it comes to limiting side reactions which may lead to cross-linking of soluble polymers.

Two main routes have been used to produce reactive polymers. Direct copolymerization of the corresponding monomers is of limited usefulness, due to frequently unfavorable copolymerization reactivity ratio (r_1, r_2) values. Thus, functionalization in the form of postpolymerization modifications is sometimes the preferred approach. An alternate synthetic route may, of course, involve copolymerization followed by further chemical modifications of the reactive comonomer. One advantage of the copolymerization technique is that the products have a more rigorously defined structure than those obtained in a postpolymerization reaction, which is subject to the selectivity of the reagents used. Consequently, isomer mixtures are often obtained in postpolymerization modifications involving direct functionalization of the polymer support.

One notably interesting application of soluble functionalized polymers pertains to the field of ionomers[5], consisting typically of organic polymers containing up to ca. 15 mole% of ionic units. The aggregation of the ions in the relatively nonpolar polymer matrix has led to new materials with greatly modified properties[6] which have already found multiple applications[7]. Two areas of ionomer research are particularly active at present. The first involves the determination of the morphology of ionomer systems, namely the structure of the ionic aggregates formed. The second involves structure-mechanical properties correlations, aiming essentially at producing tailor-made ionomers for specific applications.

In an effort to study the effects of the distance of the pendant ions from the polymer backbone on physical properties, two series of styrene ionomer precursors were produced in this work. One series involves carboxylate-terminated n-alkyl chains in the para- position of styrene, the total side chain length varying from 2 to 11 carbon units. The other consists of analogous compounds where the alkyl chain is attached through an ether linkage, rather than directly to the styrene ring. The compounds, which are obtained as methyl esters, can be hydrolyzed with a base to different extents, in order to produce ionomers of varying ion contents. A study of the dynamic mechanical properties, and a Small-Angle X-ray Scattering (SAXS) examination of ion aggregation in these ionomers will be presented in subsequent papers[8].

One reason for the interest in these materials are recent developments in the field of permselective membranes[9]. Perfluorinated polymers bearing sulfonate groups are now widely used as membrane separators in the production of chlorine and sodium hydroxide by electrolysis of sodium chloride solutions (chlor-alkali process). Several perfluorinated membrane materials are commercially available, of which some have long spacers for the pendant ionic groups, similar to the compounds prepared here. The fact that the present polymers are new materials also justifies their study.

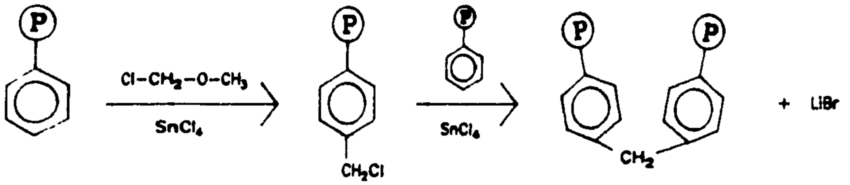
Other possible applications of the present polymers concern, among others, the intermediate bromoalkylated systems. These can indeed undergo easy nucleophilic displacement by a wealth of reagents, in analogy to the widely used chloromethylated polystyrene. The advantages of separating the reactive center from the benzene ring in functionalized styrene reagents were pointed out by a few authors[10,11]. Polymer stability was expected to be improved, compared to benzylic analogues, by incorporating alkyl chain spacers in polystyrene-supported reagents. Improved yields were also obtained in the polymer-supported reactions, presumably because of the increased mobility of the functional group-bearing chains[10,11]. These effects are obtained in the polymers prepared here, and suggests their possible usefulness as polymeric reagents.

4.2.1. Synthetic Approach - Alkyl Series

The emphasis was set on developing a general approach to attach alkyl chains of variable length (C_1 - C_{10}) in the para- position of styrene rings, eventually to produce the desired carboxylated ionomers. The attachment of linear ω-haloalkyl chains to the polymer, followed by conversion to nitriles, and then to the carboxylic acids thus seemed to be a reasonable synthetic route.

Procedures sometimes involving multistep reactions, depending on the starting materials available, have been suggested[11,12] to produce 4-(ω-bromoalkyl)styrene monomers with spacer lengths ranging from 2 to 7 carbon atoms. The postpolymerization modification approach was preferred here, because of its greater versatility, allowing the preparation of copolymers with different spacer lengths from the same parent 4-bromostyrene copolymer. An efficient technique recently suggested[13] to introduce 2-bromoethyl groups in cross-linked polystyrene involves the reaction of the lithiated polymer with ethylene oxide to produce the 2-hydroxyethyl derivative. The bromide is obtained by tosylation of the hydroxyethyl groups followed by displacement of the tosylate with magnesium bromide. The applicability of the technique is unfortunately limited to the C_2 derivative.

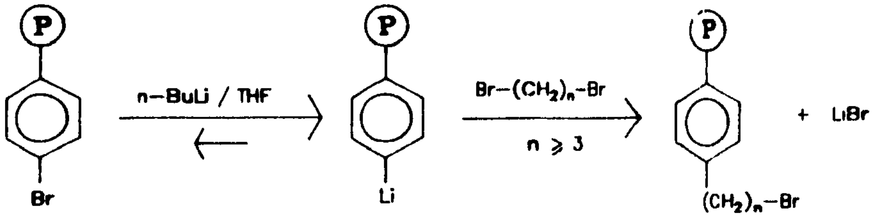
Chloromethylation with chloromethyl methyl ether is undoubtedly the most widely used route to functionalize polystyrene. Although it is a standard procedure, it is known to be difficult to control[14] and, depending on the reaction conditions used, may lead to cross-linking through electrophilic attack of the newly formed benzyl chloride groups on other styrene units:



(Eq. 4.1)

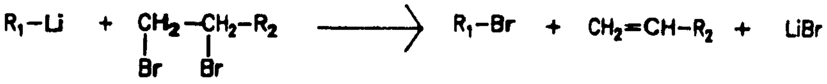
This side reaction is limited, however, when lower polymer concentrations and conversions are used[15]. Chloromethylation in the presence of stannic chloride is known to yield predominantly (ca. 95%) the para- isomer[16] and was the preferred technique to produce the C_2 carboxylic acid from styrene homopolymer.

The bromoalkyl compounds were prepared via lithiation of a styrene-4-bromostyrene copolymer, followed by reaction with a large excess of an α,ω-dibromoalkane:



(Eq. 4.2)

This approach has been suggested by Farrall and Fréchet[17] to produce cross-linked polystyrene resins with pendant bromoethyl groups via lithiation and reaction with 1,2-dibromoethane. However, attempts in this laboratory to adapt the reaction conditions for soluble styrene-4-bromostyrene copolymers were unsuccessful. A survey of the literature of organolithium compounds suggested that 1,2-dibromoalkyl compounds undergo an easy, efficient elimination reaction with organolithium compounds in general, and have been suggested as one step in the titration of solutions of organolithium compounds[18]:



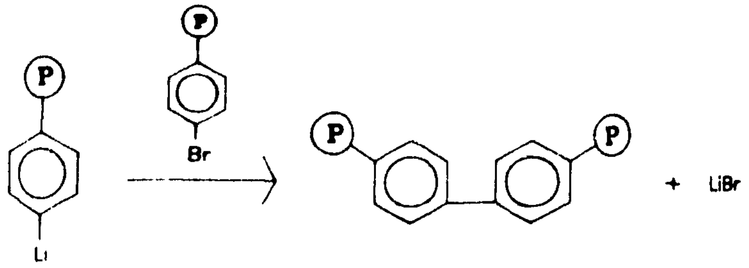
$$R_1\text{–}Li + \underset{Br}{CH_2}\text{–}\underset{Br}{CH}_2\text{–}R_2 \longrightarrow R_1\text{–}Br + CH_2{=}CH\text{–}R_2 + LiBr$$

(Eq. 4.3)

R_1 = alkyl, aryl

R_2 = alkyl

Lithiation of cross-linked polystyrene resins is now known as a routine step in the preparation of many functional polymers[17,19]. Soluble polymers, on the other hand, lead to additional experimental problems in that the lithiation via metal-halogen exchange, originally suggested by Braun[20], of halogenated styrene copolymers may very easily lead to cross-linking in a Wurtz-Fittig coupling reaction:



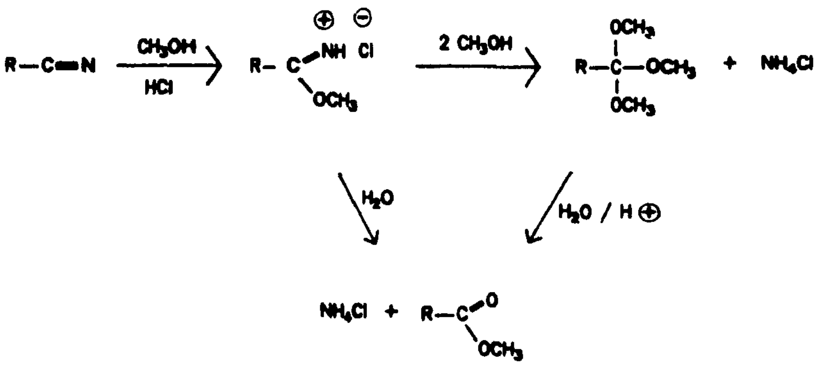
(Eq. 4.4)

Other authors[21,22] have also put much emphasis on the need to work with large (40-fold) excesses of n-butyllithium and the slow addition of dilute polymer solutions with vigorous stirring to avoid that problem in the lithiation of soluble styrene polymers.

Lithiated polystyrene has also been obtained by direct metalation with a n-butyllithium-N,N,N',N'-tetramethylethylenediamine (TMEDA) complex[23]. However, a mixture of the meta- and para- isomers was produced in the ratio 2:1 in that case[24]. The metal-halogen exchange approach was therefore preferred to produce ionomers with better defined characteristics for the structure-properties study.

The conversion of the haloalkyl groups to nitriles involved a simple nucleophilic displacement of bromide (or chloride) by the cyanide ion.

The direct hydrolysis of nitrile groups in the presence of sulfuric acid/water was used by Kusama and Hayatsu[25] for cross-linked polystyrene resins. Similar reaction conditions used for soluble polymers, however, yielded only insoluble products. A different approach was therefore necessary for soluble polymers. The use of hydrogen chloride gas and methanol was suggested a long time ago to convert alkyl nitriles directly to methyl esters[26] or ortho esters[27] via an iminoether hydrochloride intermediate, depending on the presence or absence of water in the reaction:

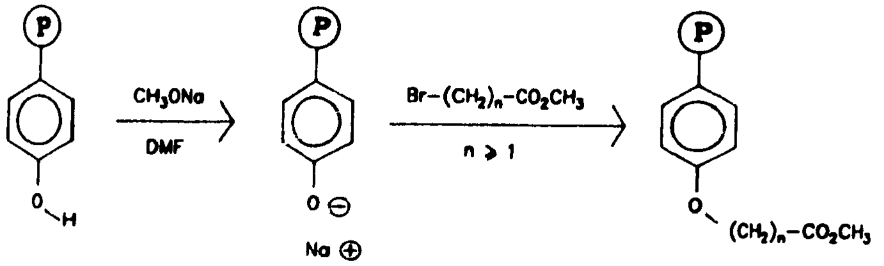


(Eq. 4.5)

While in the preparation of the ortho ester the iminoether hydrochloride intermediate is isolated, this is not deemed necessary in the case of the ester, and the conversion can be carried out in a single step. It is believed to be the first time that this reaction is applied to functionalized polymers to produce carboxylic acid esters without requiring the more vigorous reaction conditions needed for the hydrolysis of nitriles.

4.2.2. Synthetic approach - Ether series

The application of the Williamson ether synthesis in phase transfer reactions to the functionalization of polystyrene resins has already been reported[28]. However, the conditions suggested, involving relatively large excesses (10-fold) of reagents, were found to be impractical for soluble polymers. While the original reaction worked well for allyl bromide[28], these strongly basic (potassium hydroxide/water) conditions used caused quick hydrolysis of the ester reagents and/or the polymer-supported products, leading to reduced conversion and difficulty in isolating the polymer. A new set of reaction conditions involving close to equimolar reagent ratios in the absence of water were therefore developed to yield polymers with high degrees of substitution in an easy reaction:



(Eq. 4.6)

The styrene-4-hydroxystyrene copolymer itself was obtained by demethylation of a styrene-4-methoxystyrene copolymer with boron tribromide at low temperature, according to a known procedure[29]. Substitution was complete, within error limits, after three cycles of reaction and polymer isolation. The hydrolysis of the ester group was minimized by using anhydrous conditions. The procedure suggested here was used to generate ethers with chain lengths ranging from C_2 to C_{11}.

4.3. Experimental

4.3.1. Equipment

The ^{1}H NMR spectra used to characterize all the polymers and products prepared were recorded in deuterated chloroform at 45 °C on a 200 MHz Varian XL-200 Fourier Transform spectrometer. All chemical shifts reported are downfield with respect to tetramethylsilane (TMS) used as an internal standard. Infrared spectra were recorded using films on an Analect AQS-40 FT-IR spectrometer with a resolution of 4 cm^{-1}. Polymer films were obtained by compression molding of 0.05 g of material at 150 °C and ca. 10 MPa for 5 minutes between aluminum plates covered with aluminum foil.

The molecular weight distribution of the polymer samples was determined with a Varian 5000 Liquid Chromatograph system in the Gel Permeation Chromatography (GPC) mode. Two Waters Associates µStyragel (10^4 Å and 10^5 Å) columns were used in series to cover a molecular weight range of 10^4 to 10^6 g/mol with GPC-grade tetrahydrofuran (THF) used as eluent. A narrow molecular weight standards calibration technique was used with polystyrene standards ranging from 1×10^4 to 7.8×10^5 g/mol.

A special flask (Figure 4.1) was designed to allow the quick addition of 1,5-dibromopentane or 1,10-dibromodecane in the synthesis of poly(styrene-co-4-(5-bromopentyl) styrene) and poly(styrene-co-4-(10-bromodecyl)styrene) from lithiated polystyrene. The three-neck flask had one of its arms bent to 60° to allow free rotation of the modified retort-type flask to quickly transfer its content to the reaction mixture by blowing dry nitrogen through a stopcock attached on the retort. It was thus possible to add dibromoalkyl reagent volumes of the order of 400 mL to the three-neck flask in a few seconds.

4.3.2. Reagent Purification

Styrene (Aldrich, 99%) inhibited with 10-15 ppm 4-t-butylcatechol was washed three times with a 5 % aqueous sodium hydroxide solution to remove the inhibitor. The organic phase was dried over calcium hydride (Aldrich, 95+%, 40 mesh) overnight, and distilled at reduced pressure (b.p. 47-48 °C/22 mm). The other monomers, uninhibited 4-bromostyrene (Polysciences) and 4-methoxystyrene (ICN Pharmaceuticals) were both distilled at reduced pressure (b.p. 69 °C/3.2 mm and 55-56 °C/2 mm, respectively). All monomers were stored at -20 °C for at most one week before use.

Tetrahydrofuran and 1,4-dioxane (A&C American Chemicals reagents) were purified immediately before use by refluxing for a few hours and distilling over lithium aluminum hydride (Anachemia). Tetrahydrofuran was initially purified by refluxing with potassium metal and benzophenone; this technique was, however, later abandoned in view of the equivalent results obtained with the safer lithium aluminum hydride approach. Chloroform and methylene chloride (A&C reagents) were dried by refluxing and distilling over phosphorus pentoxide (Anachemia). N,N-dimethylformamide (A&C reagent), used in the Williamson ether synthesis, was dried over calcium hydride and

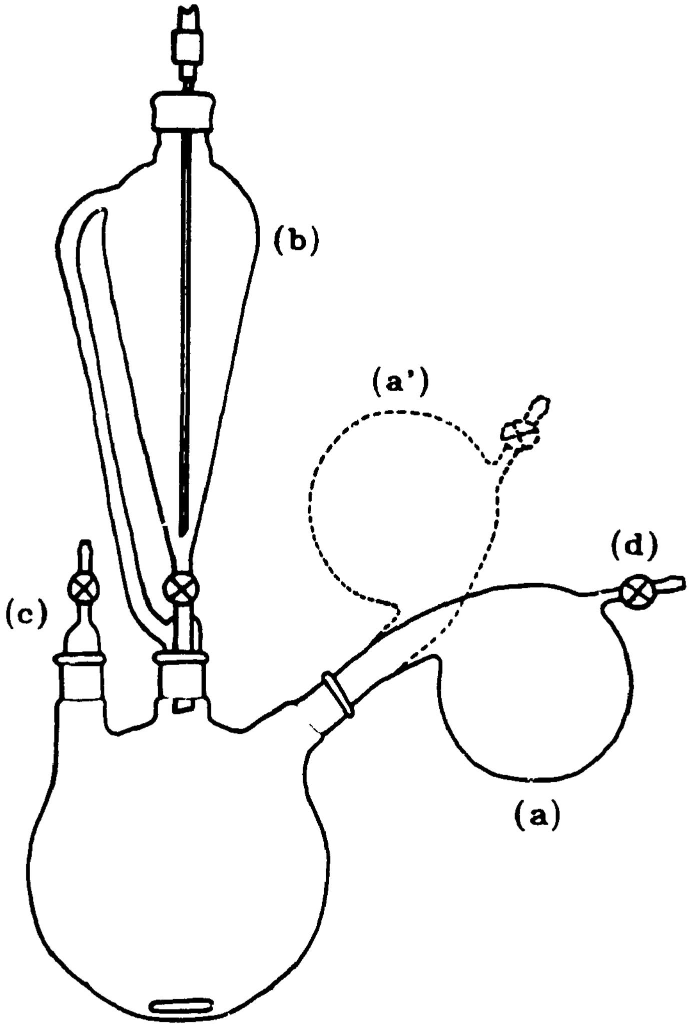


Figure 4.1. Setup used in the preparation of the C_5 and C_{10} bromoalkylstyrene copolymers. In the first part of the reaction (lithiation), the retort-type addition flask (a) is replaced with a rubber septum. System purging is effected with dry nitrogen through the septum of addition funnel (b) with purging stopcock (c) open. Polymer dissolution is achieved in the same way, after adding dry tetrahydrofuran to the funnel. The quick addition of the dibromoalkyl compound is done by rotating the retort from its lower (a) to its higher (a') position, with a dry nitrogen flow through inlet (d), the purging stopcock (c) being temporarily taken off.

distilled at reduced pressure (47-48 °C/14 mm). 1,5-dibromopentane (DBP; Aldrich, 97%) and 1,10-dibromodecane (DBD; Aldrich, 97%) were dried over type 3A molecular sieves (Aldrich) for two days. The organic phase was then decanted and distilled at reduced pressure (b.p. 92-93 °C/10 mm and 136-137 °C/2 mm for DBP and DBD, respectively). All other reagents were used as received from the suppliers.

A solution of sodium cyanide 8% w/v in N,N-dimethylformamide/water was prepared by dissolving 40 g of sodium cyanide (Anachemia) in 80 mL of distilled water, then adding 400 mL of N,N-dimethylformamide.

4.3.3. Preparation of styrene homopolymer

Styrene monomer was bulk polymerized in an ampoule at 60 °C with benzoyl peroxide (6.66 g/L), to yield a polymer with a molecular weight of approximately 10^5 g/mol[30]. The ampoule was degassed, prior to polymerization, with 3 freeze-thaw cycles, and sealed[31]. Conversion was about 50% of the monomer weight. The polymer was recovered by dilution with toluene and precipitation in methanol.

4.3.4. Preparation of poly(styrene-co-4-bromostyrene)

Styrene (119.5 g) and 4-bromostyrene (30.5 g) monomers were mixed with benzoyl peroxide (1.49 g) according to calculations for a bromostyrene content of 16.5 mole% using monomer reactivity ratios $r_1 = 0.99$ (4-bromostyrene) and $r_2 = 0.695$ (styrene)[32]. Conversion was 80%, for a calculated copolymer composition heterogeneity of 40%[33]. The copolymer was recovered in the same manner as polystyrene; its bromostyrene content was evaluated to be 13.8 mole% by IR spectroscopy from the ratio of the integrated intensities for the peaks at 1007 cm^{-1} (9.93 μm) and 1027 cm^{-1} (9.74 μm).[22]

4.3.5. Preparation of poly(styrene-co-4-methoxystyrene)

Styrene (236 g) and 4-methoxystyrene (60 g) monomers were mixed with benzoyl peroxide (0.54 g) for a methoxystyrene content of 15 mole% using copolymerization reactivity ratios $r_1 = 0.93$ (4-methoxystyrene) and $r_2 = 1.13$ (styrene)[34]. Conversion was about 60 % for a calculated composition heterogeneity of 1.6%. The methoxystyrene content of the copolymer was evaluated by NMR spectroscopy from the ratio of the integrated methoxy peak ($\delta = 3.75$ ppm) to the aromatic protons ($\delta = 6.0$-7.8 ppm) to be 15.0 mole%.

4.3.6. Preparation of poly(styrene-co-4-hydroxystyrene)

The styrene-4-methoxystyrene copolymer was demethylated with boron tribromide (Aldrich, 99.99%) in dry methylene chloride at low temperature (methanol/dry ice bath, ca. -77 °C) according to a procedure suggested by Clas and Eisenberg[29]. Completion of the reaction was confirmed by the disappearance of the methoxy peak ($\delta = 3.75$ ppm) in the NMR spectrum of the product.

4.3.7. Chloromethylation of polystyrene

Dry polystyrene (12 g, 115 mmol of styrene units) was loaded in a 500 mL round-bottomed flask and dissolved in 240 mL of dry chloroform. Technical grade chloromethyl methyl ether (4.5 mL, 59.0 mmol; A&C) was added to the flask, followed by 1.2 mL (10.3 mmol) of anhydrous stannic chloride (A&C reagent), dropwise. The polymer solution then turned yellow; 2.25 mL (29.5 mmol) of extra chlorodimethyl ether was added, and the reaction flask stirred for 75 minutes at room temperature (22 °C). During that time the solution developed a pinkish tint. The reaction was stopped by adding 25 mL of a 1:4 water/methanol (by volume) solution, and stirring was continued for 30 minutes longer. The polymer was recovered by dilution with chloroform

(180 mL), followed by precipitation in methanol. The yield was 20.3 g of 10.3 % chloromethylated (mol/mol) polystyrene, as evaluated by NMR spectroscopy (δ = 4.49 ppm, CH_2-Cl).

4.3.8. Lithiation of poly(styrene-co-4-bromostyrene)

Styrene-4-bromostyrene copolymer (5 g, 6.5 mmol of bromostyrene units) was loaded into the pressure-equilibrating addition funnel (b) of Figure 4.1. The three-neck flask was fitted, for this part of the reaction, with a purging stopcock on the straight arm side and a rubber septum on the other side. The whole flask assembly with the polymer was dried in vacuo overnight at 60 °C, together with the rest of the equipment used in the procedure. The system was then taken out of the oven and quickly purged with dry nitrogen. The three-neck flask was loaded with 500 mL of freshly purified tetrahydrofuran and lowered into a dry ice-methanol bath (-77 °C). A 40-fold excess (with respect to bromostyrene units) of a 10 M n-butyllithium solution in hexanes (26 mL, 260 mmol; Aldrich) was transferred with a syringe to the reaction flask through the septum. Dry tetrahydrofuran (500 mL) was added to the funnel, and the polymer dissolved by bubbling dry nitrogen through a long syringe needle inserted into the septum of the funnel. The polymer solution was then very slowly added to the cooled n-butyllithium solution at a rate of ca. 1 drop/second with vigorous stirring. Addition was completed in 4 to 5 hours.

4.3.9. Preparation of poly(styrene-co-4-(5-bromopentyl) styrene)

Lithiated polystyrene (5 g) was prepared as described above. When the addition of the polymer solution to the flask was completed, stirring was continued for about 5 minutes. Meanwhile, the retort-type flask was loaded with 600 g (2.60 mol) of 1,5-dibromopentane and quickly installed, in its lower (retaining) position, on the bent arm side of the three-neck flask in place of the rubber septum. A dry nitrogen line (ca. 30 kPa) was attached to the stopcock of the retort, and the reaction flask taken out of the dry ice bath. The 1,5-dibromopentane was then quickly transferred to the three-neck flask by rotating up the retort with its stopcock opened, while temporarily removing the purging stopcock on the other arm of the flask. The color of the solution quickly changed from milky to colorless. Stirring was continued at room temperature overnight under a nitrogen atmosphere. The solution was then concentrated to about 150 mL, and the polymer recovered by precipitation in methanol. The yield was 4.91 g of 11.5 %-substituted polymer. The NMR spectrum of the product showed characteristic peaks at $\delta = 3.36$ ppm (CH_2-Br) and 2.50 ppm (Ph-CH_2).

