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New Methods for Cross-linking of High Performance Polymers

by

Chunping Gao

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

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ISBN 0-612-08102-8

Acknowledgments

I would like to express my most sincere gratitude to Professor Allan S.Hay, supervisor of this thesis, for his forever patient support, enthusiasm, excellent advice during the research and in the preparation of this thesis.

I would like to thank the Department of Chemistry for providing me with the opportunity to benefit from their excellent teaching and research program.

I gratefully acknowledge Dr. Martino Paventi, Gerry Barbiero and Dr. Charles Herbert for reading part of the manuscript and their suggestions in the preparation of this thesis. Special thanks to Dr. Paventi for the French translation of the abstract.

Thanks also go to Hu Yang, Marko, Kim, Ed, Hossein, Pong, Gerry, Coromoto, Haixin, Yifeng and others for their valuable discussions and friendly help over the past years.

I am grateful to General Electric Company and NSERC for financial support.

Thanks also to Dr. Nadim Saade for mass spectrum analyses.

Abstract

A new simple method for the synthesis of novel hydroxy substituted 1,2-diphenylcyclopropanes was developed. Mono and dihydroxysubstituted-1,2-diphenylcyclopropanes were prepared by base-catalyzed decomposition of the corresponding hydroxy substituted 3,5-diphenyl-2-pyrazolines which were the products of the reaction between hydroxychalcones and hydrazine monohydrate. Some biphenols and activated aromatic difluorides containing the ethylene, chalcone and pyrazoline groups were prepared by novel, simple methods employing readily available starting materials and reagents. The monomers were used to prepare thermally cross-linkable polymers. New dianhydrides containing the 1,2-diphenylcyclopropane or diphenylacetylene group were synthesized from 1,2-bis(4-hydroxyphenyl)cyclopropane or bis(3-hydroxyphenyl)acetylene.

Subsequently, new types of poly(aryl ether sulfone)s, poly(aryl ether ketone)s, polyesters, polyformals, polyimides, poly(phenylene oxide)s and cyclic aryl ether oligomers containing the internal trans-1,2-diphenylcyclopropane, ethylene, chalcone, epoxide and 2-pyrazoline moieties were synthesized from these monomers by condensation polymerization reactions. Characterization of and cross-linking studies on these polymers were carried out utilizing DSC, TGA, TMA, GPC and NMR. The prepared polymers are high molecular weight, amorphous and soluble in common organic solvents.

The polymers can be thermally cross-linked. The glass transition temperatures of the polymers increased and their solvent resistance was improved significantly after curing. Thermogravimetric analyses showed that no significant weight loss accompanied the cross-linking reactions.

Sommaire

Une nouvelle et simple méthode pour la synthèse de nouveaux diphényl-1,2-cyclopropanes a été développée. Des diphényl-1,2-cyclopropanes substitués par des groupements mono et dihydroxy ont été préparés par la décomposition, catalysée à base, des diphényl-3,5-pyrazolines-2, substitués par le groupement hydroxy correspondant, qui sont les produits de la réaction entre les hydroxychalcones et le monohydrate d'hydrazine. Quelques biphénols et des difluorures aromatiques activés contenant les groupements éthylène, chalcone et pyrazoline ont été préparés par une nouvelle, simple méthode en employant des matières et réactifs qui sont très accessibles. Ces monomères ont été utilisés pour la préparation de polymères qui, par chauffage, forment des liaisons croisées. De nouveaux dianhydrides contenant le groupement diphényl-1,2-cyclopropanes ou le diphénylacétylène ont été synthétisés à partir du bis-1,2-(hydroxy-4-phényl)cyclopropane ou bis(hydroxy-3-phényl)acétylène.

Subséquemment, des nouveaux poly(aryl éther cétone)s, polyesters, polyformals, polyimides, poly(oxyphénylène-1,4)s et des oligomères aryls éthers cycliques contenant de groupements internes de *trans*-diphényl-1,2-cyclopropane, éthylène, chalcone, époxy et pyrazoline-2 ont été synthétisés à partir de ces monomères par une réaction de condensation polymèrique. La caractérisation et l'étude des liaisons croisées sur ces polymères ont été effectuées en utilisant le DSC, TGA, TMA, GPC, et le RMN. Les polymères préparés ont un poids moléculaire élevé, sont amorphes et solubles dans les solvants communs.

Les polymères produisent des liaisons croisées par chauffage. Les températures de transition de verre des polymères sont augmentées après un chauffage et les matières qui y résultent sont plus résistants aux solvants. Les analyses thermogravimétriques ne démontrent aucune perte de poids significative après ces réactions thermiques qui produisent des liaisons croisées.