4.3.10. Preparation of poly(styrene-co-4-(10-bromodecyl)styrene)

The procedure was similar to that described above for the analogous C_5 derivative, with a few minor changes. The lithiation reaction was scaled down to 3.3 g, in order to maintain the amount of 1,10-dibromodecane involved at a workable level (360 g, 1.20 mol). Also, the compound had to be heated to 90 °C in the retort prior to addition in order to prevent the solidification of the reaction mixture. The workup was complicated by the low volatility and limited solubility in methanol of 1,10-dibromodecane. Tetrahydrofuran was removed on a rotary evaporator, and the nonvolatile fraction precipitated in ca. 10 volumes of methanol. The resulting soft mass was soaked for one hour in hexanes to dissolve excess dibromodecane. The polymer was then dissolved in tetrahydrofuran (60 mL) and reprecipitated in methanol. The yield was proportionally lower than for the C_5 analogue - typically 2.80 g. Characteristic NMR peaks were observed at $\delta = 3.38$ ppm (CH_2-Br) and 2.49 ppm (Ph-CH_2).

4.3.11. Preparation of poly(styrene-co-4-cyanomethylstyrene), poly(styrene-co-4-(5-cyanopentyl) styrene) and poly(styrene-co-4-(10-cyanodecyl) styrene)

These polymers were prepared from the chloromethyl, 5-bromopentyl and 10-bromodecyl styrenes, respectively. The procedure used was derived from that suggested by Kusama and Hayatsu[25] for a functionalized cross-linked polystyrene resin. The halogenated copolymer (2.5 g) was dissolved in 200 mL of N,N-dimethylformamide, and a large (24 mL, ca. 25-fold) excess of the 8.0% w/v sodium cyanide solution was added. The solution was stirred for 24 hours at room temperature, then concentrated to about 150 mL and precipitated in methanol. Typical yields were 2.3-2.4 g of nitrilated polymer. The structure of the products was confirmed by NMR spectroscopy (disappearance of the CH_2-X protons and appearance of CH_2-CN peaks at $\delta = 3.56$ ppm (cyanomethyl), 2.25 ppm (cyanopentyl) or 2.29 ppm (cyanodecyl). A sharp nitrile peak also appeared in the IR spectra of the products at 2251 cm^{-1} (4.44 μm, cyanomethyl) or 2246 cm^{-1} (4.45 μm, cyanopentyl and cyanodecyl).

4.3.12. Preparation of the C_2 alkyl ester [poly(styrene-co-4-carbomethoxymethylstyrene)], C_6 alkyl ester [poly(styrene-co-4-(5-carbomethoxypentyl)styrene)] and C_{11} alkyl ester [poly (styrene-co-4-(10-carbomethoxydecyl)styrene)]

The C_2, C_6 and C_{11} alkyl esters were prepared from the corresponding nitrilated polymers in identical reaction conditions. For example, the cyanomethyl copolymer (7.5 g) was dissolved in 1.2 L of freshly purified 1,4-dioxane. A small amount (2.0 mL) of distilled water and 150 mL of methanol were added, and the flask cooled in an ice-water bath. Hydrogen chloride gas (Matheson, technical) was then bubbled in the solution to saturate it. This process was highly exothermic, and had to be repeated three times, after cooling the flask. More methanol (75 mL) was added, and the cold solution saturated with hydrogen chloride for a last time, before it was left to stand for 24 hours. The solution was then concentrated until a polymer mass precipitated out. The solid was washed twice with methanol and redissolved in 200 mL tetrahydrofuran. Distilled water (20 mL) was added, and the concentration and washing process repeated. Tetrahydrofuran (100 mL) was used to redissolve the polymer, and methanol slowly added with stirring until the solution started to look cloudy. Stirring was continued for three days before the final workup (precipitation in methanol). The yield was about 5.5 g of esterified polymer. The completion of the conversion reaction was confirmed by the virtually complete disappearance of the nitrile peak (2251 cm^{-1}, 4.44 μm) in the IR spectrum of the product. Characteristic NMR peaks were observed as follows: C_2 ester: $\delta = 3.64$ ppm (O-CH_3) and 3.50 ppm (CH_2-CO_2). C_6 ester: $\delta = 3.65$ ppm (O-CH_3) and 2.28 ppm (CH_2-CO_2). C_{11} ester: $\delta = 3.64$ ppm (O-CH_3) and 2.29 ppm (CH_2-CO_2).

4.3.13. Preparation of methyl 11-bromoundecanoate

The methyl ester of 11-bromoundecanoic acid was not commercially available and had to be prepared from the acid in a simple esterification reaction. Methanol (300 mL) was used to dissolve 100 g (0.377 mol) of 11-bromoundecanoic acid (Aldrich, 99 %). Concentrated sulfuric acid (1 mL; Mallinckrodt) was added, and the solution refluxed overnight. The sulfuric acid was then neutralized with 20 mL of a 1.0 N solution of sodium hydroxide in methanol, and the excess methanol removed on a rotary evaporator. The liquid residue was fractionally distilled (bp. 113-116 °C/1.4 mm) to yield 77.6 g of the ester (74 % of the theoretical yield). The NMR spectrum of the product exhibited peaks at $\delta = 3.63$ ppm (s, 3H, O-CH_3), 3.37 ppm (t, 2H, CH_2-Br), 2.26 ppm (t, 2H, CH_2-CO_2), 1.81 ppm (quintet, 2H, CH_2-CH_2Br), 1.58 ppm (quintet, 2H,

CH_2-CH_2CO_2), 1.38 ppm (m, 2H, CH_2-CH_2CH_2Br) and 1.25 ppm (b, 10H, alkyl chain).

4.3.14. Preparation of the C_2 ether ester [poly(styrene-co-4-carbomethoxymethyloxystyrene)]

Poly(styrene-co-4-hydroxystyrene), 15 g (21.1 meq -OH) was dissolved in 300 mL of dry N,N-dimethylformamide, and 23 mL of a methanolic 1.0 N solution of sodium methoxide (23.0 meq) added. The solution was stirred for 30 minutes, and 4 mL (42.3 mmol) of methyl bromoacetate (Aldrich, 98 %) added. Stirring was continued overnight at room temperature. The polymer was recovered by precipitation in methanol and dried in vacuo for a day; 15.72 g of 11.7 %-substituted polymer (NMR) was thus obtained. The whole procedure was repeated two more times, to yield 16.34 g of 14.7 %-substituted polymer. Partial hydrolysis of the ester groups attached to the polymer was observed in the preparation of the ether. The ester was regenerated as follows: The copolymer (13.50 g) was redissolved in tetrahydrofuran (675 mL). Methanol (525 mL) and sulfuric acid (13.5 mL) were added, and the solution refluxed overnight. Distilled water (200 mL) was then added, and the solution concentrated to precipitate out the polymer. The solids were decanted and reprecipitated in methanol, after dissolution in 225 mL tetrahydrofuran. Characteristic peaks were observed on the NMR spectrum at $\delta = 4.53$ ppm (PhO-CH_2) and 3.77 ppm (O-CH_3).

4.3.15. Preparation of the C_5 ether ester [poly(styrene-co-4-(5-carbomethoxypentyl-1-oxy)styrene)]

The procedure used was similar to that for the C_2 ether, except that methyl bromoacetate was replaced with 6 mL (42.0 mmol) of methyl 5-bromovalerate (Aldrich, 97 %). A 14.8%-substituted polymer (16.2 g) was obtained after three reaction-isolation cycles. Characteristic NMR peaks were observed at δ = 3.87 (PhO-CH_2), 3.67 ppm (O-CH_3) and 2.39 ppm (CH_2-CO_2).

4.3.16. Preparation of the C_{11} ether ester [poly (styrene-co-4-(10-carbomethoxydecyl-1-oxy) styrene)]

As in the case of the C_5 ether, methyl bromoacetate was replaced with 11.7 g (42.0 mmol) of the methyl 11-bromoundecanoate prepared above. The final yield was 17.0 g of 15.3%-substituted polymer. Characteristic NMR peaks were observed at δ = 3.83 (PhO-CH_2), 3.65 ppm (O-CH_3) and 2.30 ppm (CH_2-CO_2).

4.3.17. Acid hydrolysis of the esters

Samples (1.5 g) of the esters were completely hydrolyzed in acid conditions, in order to verify the NMR results for acid content by titration with a base. The copolymer was dissolved in 105 mL tetrahydrofuran, and distilled water (12 mL) and sulfuric acid (0.6 mL) were added, together with 60 mg of 2,6-di-t-butyl-4-methylphenol (BHT) as a preservative for the tetrahydrofuran. This mixture was refluxed for a week either in contact with air or under a nitrogen atmosphere. The solution was then concentrated to precipitate out the polymer. The soft mass was washed with methanol and again dissolved in 30 mL tetrahydrofuran, followed by reprecipitation in methanol. Complete hydrolysis was confirmed by the disappearance of the methoxy peak in the NMR spectrum of the product.

4.4. Results and discussion

4.4.1. Sample characterization

Gel Permeation Chromatography (GPC) was used to analyze the polymers after each reaction step which could possibly have affected the molecular weight distribution of the samples. The presence of functional groups was neglected in the analysis, given their relatively low concentration (10-15 mole%) and the unavailability of correction factors for them. The results are summarized in Table 4.1. No general trend seems to emerge, except perhaps a slight tendency for the polydispersity (M_w/M_n) of the samples to increase. Considering the multistep nature and relatively low overall yields of the functionalization processes for the alkyl series, it is possible that sample fractionation may have contributed to the variations in molecular weights observed.

Nuclear Magnetic Resonance (NMR) spectroscopy was used whenever possible as a quick and easy means to characterize the products. The results obtained by this technique are expected to be accurate to about 5% of the values determined, due to the effect of spectrum phasing errors on the integrated peak intensities. Two exceptions can be noted where NMR spectroscopy could not be applied; in this case, infrared spectroscopy was used. The bromostyrene content of poly(styrene-co-4-bromostyrene) was, as mentioned before, determined from the ratio of the integrated intensities for the peaks at 1007 cm^{-1} (9.93 μm) and 1027 cm^{-1} (9.74 μm), as suggested by Brockman and Eisenberg[22]. The aforementioned ratio was successfully related, in the original work of Brockman[35], to the bromine content determined by elemental analysis. Unfortunately, the accuracy of this technique was not discussed, since only 4 data points were used in the correlation, and the two IR peaks are not completely resolved. It is nevertheless used to give an approximate value of the bromine content of the polymer. The other case in which IR spectroscopy was employed was in the nitrile to ester conversion reaction. This was necessary because the chemical shift of the R-CH_2-CN and R-CH_2-CO_2 protons is essentially the same ($\delta \approx 3.6$ ppm for R = phenyl and 2.3 ppm for R = alkyl) in the polymers as in model compounds. The disappearance of the sharp IR C≡N stretch peak was thus used to confirm the completion of the reaction in this particular case.

Table 4.1. Summary of GPC data collected for the parent and functionalized styrene polymers at important reaction stages. The samples are identified according to the substituent R in the para- position of the styrene units. The values presented are, from left to right, the number- and weight-average molecular weights, polydispersity and peak molecular weight evaluated from the chromatograms (M_n, M_w, M_w/M_n and M_p, respectively). The 4-bromostyrene copolymer data is repeated for ease of comparison.

Substituent R	$M_n \cdot 10^{-3}$ (g/mol)	$M_w \cdot 10^{-3}$ (g/mol)	M_w/M_n	$M_p \cdot 10^{-3}$ (g/mol)
-H	66.5	142	2.14	124
$-CH_2Cl$	84.3	218	2.59	134
$-CH_2CO_2Me$	52.8	126	2.38	87.1
-Br	43.5	131	3.00	124
$-(CH_2)_5Br$	35.2	129	3.66	114
$-(CH_2)_5CO_2Me$	42.6	128	3.01	124
-Br	43.5	131	3.00	124
$-(CH_2)_{10}Br$	69.3	191	2.76	134
$-(CH_2)_{10}CO_2Me$	50.8	194	3.82	134
-OMe	148	253	1.72	227
$-OCH_2CO_2Me$	128	294	2.30	232
$-O(CH_2)_4CO_2Me$	161	302	1.87	249
$-O(CH_2)_{10}CO_2Me$	156	320	2.05	249

4.4.2. Synthesis of the copolymers

Although data were available to determine the initiator concentration necessary for a given molecular weight in the case of polystyrene, such was not the case for the copolymers. A few attempts were, therefore, necessary to determine the initiator concentrations needed to produce copolymers with the desired molecular weight for dynamic mechanical measurements (0.5 to 2.5 x 10^5 g/mol), keeping in mind that the molecular weight obtained is inversely proportional to the square root of initiator concentration[36].

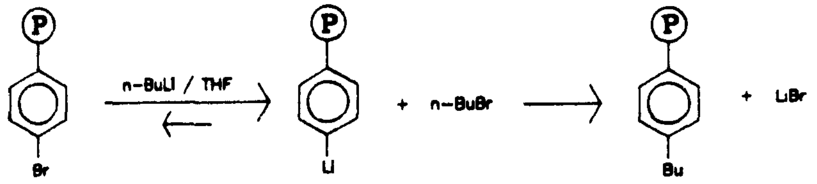
4.4.3. Chloromethylation reaction

Chloroform was freshly dried before use in the chloromethylation reaction. It was found that differing stocks of chloroform (containing presumably different amounts of water) yielded very irreproducible chloromethylation levels under otherwise identical reaction conditions. GPC analysis of the functionalized polymer reveals a slight degree of cross-linking (M_w increase of 54% versus 27% for M_n). This may be attributed to the cross-linking reaction depicted in Eq. 4.1, given the relatively long reaction time and high polymer concentration used[15].

4.4.4. Lithiation and bromoalkylation reactions

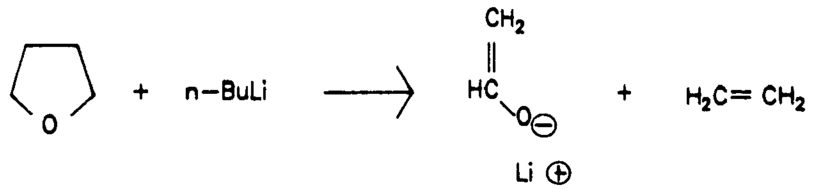
A 40-fold excess of n-butyllithium (with respect to the bromostyrene units) was used in the metal-halogen exchange reaction. As pointed out in the Introduction, large excesses of n-butyllithium were found necessary to avoid cross-linking problems[20-22]. Polymers of different molecular weights and bromostyrene contents were used in the preliminary testing phase. It was found that the n-butyllithium excess ratio necessary to avoid cross-linking problems increased with both the molecular weight and the bromostyrene content of the polymers. Satisfactory results were obtained in most cases with a 30-fold excess of n-butyllithium for the polymer used in this work. It was nevertheless preferred to use a 40:1 ratio to provide an error margin for variations in other experimental factors such as the addition and stirring rates, possibly leading to cross-linking in a Wurtz-Fittig type reaction (Eq. 4.4). The condition leading to cross-linking essentially involves a lithiated species meeting an unreacted bromostyrene unit in solution. It is therefore clearly desirable to work in dilute solution conditions (10 g/L or 1% in this case), use a large excess of n-butyllithium (40-fold) and maintain vigorous stirring conditions as well as low temperature (-77 °C). This contrasts with the techniques suggested for the lithiation of brominated cross-linked styrene resins[17,19], where a slight increase in the degree of cross-linking would not be noticed, apart from the fact that the Wurtz-Fittig reaction may itself be somewhat hindered due to the reduced mobility of the polymer chains.

The low temperature aspect is particularly important here because of the extended addition period (4-5 hours): Although the metal-halogen exchange reaction is kinetically favored, it is also known to be competing with a coupling reaction[37] leading to the thermodynamically more favorable 4-butylstyrene species:



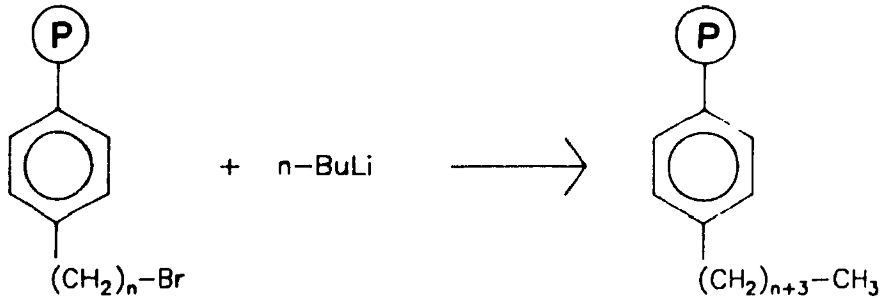
(Eq. 4.7)

The rate of the coupling reaction is slowed down at low temperatures[38]. Another important aspect of the low temperature approach is that n-butyllithium also reacts with tetrahydrofuran (and ethers in general) at room temperature[39]:


(Eq. 4.8)

It was thus reported that the molarity of a 0.79 M n-butyllithium solution in tetrahydrofuran decreased to 0.23 M after 1 hour standing at 25 °C[40].

The quick addition of the dibromoalkane in the preparation of the 5-bromopentyl and 10-bromodecyl derivatives is justified by the need for a large excess of the halogenated species compared with both lithiated styrene and n-butyllithium species. The dibromoalkyl compounds have two equally reactive ends, and could lead to cross-linking by coupling with one lithiated styrene unit (from the same or different random coils in solution) at each end of the C_5 or C_{10} alkyl chain. Furthermore, it is necessary to use a large excess of the dibromoalkyl compound with respect to n-butyllithium and not only with respect to the lithiated styrene species, because of the n-butyl coupling reaction also occurring at the end of the grafted bromoalkyl chains[41], and leading to the loss of part of the reactive groups:


(Eq. 4.9)

The different factors presented above explain the loss of part of the active bromoalkyl species in the preparation of the 5-bromopentyl- and 10-bromodecylstyrenes. The importance of the two butyl coupling reactions discussed above is supported by the appearance, in the NMR spectra of the bromoalkylated polymers prepared, of a weak methyl peak at δ = 0.8-0.9 ppm. Even though it is not very well defined, because of its weakness and its proximity to the large alkyl chain peaks, its integrated intensity can be used for a rough evaluation of the extent of both coupling reactions. Thus, in a sample containing 11.0 mole% of bromoalkyl units, a concentration of 2.1 mole% of terminal methyl groups was determined.

The bromide loss which can be attributed to coupling of the grafted bromoalkyl chains with the n-butyllithium excess is easy to quantify. It is assumed that the reaction of the dibromoalkyl compound with the lithiated styrene species is much faster than with the excess of n-butyllithium present, the former being presumed to be a better nucleophile[42]. Since a 10-fold excess of dibromoalkane (or a 20-fold excess on a functional basis) is used with respect to the n-butyllithium present, 5% of all the bromo-terminated species will be alkylated at either end, assuming a complete reaction. This process can therefore account for the disappearance of 5% of the total bromoalkyl groups on the copolymer (or 0.7% in absolute terms) being transformed to n-nonyl or n-tetradecylstyrene units. The rest of the methyl groups present (1.4 mole%) could result from the coupling reaction occurring during the slow addition of the polymer solution (Eq. 4.7). The methyl peak became much more important for polymers lithiated at room temperature according to suggested procedures[20,43] before adding 1,5-dibromopentane, providing further support for the phenyllithium-n-butyl bromide coupling scheme mentioned above (Eq. 4.7), and possibly explaining the lower than expected functional yields obtained by these authors.

The final acid contents determined by titration of the different hydrolyzed alkyl and ether esters are given in Table 4.2. The acid content of the C_6 and C_{11} alkyl polymers are clearly lower than the corresponding 13.8 mole% bromostyrene determined by IR spectroscopy, but in good agreement if the coupling losses evaluated above are included.

Table 4.2. Acid contents of the final products determined by titration of the hydrolyzed esters with methanolic sodium hydroxide.

Sample		mole%
C_2	Alkyl	9.5
C_6	Alkyl	11.4
C_{11}	Alkyl	11.2
C_2	Ether	14.1
C_5	Ether	14.8
C_{11}	Ether	14.6

Although the C_5 bromoalkyl polymer shows no significant variation in its molecular weight distribution, an increase in M_n and M_w is more noticeable for the C_{10} analogue (Table 4.1). One possible reason for this could be the increased mobility of the terminal bromoalkyl groups for the longer C_{10} compared to the C_5 unit, leading to a higher cross-linking probability. Another possibility not yet discussed is the occurrence of intramolecular, as opposed to intermolecular cross-linking. Although this occurrence could not be rigorously verified, it would seem that since dilute solution conditions are used, the random polymer coils are presumably isolated from each other, leading to a greater probability of intra- than intermolecular cross-linking.

4.4.5. Nitrile to ester conversion reaction

Although the conversion of nitriles to esters or ortho esters with the help of methanol and hydrogen chloride has long been suggested for low molecular weight compounds[26,27], this is apparently the first report of the application of this technique to a functionalized polymer. One nitrile hydrolysis reaction suggested[25] for styrene resins containing nitrile groups was tested, but yielded only insoluble products. The procedure used here involves milder (room temperature) conditions, and leads to an essentially complete conversion of the nitrile groups to the methyl ester.

Adding a very small amount (0.17%) of water to the solvent (1,4-dioxane) has a two-fold purpose. First, it ensures that the conversion is to the ester, and not to the ortho ester form, which is produced in anhydrous conditions[27]. Second, since the dioxane used to dissolve the polymer is predried, the added water constitutes a "controlled" amount. Indeed, it was found that when solvents which had not been dried were used, a large proportion (up to 70%) of the ester groups produced were actually hydrolyzed to the acid form.

The polymer solution used for the reaction was very dilute (0.625%), to prevent the precipitation of the intermediate iminoether adduct, and consequently yield a more uniform product. Washing of the polymer was necessary, even though it is probably the main cause for a reduced yield, in order to remove the ammonium chloride formed (Eq. 4.5), since ionic salt residues are undesirable in ionomers.

A three-day postreaction stirring period accounts for the slower conversion to the ester of the intermediate iminoether hydrochloride (Eq. 4.5), which is itself formed when hydrogen chloride is bubbled in the polymer solution. The polymers prepared without the three-day stirring period, even though mostly converted, cross-linked very easily upon heating at 100 °C for short periods of time, hinting at possible iminoether hydrochloride residues. No cross-linking was observed in the same conditions after the three-day treatment.

Some polymer degradation was observed in the reaction, particularly in the case of the C_2 compound (Table 4.1). The C_6 and C_{11} analogues were apparently less affected, with essentially unchanged M_w and comparable (±20-25%) M_n values.

4.4.6. Ethers series synthesis

The procedure suggested gives completely substituted (within error limits) products in good yields after three simple reaction steps. The only strict requirement of the procedure was the use of freshly dried N,N-dimethylformamide, in order to avoid, as much as possible, the hydrolysis of the ester groups of both the polymer-attached and the bromo-substituted reagent. Partial hydrolysis of the polymer-attached ester groups was nevertheless observed, in particular after the second and third reaction steps, but were regenerated in an easy esterification reaction. Extensive hydrolysis, as a result of using undried N,N-dimethylformamide on the other hand, led to solubility problems in the course of the reaction and nonuniform products.

4.4.7. Acid hydrolysis of the esters

The hydrolysis was relatively slow, owing to the low concentration (10%) of water achievable to keep the polymers in solution in the presence of sulfuric acid. Addition of 2,6-di-t-butyl-4-methylphenol (BHT), in particular, was found to be crucial to the production of the undegraded acid: A sample of the C_2 alkyl ester hydrolyzed for 6 days in contact with air and without added BHT yielded a 1:1 mixture of the C_2 acid together with the C_1 acid (styrenecarboxylic acid). The presence of the C_1 acid was attributed to clipping of the C_2 pendant group by peroxides produced in the tetrahydrofuran during the extended refluxing period. Similarly, 1,4-dioxane used in the same reaction tested positive in a potassium iodide peroxide test before, but tested negative after refluxing for a couple of days with the polymer. The preservative (BHT) was also added (as a preventive measure) to the samples hydrolyzed in a nitrogen atmosphere.