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Glossary of Abbreviation and Symbols

Å	Angstrom (1x10^{-8})
DMAc	N,N'-dimethylacetamide
DMF	N,N'-dimethylformamide
DMSO	dimethylsulfoxide
DSC	differential scanning calorimeter
E'	Young' modulus
FT	Fourier transform
HPLC	high pressure liquid chromatography
GPa	1x10^{9} Pascal (1.0 Pa = 10 dyn/cm^{2} = 0.00145 psi)
GPC	gel permeation chromatography
IR	infrared
mmol	millimole
Mn	number average molecular weight
mp	melting point
MS	mass spectrum
Mw	weight average molecular weight
Mw/Mn	polydispersity
NMP	N-methylpyrolidinone
NMR	nuclear magnetic resonance
tanδ	ratio of loss moduli to storage moduli (E'/E")
Tc	crystallizing temperature
Tg	glass transition temperature
TGA	thermogravimetric analysis

Tm	melting temperature
TMA	thermomechanical analysis
UV	ultraviolet
Noryl	blend of PPO and polystyrene
PPO	poly(phenylene oxide)
Ultem	poly(phenyl-2,2-bis(phthalimid-3-oxy-phenyl)-propane)
λ	wavelength
δ	chemical shift
μ	micro

Chapter 1

Introduction

1.1 Synthetic polymers

The substances which are referred to as polymers, or macromolecules, are giant molecules with molar masses ranging from several thousands to several millions. Polymers are the materials that are pervasive in our everyday lives. Some of these substances are recent products resulting from the ingenuity of the chemist. Some are naturally occurring and have been used by mankind for several thousands years, and some form parts of our bodies. Polymers are those large molecules constructed from. many smaller structural units called monomers, covalently bonded together in any conceivable pattern.

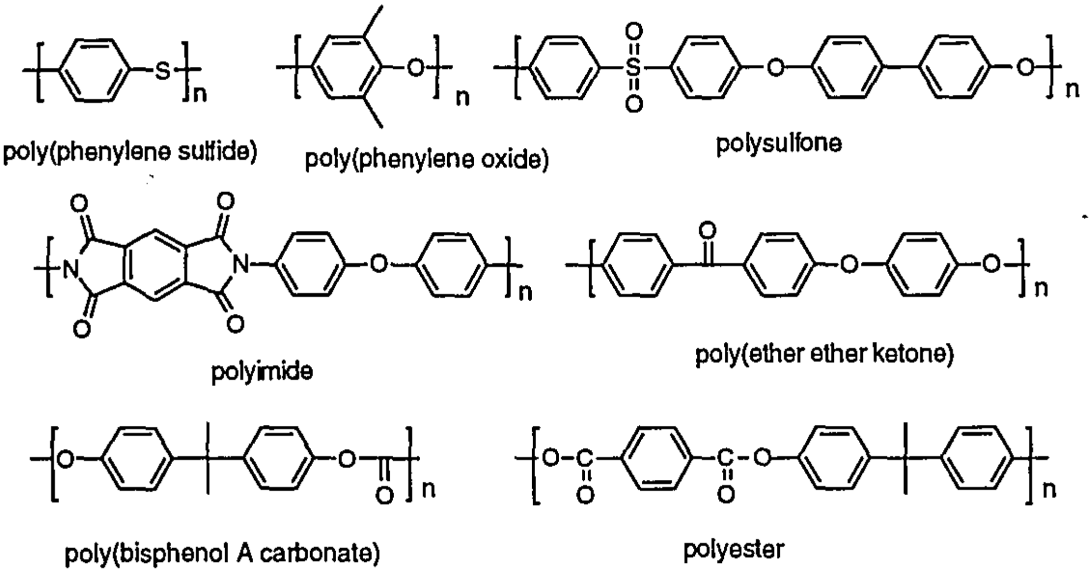
Synthetic polymers with their manifold uses have affected modern life so profoundly that our world is hardly imaginable without them.[1] A large number of synthetic polymers with a wide range of properties now exist. Thay can be grouped into the three major classes, plastics, fibers, and elastomers. Plastics and fibers are resistant to deformation and are characterized by a high modulus and low percentage elongations. Elastomers readily deform and exhibit large reversible elongations under small applied stresses, i.e. they exhibit elasticity. A polymer normally used as a fiber may make a good plastic if no attempt is made to draw it into a filament. Similarly, a plastic, if used at a temperature above its glass transition and suitably cross-linked, may make an acceptable elastomer.

1.2 Structure and property relations

The increasing use of synthetic polymers by industrial companies and engineers to replace or supplement more traditional materials, such as wood, metals, ceramics, and natural fibers, has stimulated the search for even more versatile polymeric structures covering a wide range of properties.[2] For such a quest to be effective, a fundamental knowledge of structure-property relations is required. For example, how can chain symmetry, flexibility, and tacticity, influence the individual values of both melting point (Tm) and glass transition temperature (Tg). Thus, a highly flexible chain has a low Tg, which increases as the rigidity of the chain becomes greater. Similarly, strong intermolecular forces tend to raise Tg and also increase crystallinity. Steric factors also play an important role. A high Tg is obtained when large pendent groups attached to the chain restrict its internal rotation, and bulky pendant groups tend to impede crystallization, except when arranged regularly in isotactic or syndiotactic chains. It is important to be able to regulate the degree of chain stiffness, as rigid chains are preferred for fiber formation, while flexible chains make better elastomers. An increase in the lattice energy of a crystallite is obtained when the three dimensional order is stabilized by intermolecular bonding. Cross-linking provides anchoring points for the chains and these anchor points restrain excessive movement and maintain the position of the chain in the network. When a sample is cross-linked, (1) the dimensional stability is improved, (2) the creep rate is lowered, (3) the resistance to solvents increases, and (4) it becomes less prone to heat distortion, because Tg is raised.

1.3 High temperature specialty polymers

While many of the more common polymers are remarkably resistant to chemical attack, and stable when subjected to mechanical deformation, they generally can not be used at elevated temperatures.[2-5] To overcome this low thermal stability, chains incorporating: (i) thermally unreactive aromatic rings; (ii) resonance stabilized systems; (iii) cross-linked "ladder" structures; and (iv) protective side groups, have been synthesized. Some of these characteristic structural features can be seen in most of the successfully developed high performance engineering thermoplasctics manufactured today. A few high temperature performance polymers are shown in **Scheme 1.1**:


poly(phenylene sulfide)

poly(phenylene oxide)

polysulfone

polyimide

poly(ether ether ketone)

poly(bisphenol A carbonate)

polyester

Scheme 1.1

1.4 Processing requirements for thermally stable polymers

In the initial phase of thermally stable polymer research, the inherent stability of organic compound based systems was realized. However, these highly stable polymers which characteristically contained highly rigid aromatic backbones were generally infusible and insoluble. Subsequently, efforts were focused on structural modifications which could provide processing feasibility. The general strategy was to introduce flexibility into such rigid systems to decrease the softening point and increase solubility. Almost without exception these changes led to lower stability, but were nonetheless necessary if applications were to be developed. The most common method was to incorporate flexible linkages into the backbone of rigid polymer systems[6-9].

In order to maintain high stability toward thermolysis, linkages with weak bonds must be excluded. In addition, oxidative and hydrolytic stability in the application environments is critical. This narrows the number of candidate systems significantly. To meet these requirements in aromatic systems, desirable functional groups are ether, sulfide, sulfone or ketone groups. These characteristic structural features can be seen in most of the successfully developed high performance engineering thermoplastics manufactured today.

1.5 Cross-linked polymers

One can describe polymers as linear, branched, and network. Network polymers arise when polymer chains are linked together or when polyfunctional instead of difunctional monomers are used. Network polymers are also commonly referred to as cross-linked polymers. Because of cross-linking, the polymer chains lose their ability to flow past one another and the material exhibits a considerable degree of dimensional stability. The polymer will not melt or flow and can not, therefore, be molded. Such polymers are said to be thermosetting or thermoset. To manufacture useful articles out of thermosetting polymers, one must accomplish the cross-linking reaction during processing or temporarily disrupt the cross-linking to allow the polymer to flow.

Cross-linked polymers are used in a wide variety of aerospace, automotive, building construction, and consumer product applications. Not all paints, adhesives, composites, and elastomers are cross-linked, but cross-linking systems are often used in these applications when resistance to solvents, resistance to high temperatures, and high mechanical performance are required. These important properties can be traced directly to the three-dimensional interconnected molecular network that is characteristic of cross-linked systems.[10]

1.6 Synthesis of cross-linked polymers

1.6.1 Reactive oligomers

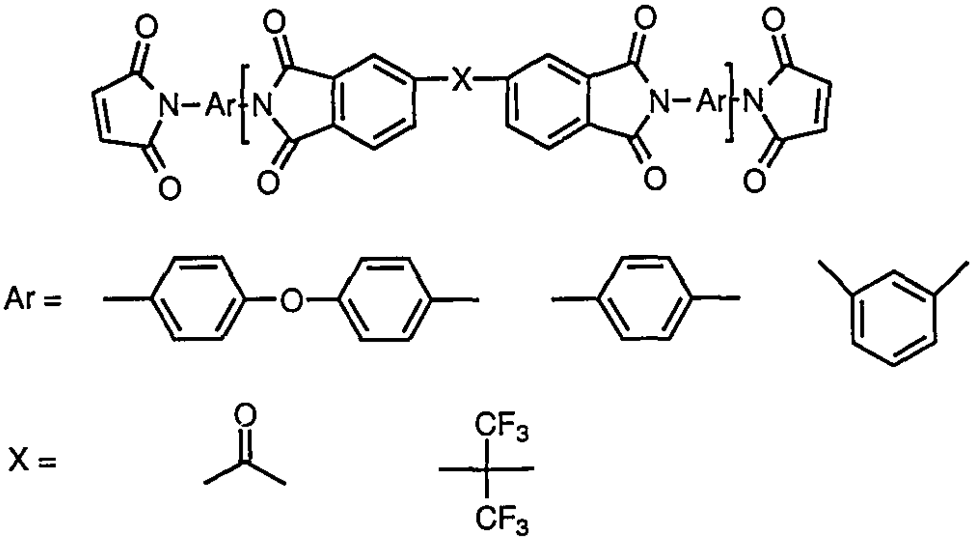
One way to synthesize cross-linked polymers is to first synthesize reactive oligomers which can then be cured. The concept of reactive oligomers involves the in situ conversion of low molecular weight compounds into high molecular weight materials which possess some assemblage of prescribed mechanical properties.[11] Reactive oligomers can be as simple as monomeric species which readily polymerize in bulk without the evolution of volatile components to yield a final manufactured article. More often than not, however, reactive oligomers are low molecular weight versions of some basic thermoset or thermoplastic polymer which are multiply substituted with mutually reactive functional groups. Upon suitable initiation, these can readily interact by an addition process to give linear chain extension and /or branching. Further, the process is often carried out in the presence of inert materials such as fibers or powders. The net result of these reactions is the one step conversion of small organic molecules into a final part in a mold or the preparation of a contiguous coating or film. The ultimate goal then of reactive oligomer technology is easily processable polymeric compositions.

The introduction of epoxy resins in the late 1930s is maybe regarded as the beginning of contemporary reactive oligomer research.[12,13] For many years, epoxy resins were refined and developed for numerous applications in a wide variety of technologies ranging from coatings to composites. As these technologies and especially the latter evolved, they set in place the modern manufacturing methodologies wherein reactive oligomers would play a key role. Epoxies worked in many of these applications but, as aircraft performance increased and as printed circuits evolved into microchips, these materials soon reached the limits of their performance and new materials were needed.