4.5. Acknowledgements

It is a pleasure to thank Dr. A.S. Hay for his helpful suggestions concerning the nitrile to ester conversion reaction, and the preparation of the ether compounds. The comments of Dr. A.S. Hay and Dr. G.D. Darling concerning the manuscript of this paper were greatly appreciated. We are also very grateful to Ms. Dieu Nguyen for her assistance in the development of the bromoalkylation reaction, and to Ms. Diep Nguyen for her help in the preparation of the C_{11} alkyl ester compound. Funding for this work was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC). One of the authors (M.G.) would also like to acknowledge the financial support of NSERC and of the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (Quebec).

4.6. References

(1) (a) *Polymer-supported Reactions in Organic Synthesis*; Hodge, P.; Sherrington, D.C.; Eds.; Wiley: New York, 1980. (b) Mathur, N.K.; Narang, C.K.; Williams, R.E. *Polymers as Aids in Organic Chemistry*; Academic: New York, 1980. (c) Akelah, A.; Sherrington, D.C. *Chem. Rev.* **1981**, *81*, 557. (d) Bailey, D.C.; Langer, S.H. *Chem. Rev.* **1981**, *81*, 109. (e) Fréchet, J.M.J. *Tetrahedron* **1981**, *37*, 663. (f) Geckeler, K.; Pillai, V.N.R.; Mutter, M. *Adv. Polym. Sci.* **1981**, *39*, 65. (g) Akelah, A.; Sherrington, D.C. *Polymer* **1983**, *24*, 1369. (h) Ford, W.T.; Tomoi, M. *Adv. Polym. Sci.* **1984**, *55*, 49. (i) *Polymeric Reagents and Catalysts*; Ford, W.T., Ed.; ACS Symposium Series 308, American Chemical Society, Washington, D.C., 1986. (j) *Chemical Reactions on Polymers*; Benham, J.L.; Kinstle, J.F.; Eds.; ACS Symposium Series 364, American Chemical Society, Washington, D.C., 1988.

(2) Pepper, K.W.; Paisley, H.M.; Young, M.A. *J. Chem. Soc.* **1953**, 4097.

(3) Merrifield, R.B. *J. Am. Chem. Soc.* **1963**, *85*, 2149.

(4) Braun, D. *Kunststoffe* **1960**, *50(7)*, 375.

(5) Eisenberg, A.; King, M. *Ion-Containing Polymers*; Academic: New York, 1977.

(6) (a) Bazuin, C.G.; Eisenberg, A. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 271. (b) MacKnight, W.J.; Earnest, T.R., Jr. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.

(7) (a) Weiss, R.A.; MacKnight, W.J.; Lundberg, R.D.; Mauritz, K.A.; Thies, C.; Brant, D.A. In *Coulombic Interactions in Macromolecular Systems*; Eisenberg, A., Bailey, F.E., Eds.; ACS Symposium Series 302; American Chemical Society: Washington, DC, 1986; pp 2-19. (b) Lundberg, R.D. In *Structure and Properties of Ionomers*; Pineri, M.; Eisenberg, A., Eds.; NATO ASI Series C Vol. 198; Reidel: Dordrecht, Holland, 1987; pp 429-438. (c) Tan, J.S. *Ibid.* pp 439-451.

(8) Gauthier, M.; Eisenberg, A. To be published.

(9) *Perfluorinated Ionomer Membranes*; Eisenberg, A., Yeager, H.L., Eds.; ACS Symposium Series 180; American Chemical Society: Washington, D.C., 1982.

(10) (a) Chiles, M.S.; Jackson, D.D.; Reeves, P.C. *J. Org. Chem.* **1980**, *45*, 2915. (b) Deratani, A.; Darling, G.D.; Horak, D.; Fréchet, J.M.J. *Macromolecules* **1987**, *20*, 767. (c) Darling, G.D.; Fréchet, J.M.J. In Ref. 1j, pp 24-36.

(11) Tomoi, M.; Ogawa, E.; Osokawa, Y.; Kakiuchi, H. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3015.

(12) (a) Braun, D.; Keppler, H.-G. *Monatsh. Chem.* **1963**, *94*, 1250. (b) Hallensleben, M.L. *Angew. Makromol. Chem.* **1973**, *31*, 147. (c) Tomoi, M.; Ogawa, E.; Hosokawa, Y.; Kakiuchi, H. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3015.

(13) Darling, G.D.; Fréchet, J.M.J. *J. Org. Chem.* **1986**, *51*, 2270.

(14) (a) Feinberg, R.S.; Merrifield, R.B. *Tetrahedron* **1974**, *30*, 3209. (b) Sparrow, J.T. *Tetrahedron Lett.* **1975**, *52*, 4637.

(15) Green, B.; Garson, L.R. *J. Chem. Soc., Sec. C* **1969**, 401.

(16) Pinnell, R.P.; Khune, G.D.; Khatri, N.A.; Manatt, S.L. *Tetrahedron Lett.* **1984**, *25*, 3511.

(17) Farrall, M.J.; Fréchet, J.M.J. *J. Org. Chem.* **1976**, *41*, 3877.

(18) (a) Gilman, H.; Cartledge, F.K. *J. Organometal. Chem.* **1964**, *2*, 447. (b) Turner, R.; Altenau, A.G.; Cheng, T.C. *Anal. Chem.* **1970**, *42(14)*, 1835. (c) Bergbreiter, D.E.; Killough, J.M. *Org. Coat. Plast. Chem.* **1979**, *41*, 213.

(19) (a) Braun, D.; Seelig, E. *Chem. Ber.* **1964**, *97*, 3098. (b) Melby, L.R.; Strobach, D.R. *J. Am. Chem. Soc.* **1967**, *89*, 450. (c) Collman, J.P.; Hegedus, L.S.; Cooke, M.P.; Norton, J.R.; Dolcetti, G.; Marquardt, D.N. *J. Am. Chem. Soc.* **1972**, *94*, 1789. (d) Weinshenker, N.M.; Crosby, G.A.; Wong, J.Y. *J. Org. Chem.* **1975**, *40*, 1966.

(20) Braun, D. *Makromol. Chem.* **1959**, *30*, 85.

(21) Greber, G.; Tölle, J.; Burchard, W. *Makromol. Chem.* **1964**, *71*, 47.

(22) Brockman, N.L.; Eisenberg, A. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 3563.

(23) (a) Chalk, A.J. *J. Polym. Sci., Polym. Lett. Ed.* **1968**, *6*, 649. (b) Evans, D.C.; George, H.H.; Barrie, J.A. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 247.

(24) Evans, D.C.; Phillips, L.; Barrie, J.A.; George, M.H. *J. Polym. Sci., Polym. Lett. Ed.* **1974**, *12*, 199.

(25) Kusama, T.; Hayatsu, H. *Chem. Pharm. Bull.* **1970**, *18(2)*, 319.

(26) (a) Pfeiffer, P.; Matton, K. *Ber. Deut. Chem. Ges.* **1911**, *44*, 1113. (b) Spiegel, L. *Ber. Deut. Chem. Ges.* **1918**, *51*, 296. (c) Drefahl, G.; Seeboth, H.; Degen, W. *J. Prakt. Chem.* **1956**, *4*, 99. (d) Betz, W.; Daub, J. *Chem. Ber.* **1972**, *105*, 1778. (e) Célérier, J.-P.; Deloisy, E.; Kapron, P.; Lhommet, G.; Maitte, P. *Synthesis* **1981**, 130.

(27) (a) Pinner, A. *Ber. Deut. Chem. Ges.* **1883**, *16*, 352, 1643. (b) McElvain, S.M.; Nelson, J.W. *J. Am. Chem. Soc.* **1942**, *64*, 1825. (c) DeWolfe, R.H. *Synthesis* **1974**, 153.

(28) Fréchet, J.M.J.; de Smet, M.D.; Farrall, M.J. *J. Org. Chem.* **1979**, *44*, 1774.

(29) Clas, S.-D.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 2743.

(30) Flory, P.J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, 1953; p 140.

(31) Navratil, M.; Eisenberg, A. *Macromolecules* **1973**, *6*, 604.

(32) Walling, C.; Briggs, F.R.; Wolfstirn, K.B.; Mayo, F.R. *J. Am. Chem. Soc.* **1948**, *70*, 1537.

(33) Odian, G. *Principles of Polymerization, 2nd. ed.*; Wiley: New York, 1981; Chapter 6.

(34) Melville, H.W.; Valentine, L. *Trans. Faraday Soc.* **1955**, *51*, 1474.

(35) Brockman, N.L. M.Sc. Thesis, McGill University: Montreal, 1980.

(36) Odian, G. *Principles of Polymerization, 2nd. ed.*; Wiley: New York, 1981; Chapter 3.

(37) Gilman, G.; Langham, W.; Moore, F.W. *J. Am. Chem. Soc.* **1940**, *62*, 2327.

(38) Gilman, H.; Moore, F.W. *J. Am. Chem. Soc.* **1940**, *62*, 1843.

(39) Bates, R.B.; Kroposki, L.M.; Potter, D.E. *J. Org. Chem.* **1972**, *37*, 560.

(40) Gilman, H.; Gaj, B.J. *J. Org. Chem.* **1957**, *22*, 1165.

(41) (a) Ziegler, K.; Colonius, H. *Annalen* **1930**, *479*, 135. (b) Cristol, S.J.; Ragsdale, J.W.; Meek, J.S. *J. Am. Chem. Soc.* **1951**, *73*, 810.

(42) Wakefield, B.J. *The Chemistry of Organolithium Compounds*; Pergamon: Oxford, 1974; Chapters 1 and 10.

(43) Houel, B. *Comp. Rend. Acad. Sci. (Paris)* **1960**, *250*, 2209.

Chapter 5. Alkylated styrene ionomers with variable length spacers. II. Physical properties

5.1. Abstract

The dynamic mechanical properties of two analogous series of alkylated styrene ionomers were examined. The samples were prepared in the partial base hydrolysis of precursors containing 10 to 15 mole% of 4-substituted styrene units with substituents $R = -(CH_2)_nCO_2Me$ (n = 1, 5, 10), or $R = -O(CH_2)_nCO_2Me$ (n = 1, 4, 10). The variation in the mechanical properties was studied as a function of ion content for the different ionomers, to form a systematic investigation of the effects of ion spacing from the polymer backbone. Three distinct factors were postulated as having contributed to the trends observed among the different series of compounds. These include the bulkiness and rigidity of the units to which the ionic groups are attached, and the immobilizing effect of the ionic groups on the polymer backbone. In the ether derivatives, the presence of alkyl aryl ether linkages led to solvation effects and reduced clustering.

5.2. Introduction

The incorporation of ions into organic polymers has been shown, on occasion, to cause dramatic changes in their physical properties[1]. It is not always clear, however, what are the exact causes for the variations in properties observed between distinct ionomer systems. The systematic variation of the structural characteristics of polymers represents a very valuable way to get some insight into the effects of certain parameters on the physical properties of ionomers. Examples of molecular parameters which were varied in previous studies are the type of counterion[2], and the placement[3] and nature[4] of pendant ionic groups. More recently, the effects of the matrix polarity and glass transition temperature[5] on ionic aggregation were also examined in styrene ionomers.

The importance of polymer structure variation, and notably of the length of the side chains, is underlined by the industrially important perfluorinated membrane materials[6]. There exists currently several different types of perfluorinated ionomers which are commercially available. Apart from the original sulfonated Nafion(R) products introduced by duPont[7] in the early 1970's, another type of perfluorosulfonate membrane material recently developed by Dow[8] has a shorter side chain length than the Nafion(R) products. Analogous carboxylated ionomers are available, among others, from the Asahi Glass Co. (Flemion(R))[9] and the Asahi Chemical Co.[10], as well as mixed sulfonate-carboxylate perfluorinated materials (Neosepta-F(R)) from the Tokuyama Soda Co.[11] Even though the different ionomers were all found to operate satisfactorily as membrane materials in the chlor-alkali industry, significant morphological differences were observed between some of them. Comparative studies of these materials to date have been oriented more towards comparing sulfonate vs. carboxylate pendant ions[12], and only to a much smaller extent towards examining the effects of the different chain lengths[13] on the physical properties of the membranes. Even though a study of chain length effects in the perfluorinated ionomers would be of considerable interest, it would be of somewhat limited generality. This is because only very few different types of perfluorinated ionomers are available, and their synthesis is highly involved. Moreover, it has been shown that the degree of crystallinity of these materials depends on different factors such as their ion content[6]. The crystallinity, in turn, would have a profound effect on the mechanical properties of the ionomers.

Ionomers based on styrene have already been the subject of much work. Their amorphous character gives them a distinct advantage over polyolefin ionomers, in that they are making the interpretation of the results correspondingly simpler. Styrene copolymerizes with a variety of functional comonomers, and the homopolymer can undergo a number of functionalization reactions. Consequently, styrene ionomers were preferred over the perfluorinated materials for this work. It is the purpose of the present study to explore the effects of systematic side chain length variation on the dynamic mechanical properties of carboxylated styrene-based ionomers.

One example of previous work dealing with systematic side chain length variation is that of Vogl and coworkers[14], who reported the synthesis of analogous poly(alkylene oxide)-based ionomers with variable chain length spacers from methyl ω-epoxyalkanoate homopolymers and copolymers with various cyclic ethers and epoxides. Unfortunately, physical properties measurements of interest to the field of ionomers, namely X-ray diffraction and dynamic mechanical measurements, were limited to very few of the materials prepared. Ionomers derived from ethylene or propylene oxide-methyl 10,11-epoxyundecanoate copolymers were also characterized more recently[15]. The early stages of the investigations done on systematic ion spacing in this group were based on ionomers of styrene-4-hydroxystyrene and styrene-4-hydroxymethylstyrene copolymers[16].

Some of the problems involved in systematic structure-properties relations studies become apparent from the examples given above. The main limitation of such investigations is the difficulty of varying a single structural parameter at a time, without affecting others at the same time; otherwise, the effects observed may not always be clearly assignable to the variation in the parameter of primary interest. Ideally, such a systematic study should be based on the same polymer matrix, with a single, well-defined characteristic used as a variable parameter.

The synthesis of styrene ionomer precursors with methyl alkanoate side chains in the para- position and varying in length from 2 to 11 carbon atoms was described in a previous paper[17]. These materials represent an excellent opportunity to examine the effects of the variation of spacing of the ionic groups from the polymer backbone on ion aggregation, and the consequent variations in the mechanical properties of the ionomers. Six different parent (esterified) copolymers were prepared, falling into two distinct families of compounds, according to the mode of attachment of the alkyl chain to the styrene ring. One family (alkyl derivatives) involved the direct attachment of the ω-carboxylated alkyl chain in the para- position. In the other family of compounds (ether derivatives), the alkyl chain was attached to the ring through an alkyl aryl ether linkage. This should allow the exploration of not only the ion spacing effects, but also of the presence of solvating groups (the ether linkages) on the properties of the resulting ionomers.

The six esterified ionomer precursors prepared were poly(styrene-co-4-carbomethoxymethylstyrene) [C_2 alkyl], poly(styrene-co-4-(5-carbomethoxypentyl) styrene) [C_6 alkyl], poly(styrene-co-4-(10-carbomethoxydecyl)styrene) [C_{11} alkyl], poly(styrene-co-4-carbomethoxymethyloxystyrene) [C_2 ether], poly(styrene-co-4-(5-carbomethoxypentyl-1-oxy)styrene) [C_5 ether], and poly(styrene-co-4-(10-carbomethoxydecyl-1-oxy)styrene) [C_{11} ether]. For the sake of simplicity, the nonsystematic names of the compounds, given above between square brackets after each systematic name, will be used throughout the rest of this paper. The alkyl derivatives had a pendant carboxyl group concentration of the order of 10 mole%; the ether derivatives, approximately 15 mole%. Ionomers of different ion contents were prepared for each series by hydrolysis with a base according to a procedure given here. This approach also insured that within a given series, only the proportion of ionized groups varied, the rest of the carboxylate moieties remaining as ester groups, thus resulting only in minimal global composition variations. A sample identified as C_2 ether 10% Na would therefore refer to an ionomer derived from the C_2 ether esterified precursor, with 10 mole% of sodium carboxylate moieties, and approximately 5 mole% of residual ester groups.

The present work deals with the dynamic mechanical and the differential scanning calorimetry analysis of these ionomers. It is the first of a series of investigations of the physical properties to be performed on these compounds; future work will involve small-angle X-ray scattering measurements and diffusion studies.

5.3. Experimental

The synthesis of the esterified ionomer precursors was described in a previous paper[17]. A brief summary of the preparation of these materials follows, for the convenience of the reader. The C_2 alkyl ester was prepared via chloromethylation of polystyrene, followed by nucleophilic displacement of the chloride ion by sodium cyanide in a N,N-dimethylformamide/water solvent mixture. The nitrile was converted to the methyl ester under mild conditions with methanol/HCl gas via an iminoether hydrochloride intermediate. The C_6 and C_{11} alkyl compounds were similarly prepared from bromoalkylated styrene analogues. These were obtained by lithiation of a styrene-4-bromostyrene copolymer, followed by the addition of a large excess of 1,5-dibromopentane and 1,10-dibromodecane for the C_5 and C_{10} derivatives, respectively. The ether compounds (C_2, C_5, and C_{11} methyl carboxylates) were obtained in a Williamson ether synthesis reaction from a styrene-4-hydroxystyrene copolymer and the corresponding ω-brominated aliphatic acid methyl ester in anhydrous DMF and in the presence of sodium methoxide.

The esterified polymers were hydrolyzed either by refluxing with sodium hydroxide in a benzene/methanol/water solvent mixture, or with sulfuric acid in tetrahydrofuran/water. The acid hydrolysis technique was used to obtain fully hydrolyzed samples of the alkyl series, and to check the total carboxylate content of the samples, as previously described[17]. This technique was also used to generate fully ionized samples of the alkyl series. Samples (1.4 g) of the acid-hydrolyzed materials were thus dissolved in 100 mL of 80/20 v/v benzene/methanol and completely neutralized with a predetermined volume of standard 0.05 N methanolic NaOH solution. The ionomers were recovered by freeze-drying.

All other samples used in this study were produced in the base hydrolysis of the esterified polymers. In a typical hydrolysis procedure, 1.3 g of polymer was dissolved in 100 mL of 80/20 benzene/methanol solvent, followed by the addition of 2 mL of water.

A calculated amount of standard methanolic 0.05 N or 0.10 N NaOH solution, based on the desired ionization level, was then added, and the solution refluxed for 3-5 days under nitrogen. Completion of the reaction was confirmed by adding a few drops of a 0.1% phenolphthalein indicator solution in ethanol to a 1 mL sample of the hydrolyzed polymer solution. The solution remained colorless if all the base initially added had been consumed in the reaction; however, it developed a pink coloration upon adding a single drop of a 0.01 N NaOH solution. The partly ionized polymer was recovered by freeze-drying. Samples with the ion contents given in Table 5.1 were prepared using either the acid hydrolysis-neutralization (alkyl series, ca. 10 mole% ions) or the direct base hydrolysis scheme described above (other samples). The total carboxylate content of the parent (esterified) polymers, as determined by titration of the acid-hydrolyzed materials, is also given for comparison.

Table 5.1. Ionomer samples prepared for each polymer series. All the values are in mole%.

Series		Parent	Samples					
C_2	Alkyl	9.5	0;	2.5;	5.0;	7.5;	9.5	
C_6	Alkyl	11.4	0;	2.5;	5.0;	7.5;	11.4	
C_{11}	Alkyl	11.2	0;		5.0;	7.5;	11.2	
C_2	Ether	14.1	0;		5.0;	7.5;	10.0;	14.0
C_5	Ether	14.8	0;		5.0;	7.5;	10.0;	14.0
C_{11}	Ether	14.6	0;	2.5;	5.0;	7.5;	10.0;	14.0

The extent of ionization of the samples was also confirmed by NMR analysis of some of the products. The ratio of the integrated intensities of the methoxy peak

(δ = 3.7-3.8 ppm) to the aromatic peaks (δ = 6.2-7.6 ppm) of a partly hydrolyzed sample thus showed a decrease, compared to the esterified polymer, which was proportional to the extent of hydrolysis.

Differential Scanning Calorimetry (DSC) was used to determine the glass transition temperature of the samples. A Perkin-Elmer DSC-2C instrument was used for this purpose. Calibration was achieved with indium and tin standards. Each sample was initially heated to ca. 40 degrees above the T_g of the material for 5 minutes, followed by quenching at the maximum rate attained by the instrument. Duplicate scans at 20 °C/min were used to insure reproducibility of the results. The agreement between two successive runs was generally better than one degree.

The samples for dynamic mechanical analysis were dried under vacuum at 100 °C for 14 to 17 days prior to molding. The mold was preheated at 180-240 °C (depending on the matrix T_g of the sample) before transferring the dried material; a pressure of 20 MPa was maintained for 10 minutes at the desired temperature. The pressure was then very slowly released, and the mold allowed to cool down on the press to ca. 10 °C below the matrix T_g of the material as determined from DSC measurements. The sample was taken out of the mold and used immediately for the dynamic mechanical measurements. Approximate sample dimensions were 2.5 mm thickness x 12 mm width x 36 mm length. These mechanical measurements were done using a Polymer Laboratories Mark II Dynamic Mechanical Thermal Analyzer (DMTA) in the dual cantilever bending mode, at frequencies of 1, 3, 10, and 30 Hz, and a heating rate of 0.5 °C/min. The furnace of the instrument was continuously purged with a flow of dry nitrogen throughout the run.

In view of the cross-linking effects observed in the samples (particularly in the ether compounds), an infrared study of the nature of thermal degradation was attempted for the C_{11} ether 10% Na sample. Films were prepared for infrared spectroscopy by compression molding of 0.1 g of the ionomer between plates covered with aluminum foil. In one case, a film was obtained by molding the sample only for a few minutes at 200 °C.

In another case, the same material was maintained at 275 °C for 5 hours. Infrared spectra were recorded for both films using an Analect AQS-40 FT-IR spectrometer with a resolution of 4 cm^{-1}.

5.4. Results

In the dynamic mechanical analysis, the storage modulus, loss modulus, and loss tangent of each sample described in Table 5.1 was obtained as a function of temperature at four different frequencies. Because of the similar behavior for the different series, only representative results will be given here in graphical form. Figure 5.1 shows the storage modulus curves obtained for the C_{11} ether series, for ion concentrations varying from 0 to 14 mole%. Because of slight scatter observed in the data (maximum log E' variations: ±0.06), the absolute values of the glassy moduli were adjusted, for ease of comparison, to the average of all the samples (8.90×10^8 Pa at 35 °C). The corresponding loss tangent curves are given in Figure 5.2. It can be seen that the general features of the system correspond to what has already been observed in other clustered styrene ionomers such as polystyrene-co-sodium methacrylate[18]. The features of interest include a 70 °C increase in the matrix glass transition temperature, and a large increase (ca. 2.5 orders of magnitude) in the ion-associated rubberlike modulus over the ion concentration range studied (0-14 mole%). The position of the rubberlike plateau is also shifted towards higher temperatures. At the same time, the height of the first loss tangent peak (matrix) decreases in favor of the second (cluster) peak with increasing degree of ionization.

The somewhat different results obtained for the C_2 ether series are presented in Figure 5.3, for comparison. It can be seen that the height of the ion-associated rubberlike modulus of these samples is significantly lower than for the corresponding C_{11} ether samples. As before, the absolute value of the glassy modulus was adjusted to the average value of all samples (log E' = 9.18 at 35 °C; maximum variations: +0.09, -0.14).