The choice of the reactive end groups resulted in the exploration of a wide variety of, new to polymer synthesis, addition reactions such as maleimide free radical addition, aryl cyanate trimerizations and arylacetylene polymerization. The key feature of these cure chemistries was that they could be thermally initiated in a controllable way and reacted by processes which did not evolve volatile components. Further, they were single component systems and cured to give thermooxidatively stable linkages. Of the wide variety of possible cure chemistries, two, free radical additions and cycloadditions, proved to come closest to meeting all of the requirements for a high performance reactive oligomer.

1.6.1.1 Bismaleimides

Bismaleimides were introduced commercially in the 1970s in various formulations and found wide application in the area of high temperature composites.[14-17] Bismaleimides are a leading class of thermosetting polyimides. The chemical structure of bismaleimides is shown in **Scheme 1.2**. Products with this sort of structure were initially synthesized by D'Alelio from pyromellitic acid dianhydride, an aromatic diamine and maleic anhydride as endcapper. Dimethylformamide was used as a solvent. Cyclodehydration was performed thermally by heating the solution of the polyamide acid to temperatures of 70-120°C. Their excellent processability and balance of thermal and mechanical properties have made them extremely popular in advanced composites and electronics. The bismaleimide resins have a good shelf life, process well and thermally cure to give high Tg thermooxidatively stable polymers and composites. They are in general rather brittle in their unmodified forms.[18-23]



Scheme 1.2

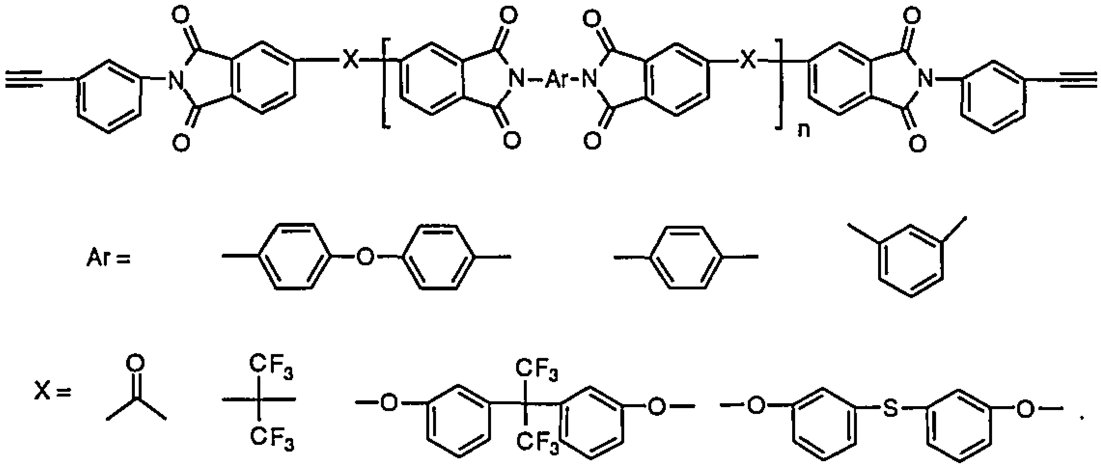
1.6.1.2 Arylene dicyanates

Arylene dicyanates form the basis of another class of reactive oligomer cure chemistry.[24-28] It is known that these compounds can undergo a thermally initiated trimerization to tris-aryloxytriazines when heated at 170 to approximately 200°C. This curing reaction can be accelerated substantially by the addition of cobalt catalysts.

1.6.1.3 Acetylene terminated polyimides

The incorporation of acetylenic moieties into polymers has been studied extensively. Polyimides containing acetylene groups have been recently reviewed.[14] The general chemical structure of acetylene terminated polyimide is shown in **Scheme 1.3** .

These resins, which are a series of aromatic oligomers end capped with primary acetylene groups,[29-36] have been largely investigated under the auspices of the U.S. Air Force and from these efforts emerged several attractive acetylene terminated reactive oligomers based on bisphenol A and arylsulfone ether center block.



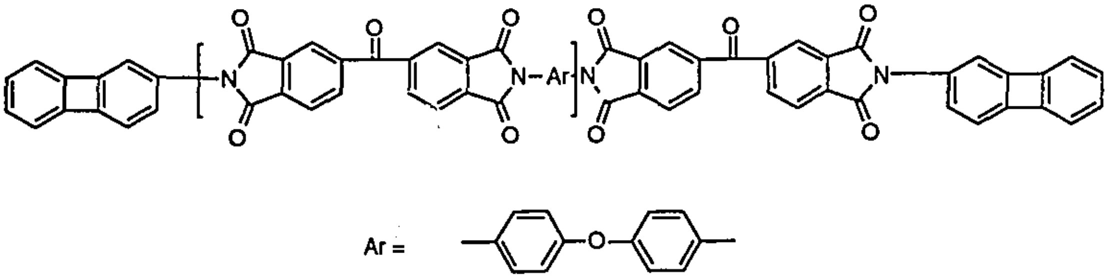
Scheme 1.3

1.6.1.4 Biphenylene reactive oligomers

A different approach to generating reactive functional groups has been taken in some work involving the use of biphenylene as a thermally activated cross-linking group. Biphenylene is known to undergo scission of one of the bonds in the four membered ring at high (300-400°C) temperature to give what are believed to be radical intermediates. These can then, as expected, couple to give addition products. Various researchers have taken advantage of this latent reactivity by incorporating low levels of biphenylene into the backbone of polyquinolines and polyether ketones.[37-39] A biphenylene endcapped polyimide is shown in **Scheme 1.4**.