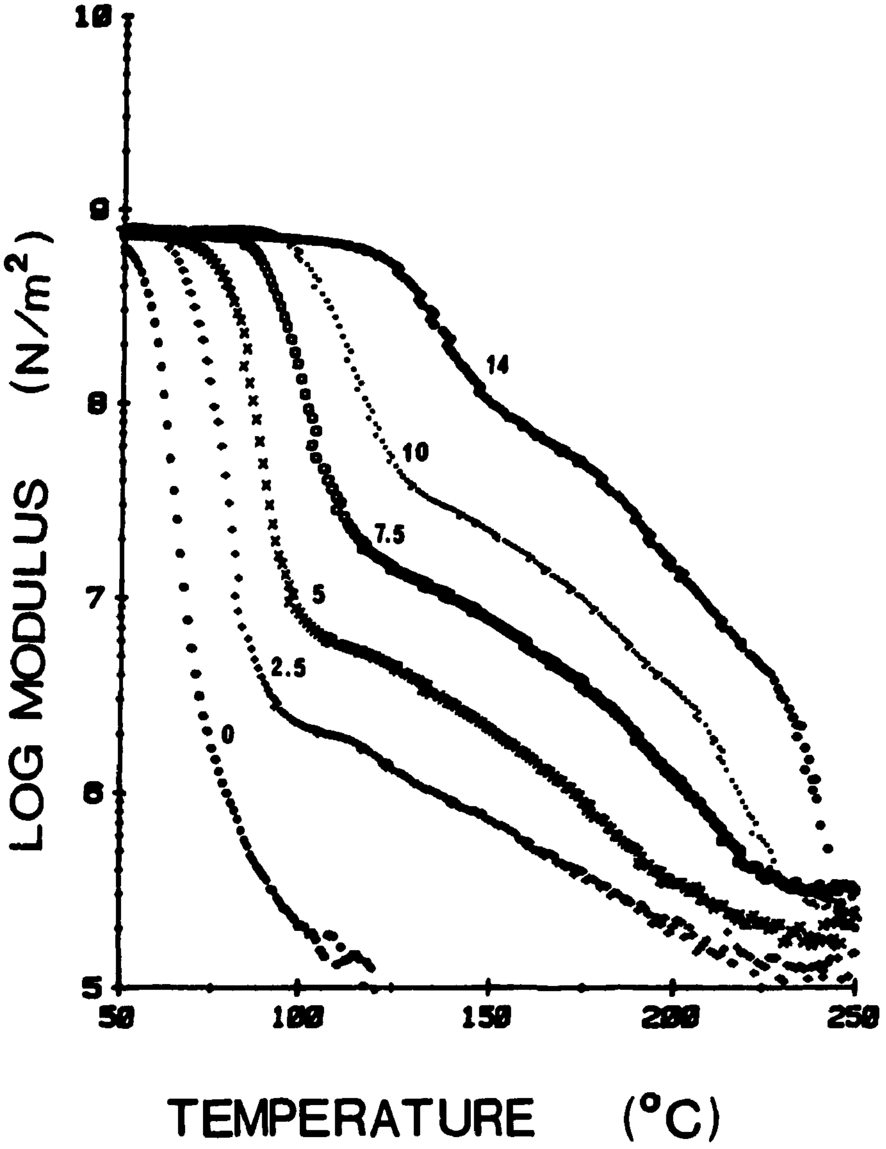


Figure 5.1. Dynamic storage modulus curves (1 Hz) for the C_{11} ether series; ion contents vary from 0 to 14 mole%, as indicated.

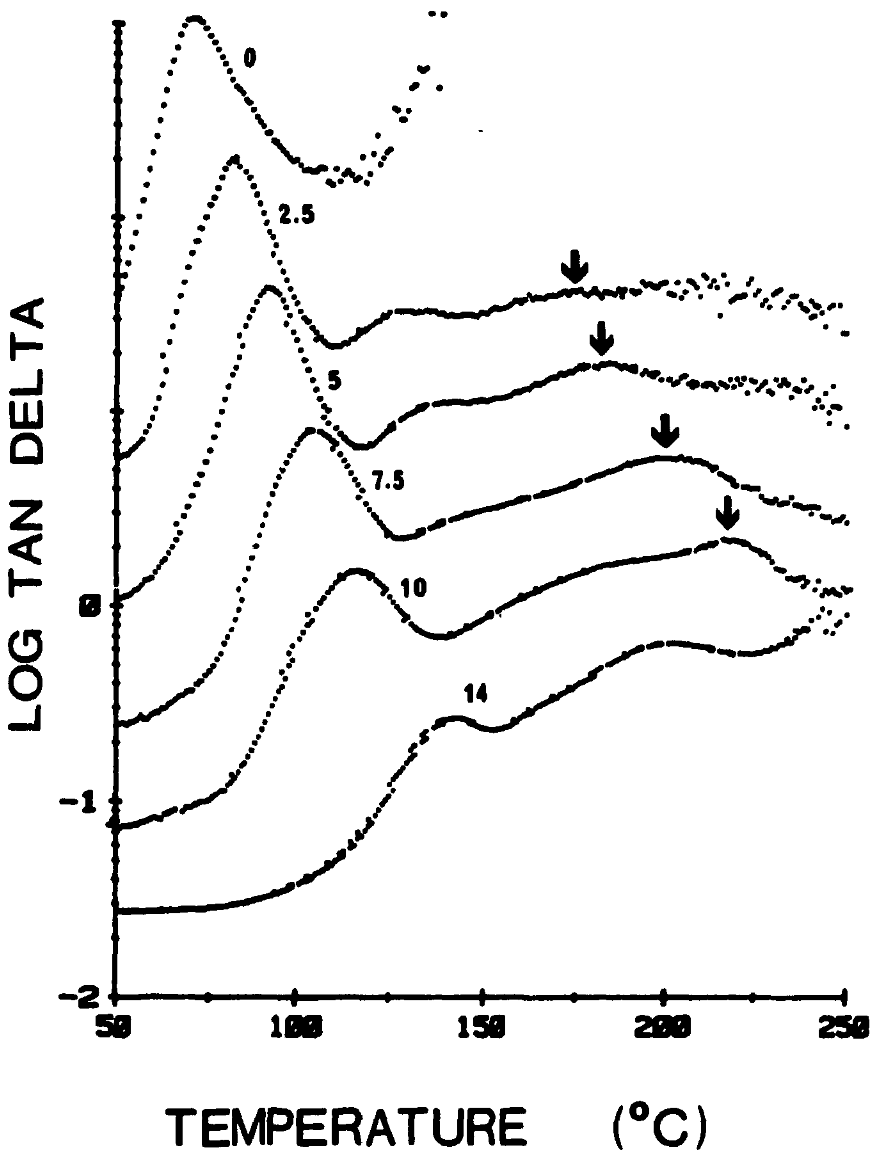


Figure 5.2. Loss tangent curves (1 Hz) for the ionomers of Figure 5.1. The scale indicated is correct for the bottom curve; each successive curve is shifted up by one half order of magnitude with respect to the previous one, for improved clarity.

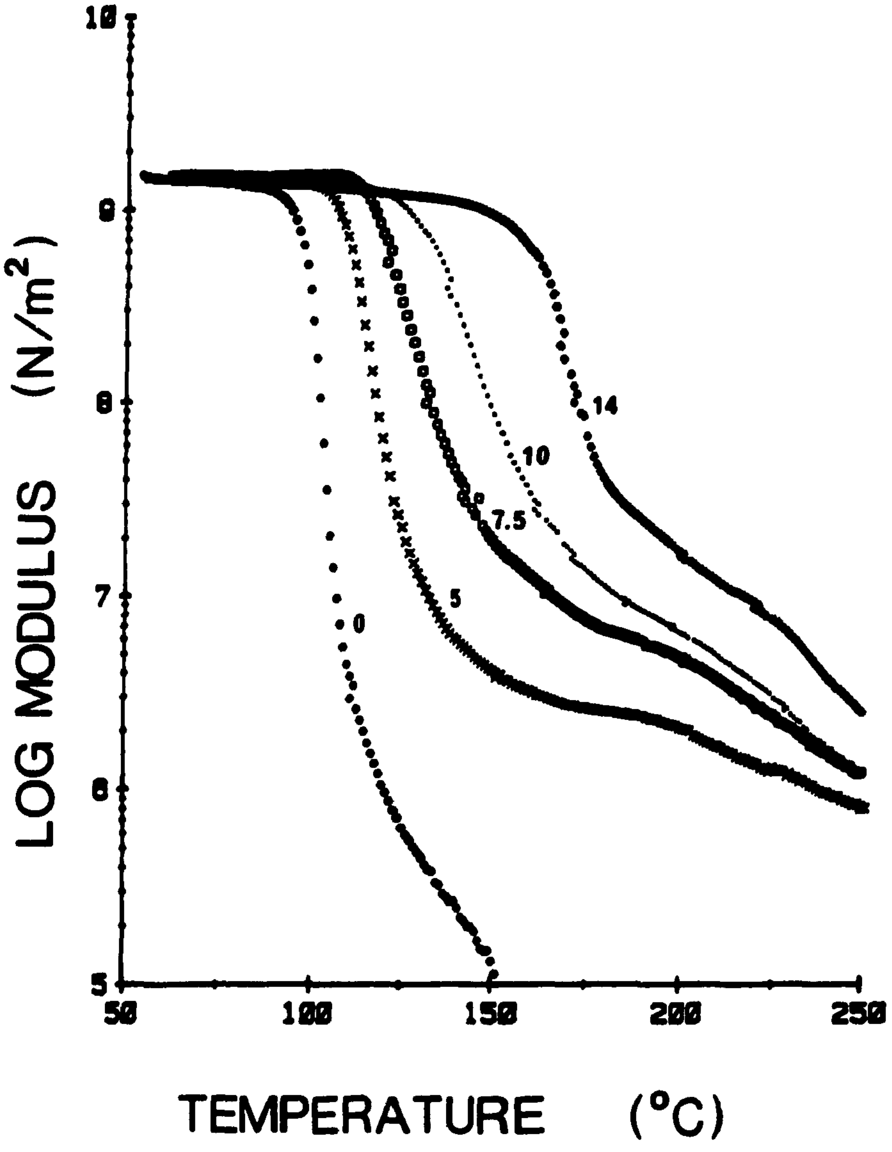


Figure 5.3. Dynamic storage modulus curves (1 Hz) for the C_2 ether series; ion contents (mole%) are as indicated.

One special feature of the tan δ vs. temperature curves (Figure 5.2) is, however, the presence of a third, high temperature loss peak (indicated by arrows in Figure 5.2), in contrast with the two normally observed for amorphous clustered styrene ionomers[18]. In fact, the presence of a third peak is characteristic of most of the systems studied here. It will be shown later that the third peak is attributable to cross-linking of the samples occurring in the course of the DMTA run at high temperatures. The presence of this third peak will therefore be neglected in the subsequent interpretation of the results. The modulus increase towards the end of the runs (starting around 225 °C for the C_{11} ethers, as shown in Figure 5.4, and at about 250 °C for the C_2 ethers) is another manifestation of cross-linking in that temperature range.

The dynamic mechanical curves were numerically analyzed on an IBM-XT compatible personal computer to extract all the useful information using a previously described program[5]. The information thus obtained includes the position and width at half height of the peaks in the tan δ curves, the magnitude of the ion-related rubberlike inflection modulus and the corresponding temperature in the storage modulus curves, as well as the activation energies calculated from the frequency shift of the tan δ maxima. These are summarized for each sample in Table 5.2. This presentation format was preferred for the results over a graphical approach, because of the quite distinct behaviors observed in comparing the different series with each other. The glass transition temperatures determined by DSC analysis are also included for comparison.

The values presented are the ion content of the samples (mole%), the T_g determined by DSC [T_g(DSC)], the 1 Hz matrix and cluster T_g [T_g(ma) and T_g(cl), respectively] and their corresponding widths at half-height ($W_{1/2}$). The calculated activation energies of the matrix [E_a(ma)] and cluster [E_a(cl)] peaks are also included, with the corresponding correlation coefficients (r^2). The experimental average molecular weight between cross-links (M_c) was calculated for each sample from the corresponding inflection modulus and temperature.

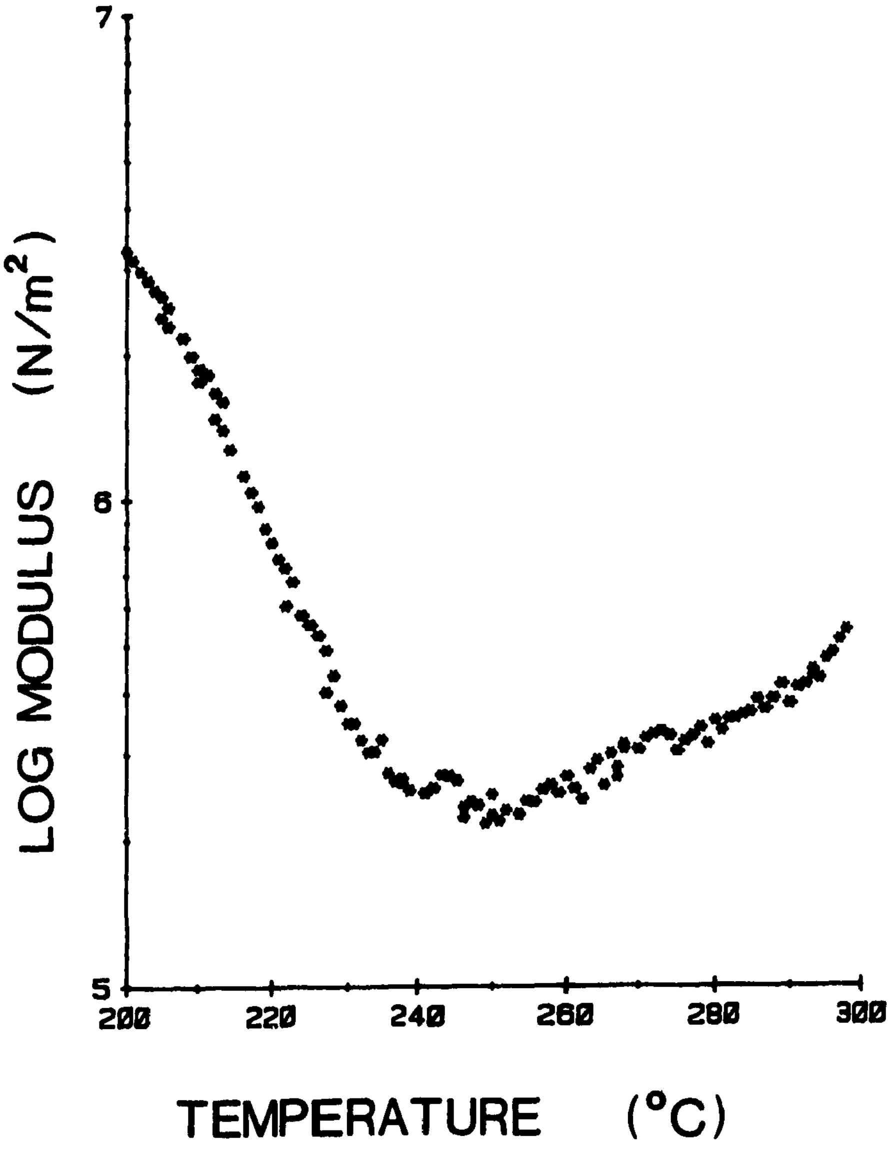


Figure 5.4. Storage modulus increase of the C_{11} ether 10% Na sample in the 200-300 °C range.

Table 5.2. Summary of data obtained by DSC and by numerical analysis of the dynamic mechar curves.

Material	EW (g/mol)	DSC T_g(°C)	Matrix T_g(°C)	$W_{1/2}$ (°C)	Clust. T_g(°C)	W_1 (°C
C_2 Alkyl ester	----	105	114	13	---	-
C_2 Alkyl 2.5% Na	4220	115	126	15	167	1
C_2 Alkyl 5% Na	2150	127	136	15	179	3
C_2 Alkyl 7.5% Na	1450	131	142	19	178	2
C_2 Alkyl 9.5% Na	1110	145	151	18	226	6
C_6 Alkyl ester	----	81	94	14	---	-
C_6 Alkyl 2.5% Na	4280	86	102	16	---	3
C_6 Alkyl 5% Na	2200	100	115	15	183	5
C_6 Alkyl 7.5% Na	1510	113	127	17	187	4
C_6 Alkyl 11.4% Na	1160	133	139	21	201	3
C_{11} Alkyl ester	----	---	78	18	---	-
C_{11} Alkyl 5% Na	2270	85	100	18	136	2
C_{11} Alkyl 7.5% Na	1580	102	117	19	166	4
C_{11} Alkyl 11.2% Na	1230	131	132	25	184	3
C_2 Ether ester	----	96	108	15	---	-
C_2 Ether 5% Na	2260	114	122	21	160	2
C_2 Ether 7.5% Na	1470	118	131	29	171	1
C_2 Ether 10% Na	1120	139	152	33	184	2
C_2 Ether 14% Na	830	169	172	18	203	2
C_5 Ether ester	----	80	94	15	---	-
C_5 Ether 5% Na	2200	99	108	16	148	4
C_5 Ether 7.5% Na	1510	104	116	19	162	3
C_5 Ether 10% Na	1160	113	125	19	171	3
C_5 Ether 14% Na	870	156	139	18	180	2
C_{11} Ether ester	----	---	71	17	---	-
C_{11} Ether 2.5% Na	4370	66	82	18	130	2
C_{11} Ether 5% Na	2290	78	92	18	138	2
C_{11} Ether 7.5% Na	1590	89	104	21	146	2
C_{11} Ether 10% Na	1250	101	115	23	173	4
C_{11} Ether 14% Na	950	133	140	19	197	4

anical

$_{1/2}$ (°C)	E'_{in}	T_{in}	M_c (g/mol)	$-E_a$(ma) (kJ/mol)	r^2	$-E_a$(cl) (kJ/mol)	r^2
--	7.9E+05	156	14200	480	0.9995	---	-.---
17	3.1E+06	151	3560	470	0.995	230	0.993
31	7.3E+06	156	1550	500	0.998	250	0.998
20	7.4E+06	164	1560	550	0.990	250	0.995
68	1.5E+07	174	790	590	0.9997	190	0.998
--	5.0E+05	122	20600	410	0.996	---	-.----
35	1.1E+06	144	10400	430	0.997	---	-.---
53	2.7E+06	137	4050	460	0.995	180	0.95
47	4.8E+06	149	2280	500	0.994	200	0.998
31	1.6E+07	160	700	580	0.997	---	-.---
--	2.8E+05	111	36300	320	0.9999	---	-.---
25	6.1E+06	123	1690	400	0.991	260	0.995
49	1.4E+07	135	790	470	1.0000	190	0.997
32	2.6E+07	155	430	560	0.997	---	-.---
--	2.4E+05	142	44900	470	0.9999	---	-.---
26	2.4E+06	181	4910	440	0.996	230	0.990
19	4.3E+06	188	2790	420	1.0000	200	0.996
20	6.7E+06	199	1850	---	-.---	300	0.994
23	1.4E+07	212	890	650	0.993	370	0.990
--	3.3E+05	124	31700	430	0.9996	---	-.----
40	1.1E+06	178	10700	430	0.995	260	0.9996
39	3.0E+06	148	3630	400	0.996	220	0.996
36	4.9E+06	152	2290	500	0.9990	270	0.9999
29	1.7E+07	156	650	560	0.998	230	0.9992
--	1.7E+05	110	58300	320	0.990	---	-.---
27	1.6E+06	110	6120	340	0.990	170	0.995
28	4.9E+06	116	2090	370	0.997	200	0.998
22	1.5E+07	128	700	380	0.997	220	0.993
42	2.7E+07	140	400	440	0.998	250	0.994
41	5.4E+07	157	210	690	0.995	---	-.---

The cross-linking efficiency of the ionic aggregates may be expressed as the ratio M_c(cal)/M_c(exp), where M_c(cal) is the theoretical value calculated for strictly multiplet-type interactions, and equal to the equivalent weight of the sample; M_c(exp) is the average molecular weight between cross-links determined from the observed rubberlike modulus. This is illustrated in Figure 5.5 for the different alkyl and ether series compounds. These are compared to data obtained for styrene-sodium methacrylate[19] and styrene-sodium 4-styrenecarboxylate ionomers[20].

5.5. Discussion

The following order will be used to discuss the experimental observations. The variation of the matrix T_g with ion concentration will be discussed first, because it is least sensitive to cross-linking effects under the conditions used. The experimental evidence for network formation and the reasons for ascribing the third loss maximum to cross-linking will then be considered. This clarification will lead to a discussion of the observed variation with ion concentration of the cluster-related glass transition temperatures, as well as of the activation energies associated with both the matrix and cluster T_g's. The discussion will be concluded by the consideration of the different molecular parameters thought to be responsible for the observed effects.

5.5.1. Matrix glass transition temperature

An examination of the data in Table 5.2 reveals a monotonic increase in the matrix T_g with ion content (dT_g/dC), as measured by both the DSC and the DMTA techniques. This is generally associated with a decrease in segmental mobility due to ionic aggregation[21]. The different slopes obtained for all 6 systems are given in Table 5.3 for comparison. In the dT_g/dC calculations for the ether series obtained by DSC, the data for the 14% samples was excluded. It is generally accepted that as the ion content of the samples increases, the width of the transition region of DSC scans

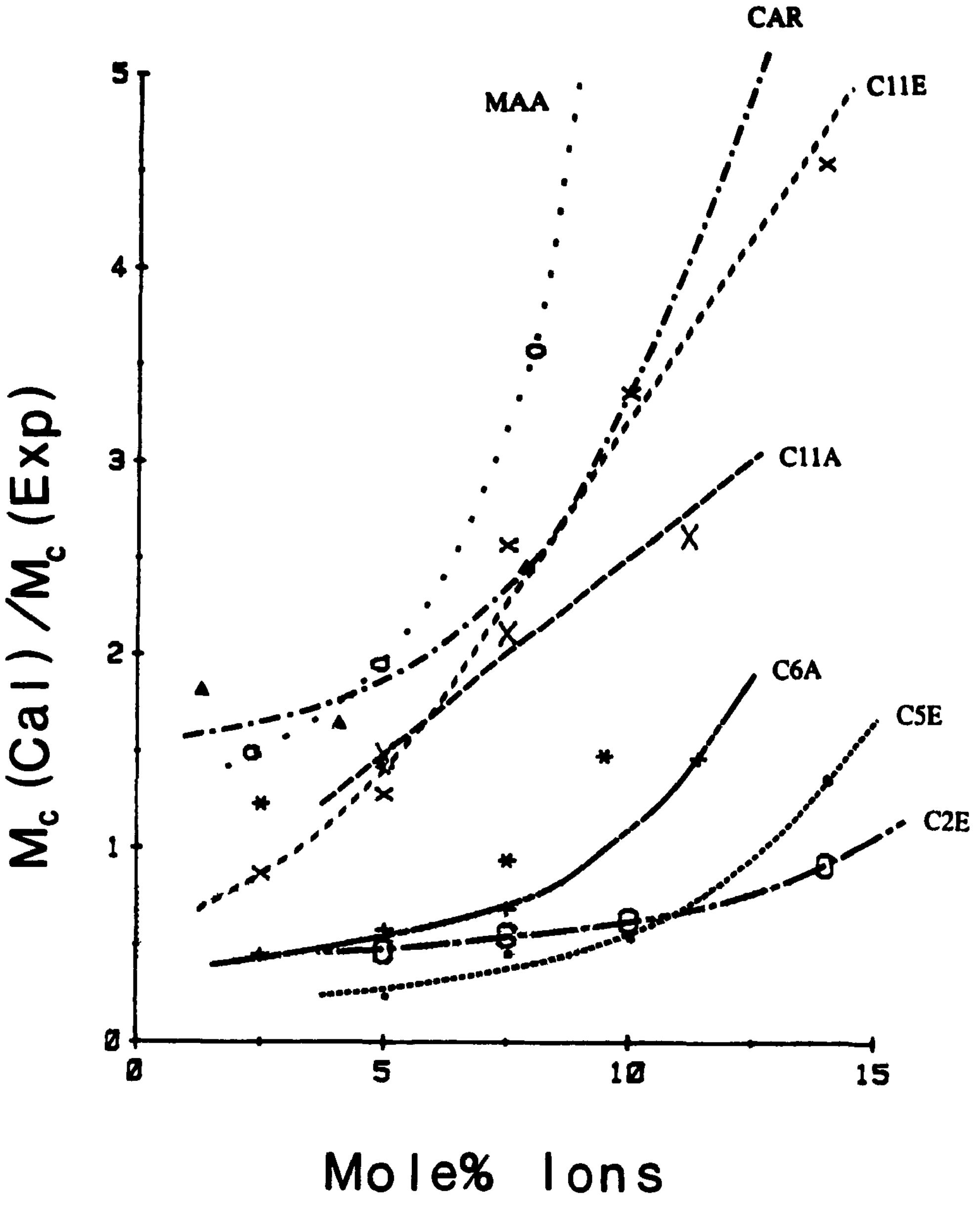


Figure 5.5. Comparison of the cross-linking efficiency of the ionic aggregates in the different families of sodium ionomers. The experimental points and the corresponding curves are identified as * (no curve): C_2 alkyl; +, C6A: C_6 alkyl; X, C11A: C_{11} alkyl; O, C2E: C_2 ether; · , C5E: C_5 ether; x, C11E: C_{11} ether; o, MAA: methacrylic acid[19]; ▲, CAR: carboxylated polystyrene[20].

increases, as a result of contributions from both the matrix- and the cluster-related glass transitions. This effect resulted in a significant deviation from linearity at 14% ion content. No calculations were performed for the C_{11} alkyl samples analyzed by DSC, because only three data points were available for the analysis and showed considerable scatter (Table 5.2). The discussion of the data for the T_g associated with the ion-rich domains (clusters) will be postponed to a later stage. Both the DSC and the DMTA techniques show a clear tendency for dT_g/dC to increase along the series C_2 alkyl < C_6 alkyl < C_{11} alkyl. However, no significant trend is observed for the ether series. In particular, the dT_g/dC values calculated for the C_5 ether derivatives is unexpectedly low. The following distinctions can be made concerning the two families of compounds. In the alkylated ionomers, the degree of functionalization is about 10-11 mole%; the ether compounds, however, have a pendant group concentration of ca. 15 mole%. Otherwise, the only difference between the two families concerns the mode of attachment of the pendant alkyl chain to the rings, namely the presence of an alkyl aryl ether linkage in the case of the ether analogs. The slightly higher concentration of ester groups in the ether than in the alkyl series appears to be an unlikely cause for the different tendencies observed. The lack of trends in the ether analogs could therefore be related to the ion-solvating properties of ethers[22]. Even though solvation effects due to ester functionalities have been linked to their somewhat different aggregation behavior[23] compared to styrene ionomers, they do not seem to cause a significant change in the dT_g/dC value: poly(ethyl acrylate-co-sodium acrylate) (3.4 °C/mol%)[23] compares to poly(styrene-co-sodium 4-styrenecarboxylate)[20] (2.7 °C/mol%), poly(styrene-co-sodium 4-styrenesulfonate) (4 °C/mol%[24] or 3.3 °C/mol%)[25], and sodium ionomers of poly(styrene-co-4-hydroxystyrene)[16] (3.2 °C/mol%).

Table 5.3. dT_g/dC by DSC and from dynamic mechanical data (matrix and cluster peaks). The values and uncertainties given were obtained by least squares fit of the data; the units are °C/mole%.

Series		DMTA (Matrix)	DMTA (Clusters)	DSC
C_2	Alkyl	3.6 ± 0.2	8.7 ± 0.8	4.0 ± 0.3
C_6	Alkyl	4.1 ± 0.2	2.9 ± 0.3	4.7 ± 0.3
C_{11}	Alkyl	4.9 ± 0.2	8 ± 1	------
C_2	Ether	4.7 ± 0.4	4.8 ± 0.1	4.0 ± 0.5
C_5	Ether	3.2 ± 0.1	3.5 ± 0.4	3.2 ± 0.2
C_{11}	Ether	4.8 ± 0.2	6.0 ± 0.6	4.6 ± 0.1

Apart from the T_g increase with the ion content of the samples, the T_g differences observed between the different families of ionomers (Table 5.2) show the expected variations of plasticized systems. Thus, between the different alkyl or ether compounds, for identical ion contents, the longer the attached chain, the lower the T_g of the sample. The T_g of the ether compounds is also lower than those in the corresponding alkyl series, presumably because of the higher degree of substitution of the ether derivatives (15 mole%) compared to the alkyls (10 mole%).

Similar trends are observed both in the dynamic mechanical and the DSC data, the two sets of curves being essentially parallel. There is, however, a systematic difference of ca. 10-15 °C between the two techniques, which becomes slightly larger for the longer chain lengths. This is attributed to the frequency effect of the dynamic mechanical experiments. It seems reasonable, however, that the larger samples (ca. 1.3 g) used in the dynamic mechanical experiments may also cause a slower thermal response of the material, even though the scanning rate is also slower in that case (DMTA: 0.5 °C/min; DSC: 20 °C/min).

5.5.2. Cross-linking effects

It was mentioned previously that three loss peaks were observed in the tan δ-temperature curves obtained by dynamic mechanical analysis of most samples. Obvious hints of the occurrence of cross-linking during the DMTA runs could be observed. These included, among others, the increase in the storage modulus with temperature in the upper temperature range (Figure 5.4), as well as the lack of sample flow. A second run performed on the same sample displayed an increased matrix T_g (first run: T_g = 115 °C, second run: T_g = 131 °C at 1 Hz). All ionic samples were insoluble after the DMTA runs; the nonionic esters, which were heated only to lower temperatures, however, remained soluble.

The cross-linking phenomena observed seemed to be more important for the ether than the alkyl compounds. Comparison of IR spectra of the 10%-hydrolyzed C_{11} ether compound before and after prolonged heating showed no clear hints concerning the nature of the reactions involved in the cross-linking process. It is suspected that the ether derivatives may undergo a thermal rearrangement reaction analogous to those reported for certain alkyl aryl ethers at elevated temperatures (200-350 °C)[26] to yield, among others, alkylated phenols. The process is known to involve free radicals, at least to some extent, which could explain the greater tendency observed for the ether than for the alkyl derivatives to cross-link. This possibility is supported by the lack of significant changes in the IR spectra before and after heating, already pointed out above. Considering the low concentration of ether linkages (15 mole%), it seems reasonable that the thermal rearrangement of a fraction of the ether groups in these polymers does not result in easily detectable changes. The fact that the carbonyl band (1750 cm^{-1}) remain unchanged both in intensity and shape also rules out the occurrence of a decarboxylation reaction.

The effects of "dynamic cross-linking" (network formation during the course of a thermal scan experiment) on the dynamic mechanical properties of epoxy resins are well known and have been the subject of a number of papers[27,28]. Of particular relevance to this work is the frequent appearance of an extra dispersion in the loss tangent-temperature curve of uncured or partially cured systems. Lee and Goldfarb[28] suggested considering the observed dynamic modulus (G or E) of curing systems as resulting from two distinct contributions, due to thermal and curing effects, respectively. The response of a sample in a temperature scan experiment may therefore be expressed as a function of these two parameters as

$$\frac{dG(n,T)}{dt} = \left[\frac{dG}{dn}\right]_T \frac{dn}{dt} + \left[\frac{dG}{dT}\right]_n \frac{dT}{dt} \qquad \text{(Eq. 5.1)}$$

where n is a loosely defined cure parameter such that $n = 0$ for an uncured sample and $n \rightarrow \infty$ for complete curing, and T is the experimental temperature. The main implication of Eq. 5.1 is that the observed modulus may be expanded into an isothermal curing contribution (first term), in addition to the conventional thermal scan contribution (second term). The relation described by Eq. 5.1 may be further simplified by assuming that the extent of cure of the system can be described by the increase in T_g, in the form of a reduced parameter $(T-T_g)$

$$\frac{dG}{dT} = \frac{dG}{d(T-T_g)} \left[\frac{dT}{dt} - \frac{dT_g}{dt}\right] \qquad \text{(Eq. 5.2)}$$

where dT/dt and dT_g/dt describe the thermal and the curing effects, respectively.

The actually observed response depends on the magnitude of each of the terms of Eq. 5.2. The authors distinguished four different possible cases for a temperature scan experiment. Type I behavior corresponds to $dT_g/dt = 0$, i.e. no curing contribution, giving rise to the response normally observed for thermoplastics in the absence of curing, or for fully cured thermoset systems. For $dT/dt > dT_g/dt \neq 0$ (stage II), $(T-T_g)$ is an increasing function, since the T_g change due to curing is small with respect to the time scale of the experiment. Stage III is identified by the condition $dT/dt < dT_g/dt$. This corresponds to a fast curing rate on the time scale of the experiment, and $(T-T_g)$ becomes a decreasing function. Finally, stage IV ($dT_g/dt < 0$) is seldom observed, and can be related to polymer degradation or the absorption of diluent by the sample.

This stage description approach was used by the authors to qualitatively describe the dynamic curing of different types of epoxy resin systems. It is suggested that the same approach may be used to describe the cross-linking effects observed in the polymers of interest to the present study. However, it should be kept in mind that since the covalent cross-link density involved in this case is significantly lower than for high-temperature epoxy resins, the features observed are correspondingly less pronounced. For the purpose of the discussion, the behavior of the C_{11} ether 10% Na sample will be considered. It is assumed that the rate of cross-linking is negligible on the time scale of the experiment at the lower temperature range (T < 175-200 °C), corresponding to a type I behavior. This assumption is based on the observation that all the nonionic (esterified) samples of the polymers analyzed by the DMTA technique up to that temperature range remained soluble. Likewise, the salts heated for short periods (ca. 1 hour) at 200 °C also remained soluble. The features observed for this part of the curve are typical of carboxylated ionomer systems: increased matrix T_g, high rubberlike modulus, appearance of a second loss tangent peak (Figures 5.1 and 5.2). At temperatures between 175 and 250 °C, however, there are two successive changes in slope of the storage modulus curve (Figure 5.1, 10 mole% curve), rather than the simple flow behavior usually observed. At around 250 °C, the modulus curve flattens, before increasing in a nonlinear fashion from 250 to 300 °C (shown in Figure 5.4). Calculations for the cross-linking density from rubberlike elasticity ($E = 3\rho RT/M_c$) have shown that the rate of increase of E' with the temperature is much more than expected for a "static" cross-linked system in the 250-300 °C range. Considering also the lack of significant sample deformation, this increase was attributed to "dynamic" cross-linking occurring during the course of the experiment. The fact that the position of the third loss maximum is shifted upwards on the temperature scale (Figure 5.2) with the degree of ionization of the sample suggests that the cross-linking rate may be diffusion controlled, being more limited in samples where ionic aggregation is more extensive, because of the increased sample viscosity.

According to the Lee and Goldfarb model, the increase in modulus would be a result of the occurrence of a stage III condition ($dT/dt < dT_g/dt$), which is equivalent in a way to retracing the modulus curve from right to left[28]. The occurrence of a stage II condition ($dT/dt > dT_g/dt$) has to be assumed because the system necessarily has to go through it to reach the stage III condition. Both stages II and III result in the increased T_g observed in the second scan ($\Delta T_g = 16$ degrees). The overall behavior of the present ionomers may therefore be described as being of type I-II-III.

Independently of the justifications brought by the stage description approach, other arguments may be used to warrant discarding the third loss peak as a dynamic cross-linking effect. The temperature of the second (cluster-related) loss maximum falls in a range typical of other carboxylated styrene ionomers (e.g. styrene-sodium methacrylate[18,19], styrene-sodium 4-styrenecarboxylate[20]), if the plasticizing effect of the pendant alkyl chains is taken into consideration. This is particularly worth noting at the lower ion contents (2.5-7.5%), where the second tan δ peak is at a much more reasonable position than the cross-linking peak, which occurs only approximately 50 degrees higher. Furthermore, the variation in the relative intensities of the first (matrix) and the second (cluster) loss maxima follows the pattern usually observed for increasing ion contents, the second peak becoming clearly dominant in the 10-14 mole% interval (Figure 5.2).

All the factors mentioned above are believed to justify the assignments made for the loss tangent-temperature peaks, namely associated with the matrix, clusters and "dynamic cross-linking", from the low to the high temperature range, respectively.

5.5.3. Cluster-related glass transition temperature

It was mentioned earlier that because of the proximity of the cross-linking peak to the cluster peak in the tan δ-temperature curves, it was necessary in many cases to "deconvolute" the peaks with the help of a numerical analysis procedure described elsewhere[5]. Because of the somewhat empirical character of baseline selection and the broader peaks associated with the ion-rich (cluster) domains, the results are expected to be less reliable than for the matrix peak. In the case of the sharper matrix peaks, variations of the order of 1 degree were obtained by intentionally selecting different possible baselines. For the cluster peaks, however, variations of the order of 2-3 degrees were observed in the same conditions. Not surprisingly, the cluster peak positions show more scatter than the matrix peaks, and approximately linear increases with ion contents (Tables 5.2 and 5.3) and dT_g/dC values ranging from approximately 3 °C/mol to 9 °C/mol. No significant trend seems to emerge from a comparison of the different series (Table 5.2).

5.5.4. Activation energies

It can be seen in Table 5.2 that the activation energy of the matrix-related transition increases with the ionic group concentration, and tends to be higher for the alkyl than for the ether derivatives. The matrix activation energies are also highest for the shorter chain compounds. The cluster-related activation energies show a similar trend; also, more scatter is present. Some experimental results were rejected (Table 5.2) on the basis of abnormal loss peak shapes within a run. The overall average trends for the activation energies may be represented (in kJ/mol) as a function of the ion concentration C (in mole%) by

$$E_a(\text{ma}) = (15 \pm 3)\cdot C + (380 \pm 20) \qquad \text{(Eq. 5.3)}$$

and

$$E_a(\text{cl}) = (7 \pm 3)\cdot C + (180 \pm 20) \qquad \text{(Eq. 5.4)}$$

for the matrix- and cluster-related transitions, respectively. The fact that the cluster-related activation energy is significantly lower than that associated with the matrix has been suggested[19] as providing strong support to the presence of two distinct phases (the ion-poor matrix and the ion-rich clusters) as detected by dynamic mechanical analysis. It was pointed out that if a single phase were present in the system, a dispersion occurring at a higher temperature should have a higher activation energy.

However, one word of caution is necessary, in that the magnitude of the uncertainties associated with the activation energies is rather large. It was explained earlier that the accuracy of the values of the matrix- and cluster-related loss maxima were expected to be of the order of 1 and 2-3 degrees, respectively. The "relative" variations expected within a set of curves for a given sample at the different frequencies were, however, expected to be significantly smaller. This is because the curves obtained at the different frequencies are essentially identical in shape. Consequently, it is possible to set the baseline in a virtually identical manner within a set of curves. The variations thus expected for the matrix and cluster peak positions were arbitrarily set to 1/3 of the values given above, leading to uncertainties of the order of 0.3 and 0.7-1.0 degree, respectively. Even though this 1/3 factor is of a very empirical nature, it proved to be consistent with the variations observed in the data. The resulting uncertainties in the temperature were included in the linear regression calculations[29] used to obtain uncertainties in the calculated activation energies. Typical errors for the matrix- and cluster-related activation energies were of about 50 and 100 kJ/mol, respectively.

5.5.5. Contributions to ionic aggregation

The aggregation efficiencies of the ions in the different ionomer series were presented as a function of the ionization level in Figure 5.5. As explained earlier, the M_c(cal)/M_c(exp) ratio was used for this purpose. The advantage of this approach is that it provides a simple way of comparing the effect of ionic aggregation in the samples with respect to a reference state. This reference state is a system in which all ion pairs are interacting in the form of multiplets only [M_c(cal)], in the absence of cluster structures. This M_c value also corresponds to the equivalent weight of the sample. A ratio greater than one (experimental M_c < calculated M_c) implies an enhanced state of aggregation, likely in the form of large-scale ionic aggregation (clustering). In contrast, a ratio of less than unity points at a reduced state of aggregation. However, because the determined M_c(exp) result from the average effect of all the ionic aggregates present in the samples, M_c(cal)/M_c(exp) < 1 does not necessarily exclude the presence of clusters, but is rather indicative of a reduced state of clustering, when compared to a system with a larger ratio.

Several clear-cut trends emerge from Figure 5.5. It can be seen that at low ion concentrations, most samples fall in or extrapolate to a band of M_c(cal)/M_c(exp) = (0.6 ± 0.2), showing that the cluster structures, if present, are not rheologically significant. Multiplet formation, therefore, seems to dominate at low ion concentration in most samples. The onset of deviation from that behavior, as well as the trends at high ion contents, however, are a function of the type of compound involved. The following trend in the ratio is observed for deviations outside the (0.6 ± 0.2) band described above:

$$C_2 \text{ ether} < C_5 \text{ ether} < C_6 \text{ alkyl} < C_{11} \text{ alkyl} \approx C_{11} \text{ ether}.$$

It can be noticed from Figure 5.5 that the C_{11} alkyl and the C_{11} ether series display very similar characteristics. This seems reasonable, considering the length of the alkyl chain (10 methylene units) separating the ionic groups from the styrene rings in both cases. For the same reason, the presence of an ether linkage does not seem to influence significantly the aggregation behavior of those samples. On the other hand, the C_2 ether and the C_5 ether series also behave very similarly. The C_6 alkyl derivatives display aggregation characteristics which are intermediate between these two groups. The results for the C_2 alkyl compounds, however, canot be explained, and will not be discussed here at great length. It is suspected that the higher matrix and cluster T_g's observed in these compounds may have led to a merging of the cluster- and thermal cross-linking loss tangent peaks, making it impossible to separate the two effects.

In order to rationalize the observed variations in the dynamic mechanical properties of the ionomers presently studied, it seemed reasonable to postulate the existence of three distinct factors affecting the ionic aggregation. These are the bulkiness and rigidity of the units to which the ionic groups are attached, the efficiency of the pendant ionic groups in immobilizing the polymer backbone, and, finally, in the case of the ether compounds, the presence of solvation effects due to the alkyl aryl ether linkages.

In consideration of the last factor, it is possible to argue that the C_2 and C_5 ether derivatives are less clustered than the C_6 alkyl series because of the presence of the solvating oxygen atom linking the relatively short alkyl chain to the styrene ring. Because of their shorter chain length, the incorporation of these ionic groups into the cluster structures also brings along solvating groups (the ether linkages), which may lead to a less favorable ion-ion interaction energy than in their absence. This solvation factor could also explain why the C_6 alkyl series is significantly more clustered than the C_5 ether at the higher (10-11 mole%) ionization level, the total chain length being otherwise identical (6 atoms in both cases). The somewhat increased state of aggregation of the C_5 ether 14% Na sample compared to the C_2 ether 14% Na sample could also be taken as indicative of more important solvation effects in the latter case. As mentioned before, the very similar behaviors of the C_{11} alkyl and the C_{11} ether series compounds could be related to the increased distance between the solvating ether linkage and the ionic chain end. The fact that the characteristics of the different series become more easily distinguishable in the higher ion concentration range is not surprizing as such, since it is known that the extent of clustering is greatly enhanced in styrene ionomers at ion concentrations above 6-7 mole%.[18]

It was already pointed out that the C_5 ether 14% Na sample displays a somewhat increased state of aggregation (Figure 5.5) relative to the analogous C_2 ether compound. Apart from the solvation effect postulated above, it seems that the increased local bulkiness (proximity of the styrene ring) of the C_2 relative to the C_5 ether compound may have contributed to the difference in aggregation. The factor involved in this case is the greater proximity of the stiff, bulky styrene ring for the C_2 than for the C_5 ether ionomers, making the incorporation of the bulkier, shorter side chains structures in the clusters energetically less favorable. This factor apparently becomes negligible in the case of the C_{11} compounds, presumably again because of the increased distance between the ionic groups and the bulky styrene rings. This is probably why the C_{11} compounds show the most efficient clustering.

The comparison of the present ionomers with previously studied systems highlights the effect of what is thought to be the effectiveness of the pendant ions in immobilizing the polymer backbone. Two additional curves are shown on Figure 5.5 for comparison, namely for poly(styrene-co-sodium methacrylate)[19] and for poly(styrene-co-sodium 4-styrenecarboxylate)[20]. The results are directly comparable in the former case, because the samples were also studied using DMTA, i.e. at a constant frequency. The carboxylated styrene analysis was done using a torsion pendulum, whose oscillation frequency varies with the stiffness of the sample; a bit more caution may therefore be necessary in that case. Once again, it is worth mentioning that the behavior of the 4-carboxystyrene ionomers is qualitatively quite similar to that of the C_6 and C_{11} alkyl compounds, but the C_2 alkyl series does not fit at all, justifying the omission of these results from this part of the discussion.

The styrene-sodium methacrylate ionomers display the characteristics of a most highly clustered system, with a M_c(cal)/M_c(exp) ratio increasing very rapidly above ion concentrations of about 8 mole%. This contrasts with the p-carboxystyrene system, and obviously even more with the ionomers prepared for this study. More specifically, the comparison of the C_{11} alkyl and ether derivatives with the styrene-sodium methacrylate polymers suggested the importance of the chain immobilization effect. Indeed, it appears that in both cases, local bulkiness alone is not a primary factor determining ionic groups aggregation. The incorporation of a sodium methacrylate unit in a cluster structure is, however, expected to have a more strongly immobilizing effect on the polymer backbone compared to a carboxylate ion at the end of a long, highly flexible alkyl chain. It seems that the aggregation of sodium methacrylate units, even though energetically approximately as favorable as for the alkylated ionomer, drags more organic material from the polymer backbone into the cluster, possibly leading to a larger overall cluster size, compared to the alkylated compound.

5.6. Conclusions

It was shown that the incorporation of ionic group spacers of variable chain length resulted in significant variations in the dynamic mechanical properties of carboxylated styrene ionomers. The results were compared, among others, in terms of ratios M_c(cal)/M_c(exp), where M_c(cal) represents the calculated molecular weight between cross-links, assuming strictly multiplet-type interactions, and M_c(exp) is the experimental molecular weight between cross-links evaluated from the value of the inflection modulus of the ion-related rubbery plateau. All the experimental cross-link densities determined were significantly lower than for other previously characterized highly clustered systems, such as poly(styrene-co-sodium methacrylate). Three distinct factors were postulated as contributing to the variations in properties observed among the different series. The bulkiness and rigidity of the units to which the pendant ionic groups are attached, as well as the efficiency of the terminal ionic groups in immobilizing the polymer backbone could explain the trends observed among both the alkyl and ether derivatives. The lower clustering tendency of the ether compounds, compared to the alkyl derivatives, could be rationalized in terms of the solvating effect of the alkyl aryl ether linkage of these ionomers.

5.7. Acknowledgements

We are most grateful to Mr. Bryn Hird for making the styrene-sodium methacrylate ionomers dynamic mechanical data available to us. Funding for this work was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC). One of the authors (M.G.) would also like to acknowledge the financial support of NSERC and of the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (Quebec).

5.8. References

(1) (a) Eisenberg, A.; King, M. *Ion-Containing Polymers*; Academic: New York, 1977. (b) Bazuin, C.G.; Eisenberg, A. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 271. (c) MacKnight, W.J.; Earnest, T.R., Jr. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41. (d) Fitzgerald, J.J.; Weiss, R.A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 99.

(2) (a) Navratil, M.; Eisenberg, A. *Macromolecules* **1974**, *7*, 84. (b) Makowski, H.S.; Lundberg, R.D.; Westerman, L.; Bock, J. In *Ions in polymers*; Eisenberg, A., Ed.; Advances in Chemistry 187; American Chemical Society: Washington, DC, 1980; pp 3-19.

(3) Brockman, N.L.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1145.

(4) (a) Lundberg, R.D.; Makowski, H.S. In *Ions in polymers*; Eisenberg, A., Ed.; Advances in Chemistry 187; American Chemical Society: Washington, DC,

1980; pp 21-36. (b) Rigdahl, M.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1641.

(5) Gauthier, M.; Eisenberg, A. Submitted for publication in Macromolecules.

(6) *Perfluorinated Ionomer Membranes*; Eisenberg, A., Yeager, H.L., Eds.; ACS Symposium Series 180; American Chemical Society: Washington, DC, 1982.

(7) Nafion is a registered trade mark of E.I. duPont de Nemours and Co.

(8) Dow Chemical, U.S. Patent 4 417 969.

(9) Ukihashi, H.; Yamabe, M. In Reference 6, p 427. Flemion is a registered trade mark of the Asahi Glass Co.

(10) Seko, M.; Ogawa, S.; Kimoto, K. In Reference 6, p 365.

(11) Sata, T.; Onoue, Y. In Refrence 5, p 411. Neosepta-F is a registered trade mark of the Tokuyama Soda Co.