1.6.1.5 Benzocyclobutene reactive oligomers

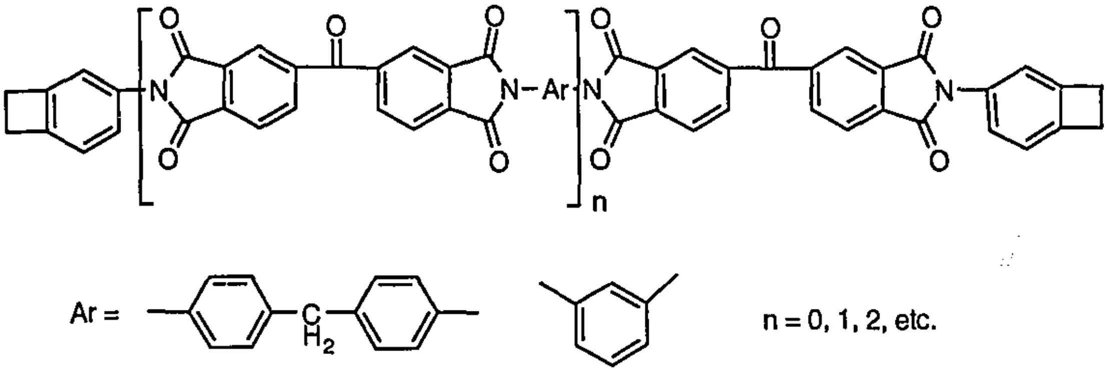
It is quite obvious that the technology of building a polyimide backbone structure is well developed. However, there is still a need for terminal groups which can undergo thermal or catalytically induced homo- or copolymerisation or cross-linking to result in new thermosetting polyimides. Benzocyclobutenes have in recent



Scheme 1.4

years been extensively employed in polymer synthesis and modification.[11] This novel cure chemistry utilizing a strained four-membered ring fused to an aromatic system has recently been described. It has been found that, under appropriate thermal conditions, the four-membered ring of benzocyclobutene undergos electrocyclic ring opening and that the o-xylylene formed undergoes homopolymerization. Researchers at the Air Force Materials Laboratory were able to synthesize 4-aminobenzocyclobutene which made it possible to prepare benzocyclobutene terminated imide oligomers (**Scheme 1.5**). The imide oligomers were synthesized by refluxing a mixture of 4-aminobenzocyclobutene and the prospective anhydride in a 2:1 stoichiometry in acetic acid under nitrogen for about 17 hours. As usual, the melting points of such relatively high molecular weight monomers or prepolymers can be tailored via the backbone structure between the benzocyclobutene terminations.

In summary, bisbenzocyclobutenes are a new family of thermosetting resins which cure via addition reactions without generation of volatiles and without the need for a catalyst. Cured bisbenzocyclobutene imides show a very low moisture absorption and exhibit the potential for use as relatively high temperature structural matrix materials in advanced composites.



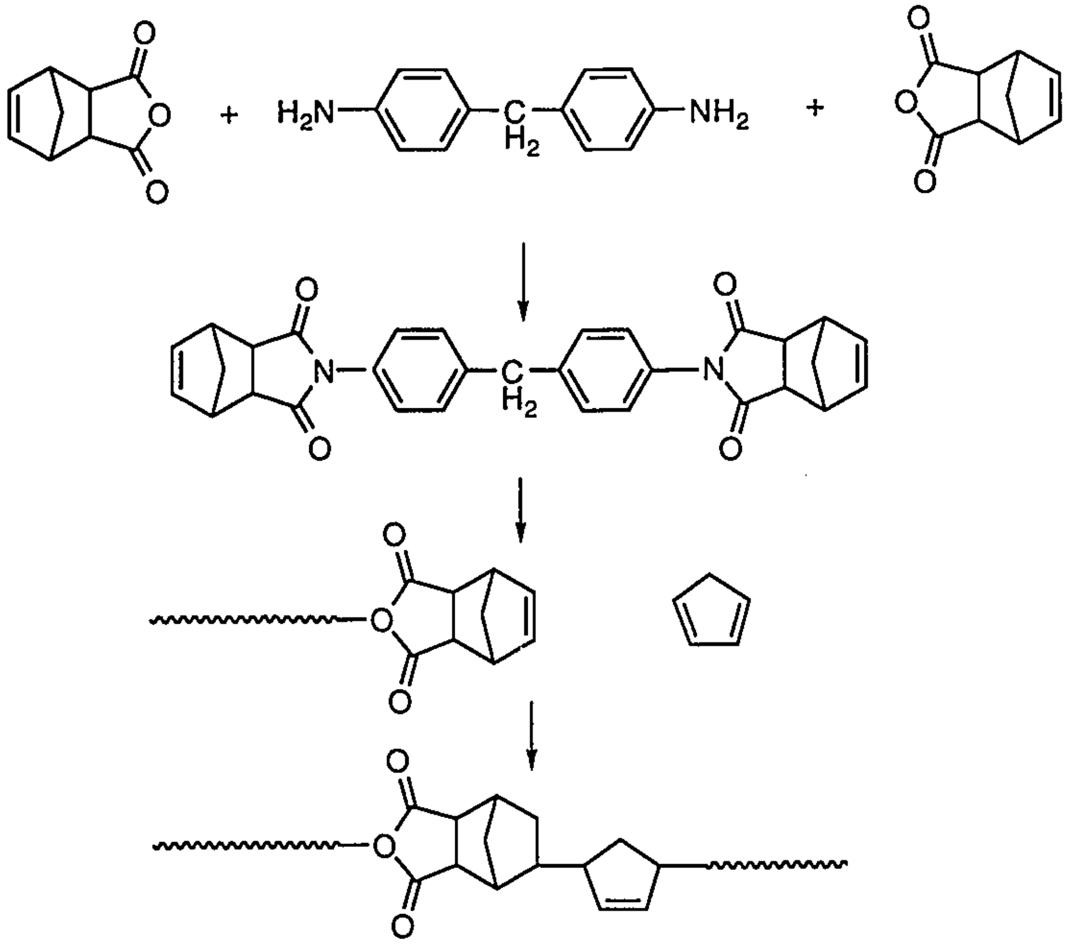
Scheme 1.5

1.6.1.6 The polymerization of monomeric reactants

The polymerization of monomeric reactants (PMR) is a unique approach to temperature-resistant cross-linked polyimides. The PMR approach, in contrast, is unique because the imide prepolymer is synthesized in situ during processing of the resin. The designation PMR-polyimides is, at least in the strict chemical sense, somewhat misleading because the monomeric (M) reactants are not polymerized. They undergo a condensation reaction to form the imide prepolymer (**Scheme 1.6**) which, after completion of the condensation reaction, polymerizes to a temperature resistant three-dimensional network.[14]

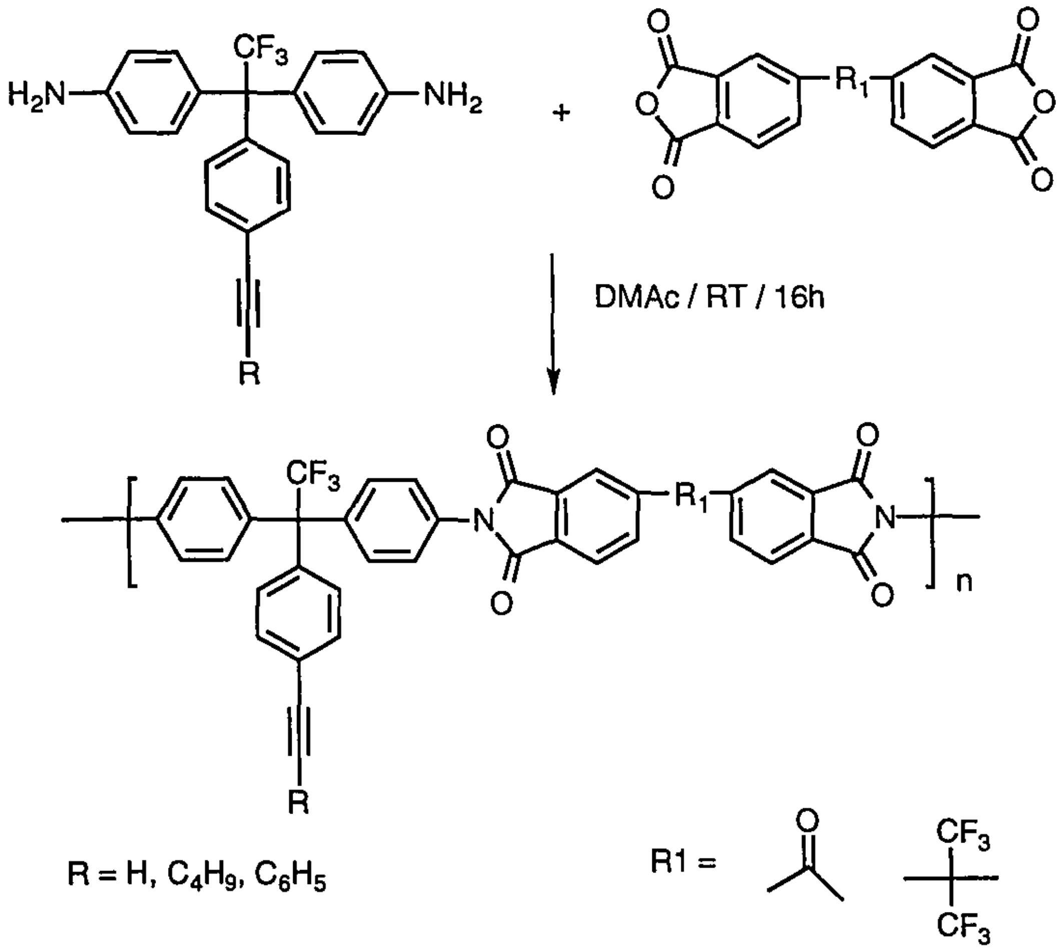
1.6.2 Polymers containing pendent acetylenic groups

Polymers with pendent acetylenic groups along the chain have also been synthesized[40-41] and attempts have been made to design polymers where the predominant reaction that occurs on heating is an intramolecular cyclization which would result in an increase in the glass transition of the cured polymers without concomitant cross-linking of the polymer. **Scheme 1.7**[41] shows a synthesis of



Scheme 1.6

polyimides with pendent ethynyl groups. The polyimides were synthesized by adding the dianhydride to a solution of the diamine in N,N-dimethylacetamide (DMAc) followed by stirring for 16 hours at room temperature under nitrogen. The polyamic acids were either thermally imidized or chemically imidized by adding acetic anhydride and triethylamine to the polyamic acid solution and stirring overnight. Those polymers can be cross-linked thermally to improve solvent resistance. The toughness and solubility can be systematically controlled by varying the amount of ethynyl containing diamine used in the synthesis, which controls the final cross-linking density.