(12) See for example Hashimoto, T.; Fujimura, M.; Kawai, H. in Reference 6, p 217.

(13) (a) Moore, R.B., III; Martin, C.R. *Macromolecules* **1988**, *21*, 1334. (b) Moore, R.B., III; Martin, C.R. To be published.

(14) (a) DeMejo, L.; MacKnight, W.J.; Vogl, O. *Polymer* **1978**, *19*, 956. (b) DeMejo, L.P.; MacKnight, W.J.; Vogl, O. *Soc. Plast. Eng., Tech. Pap.* **1978**, *24*, 5. (c) MacKnight, W.J.; DeMejo, L.; Vogl, O. *Acta Polym.* **1980**, *31*, 617. (d) Bansleben, D.A.; Janovic, Z.; Vogl, O. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3263. (e) Bansleben, D.A.; Vogl, O. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 703. (f) Muggee, J.; Vogl, O. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 2327.

(15) Huiji, L. et al. To be published.

(16) (a) Clas, S.-D.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 2743. (b) Ibid. **1986**, *24*, 2757.

(17) Gauthier, M.; Eisenberg, A. Submitted for publication in *J. Polym. Sci., Polym. Chem. Ed.*

(18) Eisenberg, A.; Navratil, M. *Macromolecules* **1974**, *7*, 90.

(19) Hird, B.; Eisenberg, A. To be published.

(20) Brockman, N.L.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1145.

(21) *Ionic Polymers*; Holliday, L., Ed.; Applied Science: London, 1975; p 36.

(22) Searles, S., Jr.; Tamres, M. In *The chemistry of the ether linkage*; Patai, S., Ed.; Interscience: New York, 1967; Chapter 6.

(23) Matsuura, H.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1201.

(24) Rigdahl, M.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1641.

(25) Weiss, R.A.; Lundberg, R.D.; Turner, S.R. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 549.

(26) (a) Hart, H.; Eleuterio, H.S. *J. Am. Chem. Soc.* **1954**, *76*, 519. (b) Elkobaisi, F.M.; Hickinbottom, W.J. *J. Chem. Soc.* **1959**, 1873. (c) See also Reference 22, Chapters 4 and 14.

(27) (a) Kenyon, A.S.; Nielsen, L.E. *J. Macromol. Sci., Chem.* **1969**, *A3*, 275. (b) Babayevsky, P.G.; Gillham, J.K. *J. Appl. Polym. Sci.* **1973**, *17*, 2067. (c) Dynes, P.J.; Kaelble, D.H. *J. Appl. Polym. Sci.* **1978**, *22*, 837. (d) Senich, G.A.; MacKnight, W.J.; Schneider, N.S. *Polym. Eng. Sci.* **1979**, *19*, 313.

(28) Lee, C.Y.-C.; Goldfarb, I.J. *Polym. Eng. Sci.* **1981**, *21*, 951.

(29) Bevington, P.R. *Data reduction and error analysis for the physical sciences*; McGraw-Hill: New York, 1969; Chapter 6.

Chapter 6. General discussion

6.1. Conclusions and contributions to original knowledge

Systematic variations were used to examine the effects of some structural parameters on the dynamic mechanical properties of carboxylated styrene ionomers. The matrix glass transition temperature of a styrene-sodium methacrylate (7 mole% ions) copolymer was lowered via alkylation with 1-decene in a Friedel-Crafts type reaction. Alkylated ionomers with 0-100 mole% substitution of the styrene rings were obtained.

Clustering was enhanced, relative to the nonalkylated ionomer, in alkylated samples with substitution levels of up to 15-20 mole%. At the higher alkylation levels, however, clustering was highly disrupted. The magnitude of the ion-related rubberlike modulus dropped by over an order of magnitude. This disruptive effect was attributed to the bulky nature of the grafted alkyl chains. It was seen that the clusters, even though still detectable in the dynamic mechanical data, did not contribute significantly to the rheological properties of the ionomers.

This plasticization study showed that T_g depression does indeed favor clustering. However, if the reduction in the glass transition temperature is achieved by the inclusion of bulky and flexible groups, beyond a certain point, clustering is disrupted, as in this case.

The novel aspects of this work relies on the use of internal plasticization to lower the T_g of the ionomers, rather than the addition of diluents, which have already been used on a few occasions. Grafting of the plasticizer onto the styrene rings has a number of advantages, of which a stable composition may be the most significant. One of the major disadvantages of low molecular weight diluents is that they may evaporate at high temperature, resulting in a composition drift during the course of the experiment. Consequently, the plasticizer content is often reported as a range in these experiments.

The nonvolatile nature of the grafted plasticizer also makes it possible to obtain samples quite devoid of moisture, which is known to be very detrimental to cluster formation. In the case of external plasticization, both the nonplasticized ionomer and the diluent have to be carefully dried separately. The process involves a number of other manipulations which have to be carried out under strictly anhydrous conditions.

The same styrene-sodium methacrylate (7 mole% ions) copolymer was also used to examine the effect of the dielectric constant (related to the polarity) of the polymer matrix on the aggregation behavior of the ionomers. Minimal composition variations of the system studied were once more obtained through postpolymerization modification of the parent copolymer. Reaction conditions were developed for the controlled nitration of the styrene-methacrylic acid copolymer; the synthesis yielded materials with a relaxed dielectric constant comparable, at the higher nitration level, to that of the acrylate ionomers. The selection of the nitro group to increase the polarity of the matrix was justified by the fact that apart from being very polar, it also lacks the capability of interacting significantly with ions. This, therefore, makes possible the clear separation of effects due to polarity as opposed to specific interactions. The results of the dynamic mechanical analysis showed no changes in the aggregation behavior of the nitrated derivatives relative to the parent ionomer.

This trend was confirmed and established more generally in a parallel study of the same ionomer plasticized with nitrobenzene. The observed variations in the matrix and cluster-related glass transition temperatures were typical of nonpolar plasticizers, two essentially parallel curves being obtained in a plot of matrix T_g and cluster T_g vs. nitrobenzene content. The results of the nitration and nitrobenzene plasticization experiments showed that the aggregation behavior of ionomers is clearly not related to the polarity of the parent polymer, but is more likely related to specific interactions, i.e. solvation effects due to the ability of the polymer to interact with the ions.

A most innovative aspect of the approach used in the polarity effects study is the variation of the dielectric constant of an ionomer over a significant range with only minimal composition variations. This contrasts with previous attempts to explore dielectric constant effects, which were limited to comparing materials of a very different structure and composition. In this case, polymers were obtained which had a dielectric constant comparable to the acrylates, by introducing nitro groups on approximately one third of the styrene rings.

Finally, the effects of the distance of the ionic groups from the polymer backbone was studied, also in carboxylated styrene ionomers. In this case, however, the ionic groups were at the end of an alkyl chain attached at the para- position of the styrene units, rather than directly on the backbone as in the two previous cases. The dynamic mechanical properties of the ionomers were examined both as a function of the ion content and of the length of the spacer chain. Two analogous families of compounds were examined, containing alkyl chains attached either directly to the styrene rings ("alkyls") or through an alkyl aryl ether linkage ("ethers"). General synthetic paths were developed for preparing derivatives of the alkyl and ether families with spacers of the desired length. The polymers prepared for this work contained either ca. 10 mole% of C_2, C_6, or C_{11} ω-carboxylated alkyl chains (alkyl derivatives), or ca. 15 mole% of C_2, C_5, or C_{11} chains for the ether compounds. The trends observed among the different series of ionomers suggested that three distinct factors may have contributed to the different clustering behaviors. The bulkiness and stiffness of the units supporting the ionic groups tend to reduce clustering, presumably because steric effects lessen the efficiency of ion-ion and dipole-dipole interactions responsible for cluster formation. The efficiency of the pendant ionic groups in immobilizing the polymer backbone was suggested to explain the lower ionic cross-link densities observed in all the the ionomers studied, compared to other highly clustered ionomer systems. Also, the decreased clustering tendency of the ether derivatives relative to the alkyl compounds was rationalized in terms of ionic solvation effects due to the presence of the alkyl aryl ether linkages.

All but the C_2 alkyl and ether derivatives are completely new materials, and none of the ionomers had been characterized in terms of mechanical properties. Given their novel character, and the possibility they offer to investigate thoroughly the effects of ionic group spacing in ionomers, these polymers will be the subject of a number of subsequent investigations.

6.2. Suggestions for further work

The studies done here have shown the importance of some molecular parameters in determining the aggregation behavior of ionomers. A number of experiments could be designed to further generalize and expand the findings of the present work. Some of these were already identified as ongoing in the different chapters. These and other suggested experiments will be summarized here, according to the relation they bear to the present studies.

6.2.1. Glass temperature variation studies

Small-angle X-ray scattering experiments are currently under way to provide further support to the interpretation presented for the dynamic mechanical data. In order to try avoiding the bulkiness effects encountered in the alkylated ionomers, it seems that it could be advantageous to try an alternate route to decreasing the T_g of the polymers. This could be possible, for example, if terpolymers containing methacrylic acid, styrene and variable proportions of a third flexible, yet not excessively bulky monomer unit (e.g. 1-hexene) were prepared. A different polymerization technique (e.g. ionic) may have to be used for this purpose, since it seems unlikely that the relative reactivities of the monomers would be such as to allow the preparation of these terpolymers whith the more common free-radical initiation techniques.

6.2.2. Matrix polarity and specific interactions

It was shown that the dielectric constant of the matrix alone does not affect ion aggregation. However, it would be possible to explicitly confirm that specific interactions (solvation effects) are mostly responsible for the variations observed among different ionomer systems. One way to do this would be through a systematic variation of the type of plasticizer used. Different types of diluents could be selected in relation to their polarity and ability to interact with ionic species. Tables of three-dimensional solubility parameters (see Chapter 3) could be used to assist in the selection of the diluents. Similar effects could also possibly be obtained in terpolymers including variable proportions of an interacting monomer unit (e.g. acrylamide).

6.2.3. Ion spacing effects

The different copolymers prepared for the systematic ionic group spacing study are new materials with interesting features justifying a number of additional properties investigations. The presence of spacers and ether linkages in these derivatives make them distantly related to the perfluorinated membrane materials, and warrants swelling, ion diffusion and transport studies accross membranes made of these materials. It was also mentioned that an extensive SAXS investigation of these ionomers is currently under way. The aim in this case would be to draw a parallel between the variations observed among the dynamic mechanical properties of the different series of compounds and the characteristic dimensions of each system. The SAXS studies would also, hopefully, show significant structural differences among the ionomer series, to account for the three factors postulated above as influencing ion aggregation.

The exact mechanisms leading to covalent cross-linking could be the subject of further investigations with the help of solid state NMR and/or IR spectroscopy, preferably on copolymers with a higher degree of substitution, or on model compounds.

Alternate synthetic routes could be used to prepare the alkyl derivatives, but would result in polymers with a structure which is less clearly defined. One possibility would be to graft methyl esters of unsaturated aliphatic acids (e.g. methyl 10-undecenoate) directly onto the styrene rings with the help of a Friedel-Crafts reaction analogous to the alkylation procedure described in Chapter 2. Rearrangement of the carbocationic intermediates would also be possible in this case, resulting likewise in a mixture of isomers. Another approach would not result in rearrangement of the chain, but would rather yield a mixture of 3- and 4-alkylated styrene units. In this case, polystyrene could be metalated directly with a TMEDA-n-butyllithium complex according to the procedure given in Reference 46 of Chapter 1. The main advantage of this technique is that much smaller excesses of dibromoalkyl derivatives would be necessary to obtain the bromoalkylated polymeric intermediate.

6.2.4. New ionomer systems

Apart from the new systems described above, a number of other functional polymers could also be suggested as possible new ionomer systems. One example of this is the synthesis, currently under way, of sulfonated analogues of the styrene derivatives. A functionalized styrene polymer containing C_4 sulfonate-terminated alkyl units in the para- position could be obtained by reacting the lithiated polymer of Chapter 4 with butane sultone. Ether derivatives could also be obtained by using terminally brominated aliphatic sulfonic acid esters in the same reaction conditions used for the Williamson ether synthesis.

Amines could be obtained by reacting the bromoalkylated polystyrene intermediates of Chapter 4 with e.g. dimethylamine. These should be thermally more stable than the vinylpyridine and N,N-dimethylaniline analogues (see Appendix B).

It may be possible to obtain systematic chain length variation in the absence of a styrene ring (i.e. without bulkiness effects) using a different approach. This would involve the preparation of a styrene-vinyl alcohol copolymer as a first step. The alcohol could be ionized by adding a strong base (e.g. butyllithium), and the polymer could then be used in a Williamson ether synthesis reaction to effect the coupling reaction as described in Chapter 4.

Appendix A. Copolymerization calculations

Structure-properties studies of ionomers require the synthesis of copolymers with well-defined characteristics. In particular, it is useful to be able to predict what proportion of monomers in the feed will result in a copolymer of the desired composition. Also important to evaluate is the degree of randomness of the monomers distribution. The random distribution of ionic groups along the polymer chain is of utmost importance in structure-properties studies of ionomers: It is well-known that the properties of ionomers (and polymers in general) with a "blocky" structure are very different from their random counterparts.

While calculations for monomer feed composition tend to be long and repetitive, it becomes almost impossible to evaluate the average copolymer composition obtained since, as will be pointed out later, numerical integration is best suited for that purpose. Two programs are suggested here to perform copolymer composition and comonomer sequence length distribution calculations. The relevant mathematical principles are reviewed for the convenience of the reader, followed by the program listings and sample calculations sessions for the materials prepared for this work.

A few styrene copolymers were prepared for this work, either as direct precursors for ionomers (methacrylic acid copolymers), or as intermediates used in functionalization reactions (bromostyrene and methoxystyrene copolymers). The reactivity of substituted unsaturated bonds in radical chain polymerization varies, depending on the ability of the substituents to stabilize the radicals formed. Furthermore, the polymerization behavior of monomers in a copolymerization reaction can be very different from that in homopolymerization. Odian[1], for example, points out that while certain monomers like maleic anhydride and stilbene have little or no tendency to homopolymerize, they easily undergo copolymerization with free-radical initiation. The following is a summary of the factors involved in determining the conditions needed to produce copolymers with the desired characteristics, as presented by Odian[1] and Flory[2].

A.1. Copolymer composition

The composition of the copolymer formed from a given monomer mixture ("feed") can intuitively be expected to depend on the relative concentrations of each monomer in the feed, but also on the reactivities of the monomer units with respect to each other. Once a polymer chain is initiated (either thermally or by a radical initiator added for this purpose), four different types of reactions may occur at the end of the chain (R) to propagate it. If M_1 and M_2 represent the two comonomers, M_1^* and M_2^* the corresponding radicals at the end of the chain, and it is assumed that the reactivity of the propagating chain only depends on the last unit added, these reactions may be described as

$$R\text{-}M_1^* + M_1 \xrightarrow{k_{11}} R\text{-}M_1^* \qquad \text{(Eq. A.1)}$$

$$R\text{-}M_1^* + M_2 \xrightarrow{k_{12}} R\text{-}M_2^* \qquad \text{(Eq. A.2)}$$

$$R\text{-}M_2^* + M_1 \xrightarrow{k_{21}} R\text{-}M_1^* \qquad \text{(Eq. A.3)}$$

$$R\text{-}M_2^* + M_2 \xrightarrow{k_{22}} R\text{-}M_2^* \qquad \text{(Eq. A.4)}$$

where k_{mn} is the rate constant for a polymer chain terminated by an M_m^* radical and propagated by adding an M_n unit. The rates of disappearance of monomers 1 and 2 are therefore

$$\frac{-d[M_1]}{dt} = k_{11}\ [M_1^*]\ [M_1] + k_{21}\ [M_2^*]\ [M_1] \qquad \text{(Eq. A.5)}$$

$$\frac{-d[M_2]}{dt} = k_{12}\ [M_1^*]\ [M_2] + k_{22}\ [M_2^*]\ [M_2] \qquad \text{(Eq. A.6)}$$

where $[M_1^*]$ and $[M_2^*]$ represent short hand notation for the concentration of propagating centers. The instantaneous copolymer composition is then given by

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}\ [M_1^*]\ [M_1]\ +\ k_{21}\ [M_2^*]\ [M_1]}{k_{12}\ [M_1^*]\ [M_2]\ +\ k_{22}\ [M_2^*]\ [M_2]} \qquad \text{(Eq. A.7)}$$

The $[M_1^*]$ and $[M_2^*]$ factors can be eliminated from Eq. A.7 if it is assumed that they are constant (steady-state assumption), in which case their rates of interconversion is equal:

$$k_{21}\ [M_2^*]\ [M_1] = k_{12}\ [M_1^*]\ [M_2] \qquad \text{(Eq. A.8)}$$

Substituting Eq. A.8 into Eq. A.7, rearranging and dividing both the numerator and denominator by $k_{21}\ [M_2^*]\ [M_2]$,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]\ (r_1\ [M_1]\ +\ [M_2])}{[M_2]\ ([M_1] + r_2\ [M_2])} \qquad \text{(Eq. A.9)}$$

is obtained where r_1 and r_2 are defined as the copolymerization reactivity ratios

$$r_1 = k_{11} / k_{12} \qquad r_2 = k_{22} / k_{21} \qquad \text{(Eq. A.10)}$$

and are a measure of the ratio of rates of homogeneous as opposed to heterogeneous addition of the monomers. Equation A.9 represents the copolymer composition expressed as a function of concentration of the monomers in the feed. It can also be more conveniently expressed in terms of mole fractions in the feed (f_n) and in the polymer (F_n) as

$$F_1 = \frac{r_1 \; f_1^2 + f_1 \; f_2}{r_1 \; f_1^2 + 2 \; f_1 \; f_2 + r_2 \; f_2^2} \qquad \text{(Eq. A.11)}$$

using the identities

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \qquad \text{(Eq. A.12)}$$

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]} \qquad \text{(Eq. A.13)}$$

Equation A.11 was used in the BASIC copolymerization calculations program given in Appendix A.4. Examples of calculations are also given for the methacrylic acid, 4-bromostyrene and 4-methoxystyrene copolymers.

The copolymerization reactivity ratios are determined experimentally from the analysis of copolymers formed at various comonomer mole fractions. An extensive tabulation of comonomer reactivity ratios is available[3] for various polymerization conditions. In the event that r_1, r_2 values are not available for a given monomer pair, the more general Q-e scheme suggested by Alfrey and Price[4] may be useful. The method is essentially based on structure-reactivity correlations in the copolymerization of a given monomer with many different comonomers. The reactivity ratios may be calculated from tabulated[5] Q and e values as

$$r_1 = \frac{Q_1}{Q_2} \quad \exp\,[-e_1\,(e_1 - e_2)] \qquad \text{(Eq. A.14)}$$

$$r_2 = \frac{Q_2}{Q_1} \quad \exp\,[-e_2\,(e_2 - e_1)] \qquad \text{(Eq. A.15)}$$

The values thus obtained, if not as accurate as the r_1, r_2 values determined experimentally, are nevertheless generally a quite reliable approximation.

A.2. Sequence length distribution

The microstructure of the polymer chains produced in a copolymerization process may be expected to vary with the comonomer concentration in the feed, but also with the r_1 and r_2 values, since these control the relative amounts of each comonomer incorporated into the chain. Because the r_1 and r_2 values are related to the probabilities of forming monomer diads, the type of polymer obtained in a copolymerization process will also depend on these values. Three limiting cases can be observed, leading to either purely random (statistical), alternating or blocky copolymer structures.

For $r_1 \cdot r_2 = 1$, both monomers get incorporated in the copolymer at rates proportional to their reactivity ratios, and result in a truly random copolymer. A special case of ideal copolymerization with $r_1 = r_2 = 1$, referred to as azeotropic copolymerization, yields a copolymer with a composition identical to the monomer feed.

Alternating copolymers are obtained when each propagating monomer radical preferentially adds a monomer unit of the other type. This happens when $r_1 \cdot r_2$ tends towards zero. On the contrary, when the propagating radical has more tendency to add to a monomer unit of its own type (i.e. $r_1 \cdot r_2 >> 1$), long sequences of the same monomer unit may be included in the polymer, leading to a "blocky" structure.

The actual monomer unit sequence probability may be calculated statistically, for given r_1, r_2 values and monomer concentrations. The probability of forming an M_1M_1 diad sequence, p_{11}, depends on the rates for the addition of M_1^* to M_1 over the sum of rates for the addition of M_1^* to M_1 and M_2, or

$$p_{11} = \frac{R_{11}}{R_{11} + R_{12}} = \frac{r_1}{r_1 + ([M_2]/[M_1])} \qquad \text{(Eq. A.16)}$$

Similarly, the probabilities of forming M_1M_2, M_2M_1, and M_2M_2 diads are

$$p_{12} = \frac{R_{12}}{R_{11} + R_{12}} = \frac{[M_2]}{r_1 [M_1] + [M_2]} \qquad \text{(Eq. A.17)}$$

$$p_{21} = \frac{R_{21}}{R_{21} + R_{22}} = \frac{[M_1]}{r_2 [M_2] + [M_1]} \qquad \text{(Eq. A.18)}$$

$$p_{22} = \frac{R_{22}}{R_{21} + R_{22}} = \frac{r_2 [M_2]}{r_2 [M_2] + [M_1]} \qquad \text{(Eq. A.19)}$$

The probability of a sequence of M_1 units of length x to be formed is therefore

$$(\underline{N}_1)_x = p_{11}^{(x-1)} p_{12} \qquad \text{(Eq. A.20)}$$

and similarly for the M_2 units,

$$(\underline{N}_2)_x = p_{22}^{(x-1)} p_{21} \qquad \text{(Eq. A.21)}$$

Equations A.16 through A.21 can therefore be used to calculate the expected monomer sequence length distribution for given r_1, r_2 values and monomer feed composition. A BASIC program performing this task is given in Appendix A.4, together with sequence length distribution calculations for the three copolymers prepared for this work.

A.3. Copolymer composition heterogeneity

It was pointed out earlier that for $r_1 = r_2 = 1$, truly random copolymers are obtained, with proportionally equal amounts of each monomer consumed as the conversion increases. Consequently, the instantaneous composition of the copolymer chains produced is the same regardless of the extent of reaction. However, this is not the case when each monomer is not included in the chains proportionally, i.e. when r_1 and

$r_2 \neq 1$. One of the monomers may get incorporated preferentially, leading to a depletion of this type of monomer unit in the feed, and a resulting decrease in the content of this monomer in the chains as the conversion increases. The net result is a drift in the average copolymer composition, since the chains formed at a later reaction stage may have a composition significantly different from that of those formed at the beginning of the polymerization.

An equation has been proposed[6] to relate the degree of conversion $(1 - M/M_0)$ to changes in feed composition as

$$1 - \frac{M}{M_0} = 1 - \left[\frac{f_1}{(f_1)_0}\right]^{\alpha} \left[\frac{f_2}{(f_2)_0}\right]^{\beta} \left[\frac{(f_1)_0 - \delta}{f_1 - \delta}\right]^{\gamma} \qquad \text{(Eq. A.22)}$$

with the factors α, β, γ, and δ defined as

$$\alpha = \frac{r_2}{(1 - r_2)} \qquad \beta = \frac{r_1}{(1 - r_1)}$$

$$\text{(Eq. A.23)}$$

$$\gamma = \frac{(1 - r_1 r_2)}{(1 - r_1)(1 - r_2)} \qquad \delta = \frac{(1 - r_2)}{(2 - r_1 - r_2)}$$

and monomers 1 and 2 defined so that $F_1 > f_1$, corresponding to a depletion of monomer 1 in the feed as the conversion increases. Although these calculations were also included initially in the copolymerization calculations program of Appendix A.4, it was found that Eq. A.22 can give rather unpredictable results for certain combinations of r_1, r_2 values, and particularly r_1 and r_2 close to 1 and $r_1 < r_2$ at low concentrations of monomer 1. It was therefore preferred to directly integrate the instantaneous copolymer composition equation (Eq. A.11) numerically in the program of Appendix A.4. to obtain the maximum conversion permissible for a specified degree of heterogeneity.