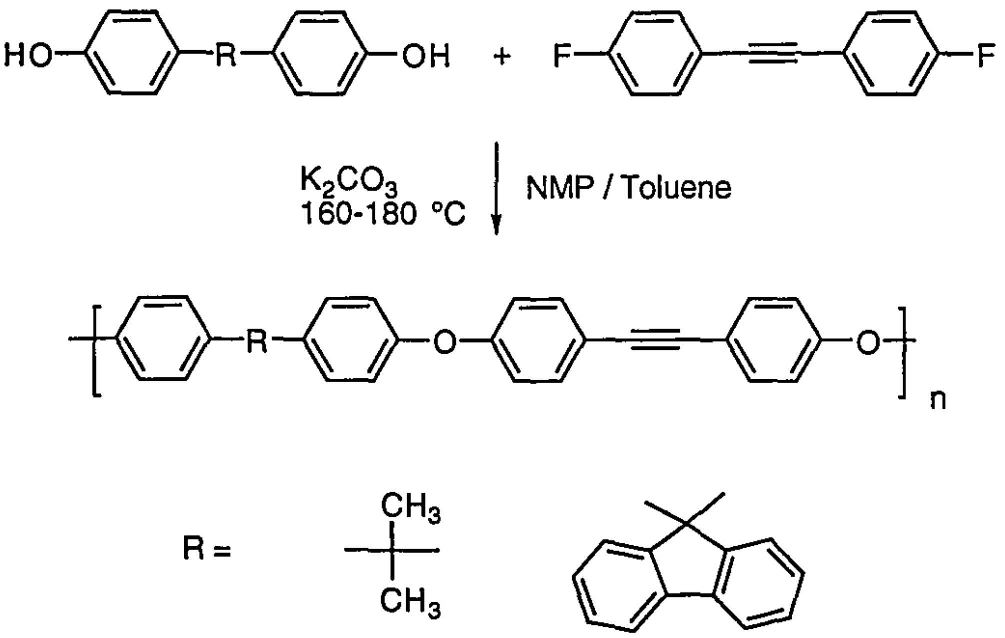
Scheme 1.7

1.6.3 Polymers containing internal acetylenic groups

Polyimide copolymers have been synthesized by using bis(3-aminophenyl)acetylene to replace some of the diamines[42], and eneyne moieties have been introduced into polyimides[43]. When all of these polymers are heated, a strong exothermic reaction takes place with the resulting cross-linking of the polymers. The position of the exotherm peak varies with the structure of the acetylene moiety.

Ethynyl groups cross-link at a much lower temperature (ca. 250 °C) than phenylethynyl groups (ca. 350°C).

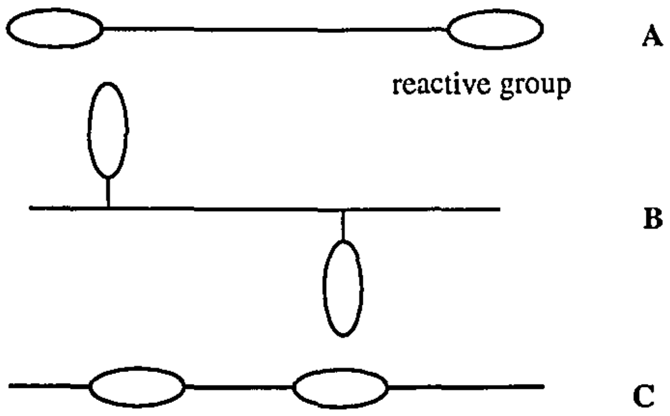
High molecular weight polymers containing internal acetylenic groups have been synthesized by solution condensation of bis(4-fluorophenyl)acetylene and bisphenols in the presence of potassium carbonate in a dipolar aprotic solvent at 160-180°C (**Scheme 1.8**)[44-45]. High molecular weight linear polymers are obtained from 4,4'-(1-methylethylidene)bisphenol (BPA) and 9,9-bis(4-hydroxyphenyl)fluorene which are readily soluble in solvents like chloroform and methylene chloride at room temperature. It was found that those polymers are thermally cross-linkable. The cured polymers are insoluble and do not swell in chloroform after being cured at 340°C.



Scheme 1.8

1.7 Goals of this project

A great deal of effort has been expended in the introduction of reactive groups into polymers in order to provide reactive functionality which will provide sites for cross-linking the polymers when heated. A major objective has been the synthesis of matrix resins for advanced composites where the potential advantage is that in the curing process no volatiles are produced which will produce voids in the final fabricated structures which would be sites for failure of the structures. The reactive groups have been introduced as terminal groups (A), as pendent groups (B) and as internal groups (C) in the polymer chains.