A.4. Program listings and examples

A.4.1. Copolymerization calculations program listing

The following listing is for a BASIC program designed for the IBM-PC computer and runs with the IBM BASIC (BASICA) or the Microsoft Quickbasic compiler. Both the source listing and the compiled version of the program are included on Supporting Data Disk #2.

```
10    REM  Copolymerization calculations
20    REM  Program COPOLY.BAS
30    REM  By Mario Gauthier -- May 5, 1984
40    REM  Modified Oct. 17, 1984
50    CLS
60    PRINT"        COPOLYMERIZATION     CALCULATIONS":PRINT:PRINT
70    LINE INPUT "Enter heading: ";H$
80    LPRINT"Copolymerization Calculations --      ";H$:LPRINT:LPRINT
90    INPUT "* Value of r1 (comonomer)";R1
100   LPRINT "* Value of r1 (comonomer) = ";R1
110   INPUT "* Value of r2 (main monomer)";R2
120   LPRINT"* Value of r2 (main monomer) = ";R2
130   INPUT "* Molecular weight of comonomer";MW1
140   LPRINT"* Molecular weight of comonomer = ";MW1
150   INPUT "* Molecular weight of main monomer";MW2
160   LPRINT"* Molecular weight of main monomer = ";MW2
170   INPUT "* Total weight of monomers used";WTOT
180   LPRINT "* Total weight of monomers used = ";WTOT
190   INPUT"* Degree of heterogeneity (0 - 1)";H
200   LPRINT"* Degree of heterogeneity = ";H
210   PRINT
220   LPRINT
230   INPUT "* Mole fraction of comonomer (999 to exit)";F1
240   IF F1<>999 THEN LPRINT"* Mole fraction of comonomer = ";F1
250   IF F1=999 THEN END
260   F2=1-F1
270   IF (R1=1) AND (R2=1) THEN X1=F1 : GOTO 290
280   GOSUB 840 : REM  Solve for f1
290   PRINT USING "  Comonomer mole fraction in feed = #.####";X1
300   LPRINT USING "  Comonomer mole fraction in feed = #.####";X1
310   X1START=X1 : REM  f1(0) for integration
320   REM  Assume 100 g of main monomer used for calculations
330   TTLMOL=100/(MW2*(1-X1))
340   W1=(TTLMOL-100/MW2)*MW1
350   W1=W1*WTOT/(100+W1) : REM  Now reconverted to proper weight
360   PRINT USING "  Main monomer weight= ####.##";WTOT-W1
370   LPRINT USING "  Main monomer weight = ####.##";WTOT-W1
380   PRINT USING "  Comonomer weight= ####.##";W1
390   LPRINT USING "  Comonomer weight = ####.##";W1
```

```
400   IF (R1=1) AND (R2=1) THEN MAXCONV=1 : GOTO 560
410   REM Integrate the copolymerization equation numerically
420   REM to evaluate the drift in the average copolymer composition
430   W2=WTOT-W1 : M1=W1/MW1 : M2=W2/MW2 : MTOT=M1+M2
440   X1=X1START : X2=1-X1START : AVGCOMP=0
450   SLICES=200 : REM Resolution of 0.5% conversion
460   FOR I=1/SLICES TO 1 STEP 1/SLICES
470   F1POL=(R1*X1^2+X1*X2)/(R1*X1^2+2*X1*X2+R2*X2^2)
480   IF (F1POL<(F1*(1-H))) OR (F1POL>(F1/(1-H))) THEN 550
490   AVGCOMP=AVGCOMP+F1POL
500   MGONE1=MTOT/SLICES*F1POL
510   MGONE2=MTOT/SLICES*(1-F1POL)
520   M1=M1-MGONE1 : M2=M2-MGONE2
530   X1=M1/(M1+M2) : X2=1-X1
540   MAXCONV=I
550   NEXT I
560   PRINT USING "  Maximum conversion: #.###";MAXCONV
570   LPRINT USING "  Maximum conversion: #.###";MAXCONV
580   IF (R1=1) AND (R2=1) THEN PRINT: PRINT : LPRINT : LPRINT : GOTO 210
590   AVGCOMP=AVGCOMP/(MAXCONV*SLICES)
600   PRINT USING "  Average composition expected: #.####";AVGCOMP
610   PRINT
620   LPRINT USING "  Average composition expected: #.####";AVGCOMP
630   INPUT "  Make calculations for a different conversion (y/n)";A$
640   IF ((LEFT$(A$,1)<>"y") AND (LEFT$(A$,1)<>"Y")) THEN 810
650   INPUT "  Enter the desired conversion: ",CONV
660   REM Reintegrate the equation over the desired range
670   W2=WTOT-W1 : M1=W1/MW1 : M2=W2/MW2 : MTOT=M1+M2
680   X1=X1START : X2=1-X1START : AVGCOMP=0
690   FOR I=CONV/SLICES TO CONV STEP CONV/SLICES
700   F1POL=(R1*X1^2+X1*X2)/(R1*X1^2+2*X1*X2+R2*X2^2)
710   AVGCOMP=AVGCOMP+F1POL
720   MGONE1=(MTOT*CONV)/SLICES*F1POL
730   MGONE2=(MTOT*CONV)/SLICES*(1-F1POL)
740   M1=M1-MGONE1 : M2=M2-MGONE2
750   X1=M1/(M1+M2) : X2=1-X1
760   NEXT I
770   AVGCOMP=AVGCOMP/SLICES
780   PRINT USING "  Average composition expected: #.####";AVGCOMP
790   PRINT : PRINT
800   LPRINT USING "  Average composition for ###% conversion:
            #.####";CONV*100;AVGCOMP
810   LPRINT : LPRINT
820   GOTO 210
830   REM Subroutine to solve for f1 (Called X1 here)
840   A=F1*R1-R1-2*F1+1+F1*R2
850   B=2*F1-1-2*F1*R2
860   C=F1*R2
870   X1R=(-B+SQR(B^2-4*A*C))/2/A
880   X2R=(-B-SQR(B^2-4*A*C))/2/A
890   IF ((X1R>=0) AND (X1R<=1)) THEN X1=X1R
900   IF ((X2R>=0) AND (X2R<=1)) THEN X1=X2R
910   RETURN
```

A.4.2. Running the program

The program is started by simply typing its name from the currently logged drive (assumed to be drive A in this example):

```
A>COPOLY
```

It should be noted that the run-time library module BRUN20.EXE also has to be on the same diskette, if the compiled version of the program is to be used. What follows is a sample session involving calculations for a styrene-methacrylic acid copolymer with an initial composition of 10 mole% acid (Chapters 2 and 3). The screen output used to obtain input data from the user is given first:

```
      COPOLYMERIZATION CALCULATIONS

Enter heading: Methacrylic acid copolymer
* Value of r1 (comonomer)? .7
* Value of r2 (main monomer)? .15
* Molecular weight of comonomer? 86.09
* Molecular weight of main monomer? 104.16
* Total weight of monomers used? 100
* Degree of heterogeneity (0 - 1)? .3

* Mole fraction of comonomer (999 to exit)? .1
 Comonomer mole fraction in feed = 0.0181
 Main monomer weight=  98.50
 Comonomer weight=    1.50
 Maximum conversion: 0.085
 Average composition expected: 0.0854

 Make calculations for a different conversion (y/n)? y
 Enter the desired conversion: .15
 Average composition expected: 0.0738


* Mole fraction of comonomer (999 to exit)? 999
```

The maximum conversion calculated (accurate to ca. 0.005 or 0.5%) is for the degree of heterogeneity specified by the user (here 0.3 or 30%). The average copolymer composition resulting from changes in monomer feed composition is also estimated by numerical integration of the instantaneous copolymer composition equation (Eq. A.11). As can be seen above, it is possible, however, to re-do the expected composition calculations for a different degree of conversion, if the maximum conversion suggested is impractical (e.g. too high). A hard copy of the calculations done is also obtained on the printer:

```
Copolymerization Calculations -- Methacrylic acid copolymer

* Value of r1 (comonomer) =  .7
* Value of r2 (main monomer) = .15
* Molecular weight of comonomer =  86.09
* Molecular weight of main monomer =  104.16
* Total weight of monomers used =  100
* Degree of heterogeneity =  .3

* Mole fraction of comonomer = .1
  Comonomer mole fraction in feed = 0.0181
  Main monomer weight =  98.50
  Comonomer weight =   1.50
  Maximum conversion: 0.085
  Average composition expected: 0.0854
  Average composition for  15% conversion: 0.0738
```

The printouts of the copolymerization calculations for the 4-bromostyrene and 4-methoxystyrene copolymers prepared in Chapter 4 are also included here.

```
Copolymerization Calculations  --  4-Bromostyrene copolymer

* Value of r1 (comonomer) =  .97
* Value of r2 (main monomer) = .695
* Molecular weight of comonomer =  183.06
* Molecular weight of main monomer =  104.16
* Total weight of monomers used =  100
* Degree of heterogeneity =  .3

* Mole fraction of comonomer = .165
  Comonomer mole fraction in feed = 0.1271
  Main monomer weight =  79.63
  Comonomer weight =  20.37
  Maximum conversion: 0.705
  Average composition expected: 0.1443
```

```
Average composition for 80% conversion: 0.1396
```

```
Copolymerization Calculations -- 4-Methoxystyrene copolymer

* Value of r1 (comonomer) =  .93
* Value of r2 (main monomer) =  1.13
* Molecular weight of comonomer =  134.19
* Molecular weight of main monomer =  104.16
* Total weight of monomers used =  100
* Degree of heterogeneity =  .3

* Mole fraction of comonomer =  .15
 Comonomer mole fraction in feed = 0.1652
 Main monomer weight =  79.68
 Comonomer weight =  20.32
 Maximum conversion: 0.980
 Average composition expected: 0.1638
 Average composition for  60% conversion: 0.1548
```

A.4.3. Sequence length distribution program listing

The following BASIC program provided here performs sequence length distribution calculations according to equations A.16 through A.21. The source listing and the compiled version of the program can also be found on Supporting Data Disk #2.

```
10      REM   Sequence-length distribution calculations
15      REM     Program DISTR.BAS
20      REM     by Mario Gauthier --  Oct. 31, 1984
30      CLS
40      PRINT TAB(10) "SEQUENCE LENGTH DISTRIBUTION CALCULATIONS"
50      PRINT:PRINT
60      INPUT "* Value of r1 (comonomer): ",R1
70      LINE INPUT "* Identification of comonomer: ";I1$
80      INPUT "* Value of r2 (main monomer): ",R2
90      LINE INPUT "* Identification of main monomer: ";I2$
100     INPUT "* Maximum value of sequence length: ",XMAX
110     PRINT:PRINT:PRINT
120     LPRINT TAB(10) "SEQUENCE-LENGTH DISTRIBUTION"
130     LPRINT:LPRINT
140     LPRINT "Comonomer: ";I1$;"    r1= ";R1
150     LPRINT "Main monomer: ";I2$;"    r2= ";R2
160     LPRINT:LPRINT:LPRINT
170     LINES=8
180     INPUT "* Mole fraction of comonomer in feed (0 to END): ",M1
190     M2=1-M1
```

```
200   IF M1=0 THEN END
210   LPRINT "* Mole fraction of comonomer in feed: ";M1
220   F1POL=(R1*M1^2+M1*M2)/(R1*M1^2+2*M1*M2+R2*M2^2)
230   LPRINT USING "                        in polymer: #.####";F1POL
240   LPRINT:LINES=LINES+4
250   LPRINT "   X" TAB(8) "N1(X)" TAB(18) "N1(tot)" TAB(28) "N2(X)";
260   LPRINT TAB(38) "N2(tot)"
270   P11=R1/(R1+(M2/M1))
280   P12=M2/(R1*M1+M2)
290   P21=M1/(R2*M2+M1)
300   P22=R2*M2/(R2*M2+M1)
310   NTOT1=0 : NTOT2=0
320   FOR X=1 TO XMAX
330   IF LINES <= 55 THEN 360
340   FOR J=LINES TO 66:LPRINT:NEXT J
350   LINES=0
360   N1X=P11^(X-1)*P12
370   N2X=P22^(X-1)*P21
380   NTOT1=NTOT1+N1X : NTOT2=NTOT2+N2X
390   LPRINT USING "#### #.##### #.##### #.##### ";X;N1X;NTOT1;N2X;
400   LPRINT USING "#.##### ";NTOT2
410   LINES=LINES+1
420   NEXT X
430   LPRINT:LPRINT:LINES=LINES+2
440   PRINT:PRINT
450   GOTO 180
```

A.4.4. Running the program

As before, the program is started by typing its name from the currently logged drive:

```
A>DISTR
```

The following information is requested from the user on the console (using the styrene-methacrylic acid copolymer as an example, as before):

```
      SEQUENCE LENGTH DISTRIBUTION CALCULATIONS


* Value of r1 (comonomer): .7
* Identification of comonomer: Methacrylic acid
* Value of r2 (main monomer): .15
* Identification of main monomer: Styrene
* Maximum value of sequence length: 20


* Mole fraction of comonomer in feed (0 to END): .0181
```

```
* Mole fraction of comonomer in feed (0 to END): 0
```

The printer output provides the probabilities of finding sequences of X consecutive monomer units (X=1 to the upper boundary specified by the user; here 20 was used) along the chain. These are denoted N1(X) and N2(X) for the comonomer and the main monomer, respectively. The cumulative probabilities N1(tot) and N2(tot) are also given, as a measure of the total amount of monomers 1 and 2 accounted for so far in the analysis.

```
      SEQUENCE-LENGTH DISTRIBUTION

Comonomer: Methacrylic acid   r1= .7
Main monomer: Styrene    r2= .15


* Mole fraction of comonomer in feed: .0181
                       in polymer: 0.0998

      X     N1(X)       N1(tot)     N2(X)       N2(tot)
      1     0.98726     0.98726     0.10944     0.10944
      2     0.01258     0.99984     0.09746     0.20691
      3     0.00016     1.00000     0.08680     0.29370
      4     0.00000     1.00000     0.07730     0.37100
      5     0.00000     1.00000     0.06884     0.43984
      6     0.00000     1.00000     0.06130     0.50114
      7     0.00000     1.00000     0.05460     0.55574
      8     0.00000     1.00000     0.04862     0.60436
      9     0.00000     1.00000     0.04330     0.64766
      10    0.00000     1.00000     0.03856     0.68622
      11    0.00000     1.00000     0.03434     0.72056
      12    0.00000     1.00000     0.03058     0.75114
      13    0.00000     1.00000     0.02724     0.77838
      14    0.00000     1.00000     0.02425     0.80263
      15    0.00000     1.00000     0.02160     0.82423
      16    0.00000     1.00000     0.01924     0.84347
      17    0.00000     1.00000     0.01713     0.86060
      18    0.00000     1.00000     0.01526     0.87586
      19    0.00000     1.00000     0.01359     0.88944
      20    0.00000     1.00000     0.01210     0.90154
```

It can be seen that the comonomer units are obtained mostly (98.7%) as isolated species along the chain, satisfying the requirements for random (as opposed to blocky or alternating) microstructure. This is also the case of the 4-bromostyrene and 4-methoxystyrene copolymers:

SEQUENCE-LENGTH DISTRIBUTION

Comonomer: 4-Bromostyrene r1= .99
Main monomer: Styrene r2= .695

* Mole fraction of comonomer in feed: .1268
in polymer: 0.1650

X	N1(X)	N1(tot)	N2(X)	N2(tot)
1	0.87431	0.87431	0.17283	0.17283
2	0.10989	0.98420	0.14296	0.31579
3	0.01381	0.99801	0.11825	0.43404
4	0.00174	0.99975	0.09781	0.53185
5	0.00022	0.99997	0.08091	0.61276
6	0.00003	1.00000	0.06693	0.67969
7	0.00000	1.00000	0.05536	0.73505
8	0.00000	1.00000	0.04579	0.78084
9	0.00000	1.00000	0.03788	0.81872
10	0.00000	1.00000	0.03133	0.85005
11	0.00000	1.00000	0.02592	0.87596
12	0.00000	1.00000	0.02144	0.89740
13	0.00000	1.00000	0.01773	0.91513
14	0.00000	1.00000	0.01467	0.92980
15	0.00000	1.00000	0.01213	0.94193
16	0.00000	1.00000	0.01004	0.95197
17	0.00000	1.00000	0.00830	0.96027
18	0.00000	1.00000	0.00687	0.96714
19	0.00000	1.00000	0.00568	0.97282
20	0.00000	1.00000	0.00470	0.97751

SEQUENCE-LENGTH DISTRIBUTION

Comonomer: 4-Methoxystyrene r1= .93
Main monomer: Styrene r2= 1.13

* Mole fraction of comonomer in feed: .1652
in polymer: 0.1500

X	N1(X)	N1(tot)	N2(X)	N2(tot)
1	0.84457	0.84457	0.14903	0.14903
2	0.13127	0.97584	0.12682	0.27584
3	0.02040	0.99624	0.10792	0.38376
4	0.00317	0.99942	0.09184	0.47560
5	0.00049	0.99991	0.07815	0.55375
6	0.00008	0.99999	0.06650	0.62025
7	0.00001	1.00000	0.05659	0.67685
8	0.00000	1.00000	0.04816	0.72500
9	0.00000	1.00000	0.04098	0.76599
10	0.00000	1.00000	0.03487	0.80086
11	0.00000	1.00000	0.02968	0.83054
12	0.00000	1.00000	0.02525	0.85579
13	0.00000	1.00000	0.02149	0.87728
14	0.00000	1.00000	0.01829	0.89557
15	0.00000	1.00000	0.01556	0.91113
16	0.00000	1.00000	0.01324	0.92438
17	0.00000	1.00000	0.01127	0.93565
18	0.00000	1.00000	0.00959	0.94524
19	0.00000	1.00000	0.00816	0.95340
20	0.00000	1.00000	0.00694	0.96034

A.5. References

(1) Odian, G. *Principles of Polymerization, 2nd ed.*; Wiley: New York, 1981.

(2) Flory, P.J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, 1953; p 140.

(3) Young, L.J. In *Polymer Handbook, 2nd ed.*; Brandrup, J., Immergut, E.H., Eds.; Wiley: New York, 1974; p II-105.

(4) Alfrey, T., Jr.; Price, C.C. *J. Polym. Sci.* **1947**, *2*, 101.

(5) Young, L.J. In *Polymer Handbook, 2nd ed.*; Brandrup, J., Immergut, E.H., Eds.; Wiley: New York, 1974; p II-387.

(6) (a) Meyer, V.E.; Lowry, G.G. *J. Polym. Sci. A3*, **1965**, 2843. (b) *J. Polym. Sci. C25*, **1968**, 11. (c) *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 701.

Appendix B. Preparation of poly(styrene-co-4-N,N-dimethylaminostyrene)

B.1. Introduction

Previous dynamic mechanical studies of styrene-methylpyridinium iodide ionomers[1] have shown no evidence of large scale ionic aggregation (clustering). In order to further the knowledge of styrene-based ionomers containing quaternized amine groups, a study of 4-N,N-dimethylaminostyrene (DMAS) ionomers was undertaken to form a comparative structure-properties investigation together with the vinylpyridinium series. Given the very distinct nature of 4-N,N-dimethylaminostyrene (a tertiary amine) compared with 4-vinylpyridine (a heterocyclic aromatic amine), it seemed interesting to compare the dynamic mechanical properties of the two series.

The preparation of 4-N,N-dimethylaminostyrene has been described on a few occasions in the chemical literature[2-7]. Although von Braun and Blessing[2] initially obtained it by dehydrating trimethyl-β-(4-N,N-dimethylaminophenyl) ethyl ammonium hydroxide, the dehydration of 4-N,N-dimethylaminophenylmethyl carbinol is usually the preferred synthetic route. The carbinol is prepared in a Grignard reaction from methyl iodide and 4-N,N-dimethylaminobenzaldehyde. Dehydration of the carbinol has been reported by simple distillation at reduced pressure[3], flash distillation in the same conditions[4,5], and flash distillation[6] or passage of the vapors[7] over activated alumina. Other carbinols have also been dehydrated over fused potassium acid sulfate in the presence of inhibitors[8]. Of all the techniques tested, flash distillation over activated alumina gave the highest yield, and was the preferred approach here.

Copolymers of 4-N,N-dimethylaminostyrene with styrene have been reported in the literature[7,9]. In one case[9], differential scanning calorimetry (DSC) was used to characterize both random and block copolymers with amine contents ranging from 30 to 100 mole%. No studies of the quaternized amine were found, however. Random dimethylaminostyrene (DMAS) copolymers containing about 2.5 to 10 mole% amine were therefore prepared for this work in a radical bulk copolymerization process with 2,2'-azobis-isobutyronitrile (AIBN) used as initiator. The ionomers were obtained by quaternization of the amine with methyl iodide according to a known technique[1].

Differential scanning calorimetry measurements on the ionomers, preliminary to the dynamic mechanical analysis, were unfortunately very deceptive: dequaternization of the products was observed at about the glass transition temperature of the polymers, making them unsuitable for the intended dynamic mechanical analysis. Nevertheless, this may not preclude their study in the form of ionic-ionic blends with low T_g materials (e.g. ethyl acrylate-sodium acrylate ionomers), or particularly as alkylated samples (1-decene with aluminum chloride, see Chapter 2), in the light of recent analogous studies done on 4-vinylpyridinium ionomers[10].

B.2. Experimental

B.2.1. Preparation of 4-N,N-dimethylaminostyrene

The method used was a combination of the techniques suggested by Hall et al.[5] and by Sélégny[6]. A solution of methyl iodide (60 g, 0.21 mol, A&C American Chemicals reagent) in anhydrous diethyl ether (Mallinckrodt) was added with stirring to 10.0 g (0.412 mol) of dry magnesium turnings (A&C reagent) contained in a 2 L three-neck flask fitted with a condenser and in a dry nitrogen atmosphere. The reaction, initially vigourous, was moderated by cooling the flask in an ice-water bath. The solution was refluxed with stirring for 1 hour longer, followed by the slow addition of a solution of 4-N,N-dimethylaminobenzaldehyde (A&C reagent, 50 g, 0.17 mol) in anhydrous ether (1 L) over about 3 hours. The organomagnesium product was decomposed with a saturated solution of ammonium chloride (100 mL) with added hydrochloric acid (10M, 10 mL). The organic layer was dried over anhydrous sodium sulfate and the ether removed, to give the lemon-yellow 4-N,N-dimethylaminophenylmethylcarbinol in 85-95% yield.

The substituted styrene was obtained in about 85-90% purity (NMR) by dehydration in the flash distillation of the carbinol over activated alumina at 3.3mm/155-165 °C. The product was further purified by two fractional distillations at reduced pressure (b.p. 95-97 °C/1.5 mm, lit.: 98 °C/ 3mm[9]).

B.2.2. Preparation of poly(styrene-co-4-N,N-dimethylaminostyrene)

Styrene monomer (Aldrich 99%, inhibited with 10-15 ppm 4-t-butylcatechol) was washed three times with a 5% aqueous sodium hydroxide solution in a separatory funnel to remove the inhibitor. The organic phase was dried overnight and distilled over calcium hydride (Aldrich, 95+%, 40 mesh) at reduced pressure (bp. 47-48 °C/22 mm).

The two monomers were mixed in different proportions (Table B.1) for 4-N,N-dimethylaminostyrene contents in the polymer ranging from about 2.5 to 10 mole% calculated from copolymerization reactivity ratios $r_1 = (1.015 \pm 0.06)$ and $r_2 = (0.84 \pm 0.05)$[11]. Azobisisobutyronitrile (AIBN) was used as a radical initiator in the bulk copolymerization of the monomers. The monomer mixtures were transferred to 250 mL ampoules which were degassed with three freeze-thaw cycles under vacuum and sealed. Polymerization was carried out at 60 °C for the times indicated in Table B.1. The polymers were recovered by dilution with 1-2 volumes of toluene followed by precipitation in methanol with vigourous stirring. The recovered copolymers were finally dried in a vacuum oven at 60 °C for a few days.

B.2.3. Copolymers analysis

The DMAS content of the copolymers was determined in acid-base titrations of 0.3 to 0.7 g samples (depending on their amine concentration) in chlorobenzene or

Table B.1. Monomer feed compositions in the preparation of styrene-4-N,N-dimethylaminostyrene (DMAS) copolymers. The weight of styrene monomer used was 100g in all cases; f_1 represents the mole fraction of amine in the feed.

Weight DMAS (g)	Weight AIBN (g)	f_1	Polymerization time (hours)
3.69	0.90	0.0255	9.50
7.61	0.90	0.0511	9.50
11.76	0.50	0.0768	11.00
16.18	0.35	0.1027	13.67

1,2-dichlorobenzene with perchloric acid in glacial acetic acid, according to a technique suggested by Burleigh et al.[12] for butadiene-4-vinylpyridine copolymers. The perchloric acid solution was standardized against anhydrous sodium carbonate in a 4:1 chlorobenzene/acetic acid solvent. This standardization technique was preferred to the original approach[12] using only glacial acetic acid, because of the much sharper end point thus obtained. Blank corrections were included in the DMAS content calculations.

The molecular weights of the nonquaternized polymers were determined by viscometric measurements in toluene at (25.00 ± 0.02) °C using Ubbelohde-type viscometers. The data were analyzed by neglecting the presence of the amine, and taking the average of two values calculated for Mark-Houwink constants of $k = 1.34 \times 10^{-2}$ mL/g, $\alpha = 0.71$ [13], and $k = 1.7 \times 10^{-2}$ mL/g, $\alpha = 0.69$ [14], respectively.

B.2.4. Quaternization and dequaternization studies

The DMAS copolymers were quaternized by refluxing in dry tetrahydrofuran with a 5-fold excess of methyl iodide, according to the procedure suggested by Gauthier et al.[1] for styrene-4-vinylpyridine copolymers. The glass transition temperatures of the quaternized and nonquaternized polymers were determined on a Perkin-Elmer DSC-2C Differential Scanning Calorimeter with a heating rate of 20 °C/min. Triplicate runs were done to ensure the reproducibility of the results; the agreement between the second and third runs was generally better than 0.5 degree. The first run was obtained without annnealing of the sample. The second and third scans were obtained after annealing for 3 minutes at T_g + 40 degrees followed by quick quenching of the sample.

Given the apparent dequaternization problems observed on the DSC traces, further dequaternization studies were undertaken. A sample (1.0 g) of the quaternized copolymer containing 10% amine was heated for 1 hour at 150 °C in a flow of nitrogen. A portion of this very slightly cross-linked sample (0.3 g) was dispersed by stirring overnight in o-dichlorobenzene and titrated to a stable end point (over a few minutes) with perchloric acid as described above. A 0.3 g sample of the quaternized amine was also dissolved in 100 mL of 4:1 solution by volume of o-dichlorobenzene/glacial acetic acid and titrated to evaluate the degree of quaternization, and for comparison with the heated sample.

Films for IR spectroscopy were obtained either by casting over teflon of 10% polymer solutions in tetrahydrofuran (nonquaternized and quaternized samples), or by compression molding at 180 °C for 10 minutes at ca. 10 MPa (dequaternized sample). Spectra were recorded in the 400-4400 cm^{-1} range on an Analect AQS-18 Fourier Transform spectrometer with a resolution of 4 cm^{-1}.

B.3. Results and discussion

B.3.1. Synthesis

As mentioned in the introduction, of all the dehydration techniques mentioned, flash distillation over activated alumina (3.3 mm/155-165 °C) gave the best results. The technique suggested by Braun and Sterzel[7] was the only experimental approach not tested. The temperature and pressure used also represent optimized conditions for the dehydration reaction. It was found that at very low pressures (less than 1 mm Hg), the carbinol had the tendency to volatilize without decomposition, leading to very impure products. At higher pressures (over 5-10 mm Hg), on the contrary, the dimethylaminostyrene momoner formed apparently did not get vaporized quickly enough, resulting in large losses from polymerization.

Azobisisobutyronitrile (AIBN), rather than benzoyl peroxide, was used as a free-radical initiator in the copolymerization of dimethylaminostyrene with styrene, because the latter is known to undergo a charge transfer reaction with tertiary amines, leading to undesirable side reactions[15].

The results of the titrations and the viscosity measurements, as well as the degrees of conversion for each copolymer are summarized in Table B.2. Titrant volumes were approximately 6 mL, the relatively diffuse end point of the titrations in organic solvents leading to errors estimated at 2 drops or 0.05 mL for both the sample and the blank. This leads to a relative error of approximately 1.6% on the DMAS content (F_1) values reported in Table B.2. The very favorable r_1, r_2 values ($r_1 \cdot r_2 = 0.85$) are reflected in a DMAS content of the copolymers (F_1) very similar to the monomer feed (f_1). The variations in the viscosity average molecular weight (M_v) observed are a result of the adjustment of the initiator concentration (see Table B.1) to compensate for the apparent lowering in M_v observed in going from 2.5 to 5% amine content, and possibly due to chain transfer to the amine.

Table B.2. Characterization of the dimethylaminostyrene copolymers prepared. The mole fraction of amine in the monomer feeds and the polymers are represented by f_1 and F_1, respectively. The viscosity-average molecular weight (M_v) is the average value obtained with two different sets of k, α values, as described above.

f_1	F_1	Conversion	M_v (g/mol $\cdot 10^{-3}$)
0.0255	0.0261	0.59	114
0.0511	0.0531	0.57	90
0.0768	0.0797	0.43	120
0.1027	0.104	0.48	154

B.3.2. DSC Analysis

The first hints of dequaternization of the ionomers originated from the DSC analysis done prior to the intended dynamic mechanical studies. The DSC traces obtained for samples of similar weight (10 ± 2 mg) in the first and second scans for the nonquaternized and quaternized PS-0.104DMAS copolymer are compared in Figure B.1. It can be seen that the first scan of the quaternized material shows a large endotherm at a temperature ca. 20 degrees higher than the nonquaternized polymer. The second scans, however, are very comparable for the two materials.

The DSC results are summarized in Table B.3. The onset of dequaternization of the ionomers is clearly higher than the T_g of the corresponding nonquaternized materials. The average T_g measured in the second and third scans for the nonquaternized and the quaternized polymers, on the other hand, are very similar. This suggests that the large endotherm observed in the first scan of the ionomers corresponds to the dequaternization of the ammonium salt.

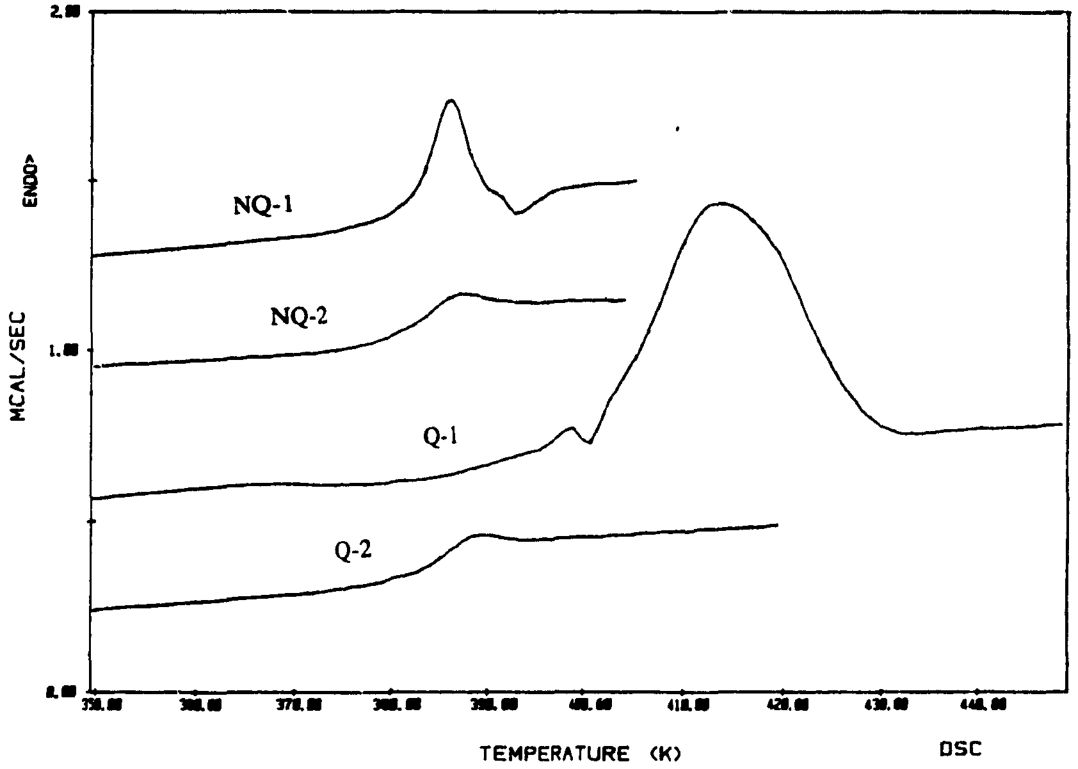


Figure B.1. Comparison of the first (1) and second (2) DSC scans obtained for PS-0.10 DMAS copolymers nonquaternized (NQ) and quaternized with methyl iodide (Q).

Table B.3. Summary of DSC data for the dimethylaminostyrene copolymers nonquaternized and quaternized with methyl iodide. The symbols used are T_g(NQ): average T_g obtained in the second and third runs of the nonquaternized polymers; T_{on}(Q): onset temperature of dequaternization peak in the first run of the quaternized polymers; T_g(Q): average of T_g determinations in the second and third DSC runs for the quaternized polymers.

DMAS (mol%)	T_g(NQ) (°C)	T_{on}(Q) (°C)	T_g(Q) (°C)
2.6	106.5	121.5	109.5
5.3	107.1	125.5	110.5
8.0	109.2	126.7	108.3
10.4	109.3	128.3	111.5

B.3.3. Other dequaternization studies

Further support for the nature of the problems observed in the DSC analysis was obtained from titrations of a dequaternized sample and the comparison of IR spectra of the different materials.

The titration of a quaternized amine sample (10.4 mole% DMAS) yielded a residual amine content of 0.9%, corresponding to approximately 90% quaternization, comparable with the results of Gauthier et al. in the case of 4-vinylpyridine (4-VP) copolymers[1] analyzed by IR spectroscopy. This is not surprising, considering the very similar basicity of model compounds for DMAS and 4-VP (N,N-dimethylaniline: pK_a = 5.15; pyridine: pK_a = 5.25 [16]). The sample which was heated at 150 °C in a flow of nitrogen, on the contrary, gave an amine content of 10.5%, identical, within error limits (absolute error ca. 0.2%), with the nonquaternized material.

IR spectra of films of the nonquaternized polymer, and for the quaternized material before and after heat treatment also confirm these results. The spectrum of the quaternized 10.4% DMAS copolymer displays a sharp, strong band at 940 cm^{-1} (10.64 μm), which has already been attributed to the $C\text{-}N^+$ stretch in phenyltrimethylammonium halides[17]. This band is very weak, however, in both the nonquaternized and the dequaternized samples.

The inherent instability of quaternary ammonium salts of dimethylaminostyrene has already been pointed out by a few authors. Ho[18] reported the easy demethylation of phenyltrimethylammonium iodide by boiling with reagents like thiourea or sodium thiosulfate in N,N-dimethylformamide or 1,4-dioxane for 2-3 hours. Petrariu and Stamberg[19] showed the greater ease of degradation of cross-linked poly[(4-vinylphenyl)trimethylammonium hydroxide] anion exchangers, compared to the poly[(4-vinylbenzyl)trimethylammonium hydroxide] analogue at 95 °C in aqueous sodium hydroxide solutions. Similarly, Snyder and Speck[20] pointed out that benzyldimethylphenylammonium chloride is easily cleaved by aqueous sodium sulfide, yielding dimethylaniline and benzyl sulfide. Westaway and Poirier[21] used sodium thiophenoxide at 0 °C in N,N-dimethylformamide to cleave para- substituted benzyldimethylphenylammonium nitrates.

It was already known that the methyl iodide-quaternized styrene-4-vinylpyridine copolymers dequaternize rapidly in the 160-190 °C range, and more slowly at 100 °C under vacuum[1]. It was nevertheless hoped that the thermal stability of the analogous N,N-4-dimethylaminostyrene system would be, if not better, at least comparable, which turned out not to be the case. In view of the significantly lower stability of these ionomers, it therefore became impossible to use them for the intended dynamic mechanical measurements.

More recent ongoing studies in this laboratory of ionic-ionic blends and internal plasticization involving 4-vinylpyridine copolymers suggest that in spite of their limited thermal stability, these approaches could also be useful to study the dimethylaminostyrene ionomers synthesized here. One possibility would thus be the blending of the quaternized copolymer with a low T_g ethyl (or butyl) acrylate-sodium acrylate ionomer followed by extraction of the sodium iodide formed. The other possibility involves the use of the alkylation procedure described in Chapter 2 to lower the T_g of the material. This technique has indeed recently been applied to styrene-4-vinylpyridinium ionomers[10], and could indirectly provide a more complete picture of ionic aggregation in amine-containing ionomers.

B.4. Conclusions

The preparation of 4-N,N-dimethylaminostyrene and its copolymerization with styrene was described to produce copolymers with amine contents ranging from 2.5 to 10 mole%. Corresponding ionomers were prepared by quaternization with methyl iodide. Differential scanning calorimetric analysis of both the nonquaternized and the quaternized polymers revealed the unexpectedly low thermal stability of the quaternized materials, making them unsuitable for dynamic mechanical analysis. Dequaternization was also confirmed by comparison of titrations performed before and after heating the quaternized polymer, and by IR spectroscopy. It is suggested that the polymers prepared may nevertheless be useful if studied in the form of blends with low T_g ionomers or alkylated using a previously described procedure, leading to materials with a glass transition temperature hopefully below the dequaternization temperature of the quaternized amine.

B.5. References

(1) Gauthier, S.; Duchesne, D.; Eisenberg, A. *Macromolecules* **1987**, *20*, 753.

(2) von Braun, J.; Blessing, G. *Ber. Deut. Chem. Ges.* **1923**, *56*, 2153.

(3) (a) Marvel, C.S.; Overberger, C.G.; Allen, R.E.; Saunders, J.H. *J. Am. Chem. Soc.* **1946**, *68*, 736. (b) Strassburg, R.W.; Gregg, R.A.; Walling, C. *Ibid.* **1947**, *69*, 2141.

(4) Wiley, R.H.; Schmitt, J.M. *J. Am. Chem. Soc.* **1958**, *80*, 1389.

(5) Hall, H.K., Jr.; Dunn, L.C.; Padias, A.B. *J. Org. Chem.* **1980**, *45*, 835.

(6) Sélégny, E. *Bull. Soc. Chim. France* **1959**, 1275.

(7) Braun, D.; Sterzel, H.-J. *Ber. Bunsen-Ges.* **1972**, *76*, 551.

(8) (a) Marvel, C.S.; Schertz, G.L. *J. Am. Chem. Soc.* **1943**, *65*, 2054. (b) Marvel, C.S.; Saunders, J.H. *Ibid.* **1946**, *68*, 1085.

(9) Noël, C. *Bull. Soc. Chim. France* **1967**, 3733.

(10) Wollmann, D.; Eisenberg, A. To be published.

(11) Walling, C.; Briggs, E.R.; Wolfstirn, K.B.; Mayo, F.R. *J. Am. Chem. Soc.* **1948**, *70*, 1537.

(12) Burleigh, J.W.; McKinney, O.F.; Barker, M.G. *Anal. Chem.* **1959**, *31*, 1684.

(13) Bawn, C.E.H.; Freeman, C.; Kamaliddin, A. *Trans. Faraday Soc.* **1950**, *46*, 1107.

(14) Outer, P.; Carr, C.I.; Zimm, B.H. *J. Chem. Phys.* **1950**, *18*, 830.

(15) (a) Horner, L.; Schwenk, E. *Angew. Chem.* **1949**, *61*, 411. (b) Horner, L. *Ibid.* **1949**, *61*, 458.

(16) *CRC Handbook of Chemistry and Physics, 61st ed.*; Weast, R.C., Astle, M.J., Eds. Chemical Rubber Company: Boca Raton, 1981; p D-161.

(17) Hume, A.S.; Holland, W.C.; Fry, F. *Spectrochim. Acta* **1968**, *24A*, 786.

(18) Ho, T.-L. *Synt. Commun.* **1973**, *3*, 99.

(19) Petrariu, I.; Stamberg, J. *Coll. Czech. Chem. Commun.* **1967**, *32*, 798.

(20) Snyder, H.R.; Speck, J.C. *J. Am. Chem. Soc.* **1939**, *61*, 2895.

(21) Westaway, K.C.; Poirier, R.A. *Can. J. Chem.* **1975**, *53*, 3216.

Appendix C. Supporting data

C.1. Data for the figures

Figure 2.1. Conversion curves for the Friedel-Crafts alkylation of the PS-0.07MAA copolymer.

i. Dilute reaction conditions

Time (min)	Conversion (mol%)
145	8.8
280	16.5
900	34.0

ii. Concentrated reaction conditions

Time (min)	Conversion (mol%)
160	27
445	53
655	67
1 345	74
3 120	103

Figure 2.5. Peak positions of the loss tangent maxima associated with the matrix and ion-rich domains for the alkylated PS-0.07MAA-Na ionomers.

Alkylation (mol%)	Matrix T_g (°C)	Clusters T_g (°C)
0	133	186
8.8	119	191
16.5	101	166
34	75	148
53	63	---
74	43	126
103	32	121

Figure 2.6. Extent of aggregation observed in the alkylated ionomers expressed as the ratio of calculated M_c for multiplet-type interactions to experimental M_c.

Alkylation (mol%)	M_c(cal)/M_c(exp)
0	2.42
8.8	3.25
16.5	2.98
34	1.45
53	1.07
74	0.79
103	0.62

Figure 3.1. Nitration of polystyrene in a 3:1 nitrobenzene/ 1,2-dichloromethane with fuming nitric acid at 20 °C after 60 minutes.

[HNO_3] (mol/L)	Nitration (mol%)
1.50	3.8
2.00	7.4
2.25	12.5
2.50	16.7
2.75	19.9
3.00	26.8
3.25	36.4
3.50	44.0

Figure 3.3. Matrix and cluster glass transition temperatures of PS-0.05MAA-Na ionomers plasticized with diethylbenzene.

Diethylbenzene (mol%)	Matrix T_g (°C)	Clusters T_g (°C)
22.3	9	48
13.2	38	107
6.3	93	143
0	124	163

Figure 3.4. Peak positions of the dynamic loss tangent maxima in PS-0.07MAA-Na nitrated and plasticized with nitrobenzene for the matrix and ion-rich domains.

i. Data for nitrated samples

Nitration (mol%)	Matrix T_g (°C)	Clusters T_g (°C)
0	138	210
8.0	147	208
20.8	157	205
32.3	170	212

ii. Data for nitrobenzene-plasticized samples

Nitrobenzene (mol%)	Matrix T_g (°C)	Clusters T_g (°C)
0	138	210
9.5	90	187
25	41	122

Figure 5.5. **Comparison of the cross-linking efficiency of the ionic aggregates in the different families of sodium ionomers.**

i. Data for the C_2 alkyl ionomers.

Concentration (mole%)	M_c(cal)/ M_c(exp)
2.5	1.23
5.0	1.42
7.5	0.94
9.5	1.48

ii. Data for the C_6 alkyl ionomers.

Concentration (mole%)	M_c(cal)/ M_c(exp)
2.5	0.45
5.0	0.58
7.5	0.69
11.4	1.47

iii. Data for the C_{11} alkyl ionomers.

Concentration (mole%)	M_c(cal)/ M_c(exp)
5.0	1.48
7.5	2.11
11.2	2.62

iv. Data for the C_2 ether ionomers.

Concentration (mole%)	M_c(cal)/ M_c(exp)
5.0	0.47
7.5	0.55
10.0	0.63
14.0	0.92

v. Data for the C_5 ether ionomers.

Concentration (mole%)	M_c(cal)/ M_c(exp)
5.0	0.23
7.5	0.45
10.0	0.53
14.0	1.35

vi. Data for the C_{11} ether ionomers.

Concentration (mole%)	M_c(cal)/ M_c(exp)
2.5	0.87
5.0	1.28
7.5	2.57
10.0	3.36
14.0	4.56

vii. Data for the styrene-sodium methacrylate ionomers.

Concentration (mole%)	M_c(cal)/ M_c(exp)
2.3	1.49
4.9	1.95
8.0	3.58
10.0	9.51
14.0	18.7

viii. Data for the styrene-sodium p-carboxylate ionomers.

Concentration (mole%)	M_c(cal)/ M_c(exp)
1.2	1.79
4.0	1.62
7.8	2.44
13.5	6.19

C.2. Torsion pedulum and DMTA data files access

The data collected in the dynamic mechanical analysis of the polymers studied in the present work are included as part of the supporting data in the form of two computer diskettes. Two types of data files are included, as obtained in the Torsion Pendulum (TP) or the Dynamic Mechanical Thermal Analyzer (DMTA) experiments, and are included with programs which can be used to display and print the data on IBM-PC compatible computers. The data files included and the corresponding programs to read them are as follows:

- Torsion pendulum files (supporting data for Chapter 2)

Readable with program READTP. The samples are identified according to their degree of alkylation, following the nomenclature rules of Chapter 2.

CMA7NA.TP	PS-0.07MAA-Na
CMA09D.TP	PS-0.088Dec-0.07MAA-Na
CMA17D.TP	PS-0.17Dec-0.07MAA-Na
CMA34D.TP	PS-0.34Dec-0.07MAA-Na
CMA53D.TP	PS-0.53Dec-0.07MAA-Na
CMA74D.TP	PS-0.74Dec-0.07MAA-Na
CMA103D.TP	PS-1.03Dec-0.07MAA-NA

- DMTA files (supporting data for Chapters 3 and 5)

Readable with program READDMTA. The files are identified as follows:

MARIO4.MFQ	PS-0.07MAA-Na

MARIO7.MFQ	8.0% Nitrated PS-0.07MAA-Na
MARIO5.MFQ	20.8% Nitrated PS-0.07MAA-Na
MARIO6.MFQ	32.3% Nitrated PS-0.07MAA-Na
MARIO9.MFQ	PS-0.07MAA-Na + 9.5% Nitrobenzene
MARIO11.MFQ	PS-0.07MAA-Na + 32% Nitrobenzene
MARIO80F.MFQ	C_2 Alkyl ester
MARIO23.MFQ	C_2 Alkyl 2.5% Na
MARIO21.MFQ	C_2 Alkyl 5% Na Part 1
MARIO22.MFQ	C_2 Alkyl 5% Na Part 2
MARIO92F.MFQ	C_2 Alkyl 7.5% Na
MARIO20.MFQ	C_2 Alkyl 9.5% Na
MARIO89F.MFQ	C_6 Alkyl ester
MARIO40F.MFQ	C_6 Alkyl 2.5% Na
MARIO41F.MFQ	C_6 Alkyl 5% Na
MARIO42F.MFQ	C_6 Alkyl 7.5% Na
MARIO43F.MFQ	C_6 Alkyl 11.4% Na
MARIO83F.MFQ	C_{11} Alkyl ester
MARIO75.MFQ	C_{11} Alkyl 5% Na
MARIO76.MFQ	C_{11} Alkyl 7.5% Na
MARIO77.MFQ	C_{11} Alkyl 11.2% Na
MARIO87F.MFQ	C_2 Ether ester
MARIO71.MFQ	C_2 Ether 5% Na
MARIO72.MFQ	C_2 Ether 7.5% Na

MARIO73.MFQ	C_2 Ether 10% Na
MARIO74.MFQ	C_2 Ether 14% Na

MARIO86F.MFQ	C_5 Ether ester
MARIO60.MFQ	C_5 Ether 5% Na
MARIO61F.MFQ	C_5 Ether 7.5% Na
MARIO62.MFQ	C_5 Ether 10% Na
MARIO63.MFQ	C_5 Ether 14% Na

MARIO90F.MFQ	C_{11} Ether ester
MARIO51F.MFQ	C_{11} Ether 2.5% Na
MARIO52.MFQ	C_{11} Ether 5% Na
MARIO53.MFQ	C_{11} Ether 7.5% Na
MARIO54.MFQ	C_{11} Ether 10% Na
MARIO55.MFQ	C_{11} Ether 14% Na

The two data reading programs included on the supporting data diskettes are very simple to use. Similarly to the programs described in Appendix A, they are called simply by typing the name of the program (READTP or READDMTA) from the currently logged drive (normally drive A). The user is prompted as to whether printer output is required, and asked to enter the name of the file to read (as taken from the lists above).