The largest effort has been centered on the synthesis of polymers which contain terminal reactive groups such as acetylene containing moieties. Generally this involves the preparation of oligomers[46-50] with reactive end groups which can be subsequently be thermally chain extended to produce a highly cross-linked polymer matrix. Polymers containing reactive pendent groups have been synthesized and these polymers have been thermally cured. Polymers containing internal reactive groups have been less studied. High temperature cross-linkable polymers containing internal reactive groups such as acetylene and benzocyclobutene have been investigated.[45,51]

The goals of this thesis are the synthesis of monomers which contain reactive functionality which can be incorporated into high molecular weight linear homopolymers and copolymers which can be cross-linked on heating or by photochemical means.

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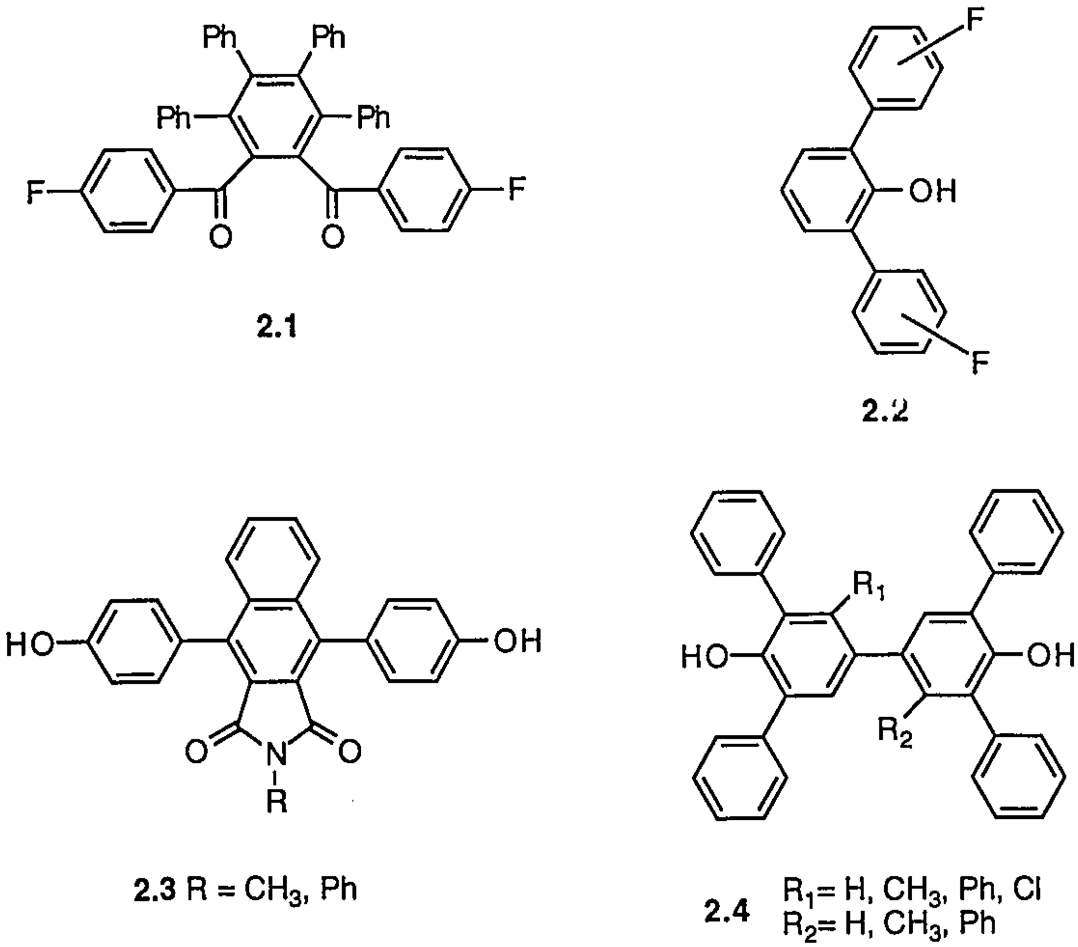
Chapter 2

Monomer Design and Synthesis

2.1 Introduction

The design of new polymeric materials with specific property profiles offers an exciting challenge to chemists. The synthesis of a new polymer may first require the synthesis of a new monomer which can then be polymerized to give a high molecular weight linear structure. Alternatively, a known molecule may be polymerizable by the discovery of new chemistry or the adaptation and optimization of an existing chemical reaction since any chemical reaction in which two molecules can be coupled together in high yield is conceptually adaptable to a polymer forming reaction.

Properties, such as melting point, glass transition temperature, thermal stability and mechanical properties, etc., depend on the structure of the monomer unit making up the polymer. Therefore specific monomers when incorporated into polymers are advantageous for tailoring the properties of the material for the specific applications. To synthesize certain polymers with specific properties which meet the requirements for applications, a monomer has to be designed and synthesized. Significant improvements in materials technology have been made by designing strategically substituted monomer units in the polymer architecture.[1-8] Introducing bulky substituents on the polymer backbone which suppress crystallization of the polymer, and improve solubility, is an example to demonstrate the significance of new polymer forming monomers. Reaction of the novel fluoro substituted monomers containing the 1,2-dibenzoylbenzene moiety (structure **2.1**) with bisphenates in the presence of excess anhydrous potassium carbonate in N,N-dimethylacetamide (DMAc) gave high molecular weight amorphous



2.1

2.2

2.3 R = CH_3, Ph

2.4 R_1= H, CH_3, Ph, Cl
R_2= H, CH_3, Ph

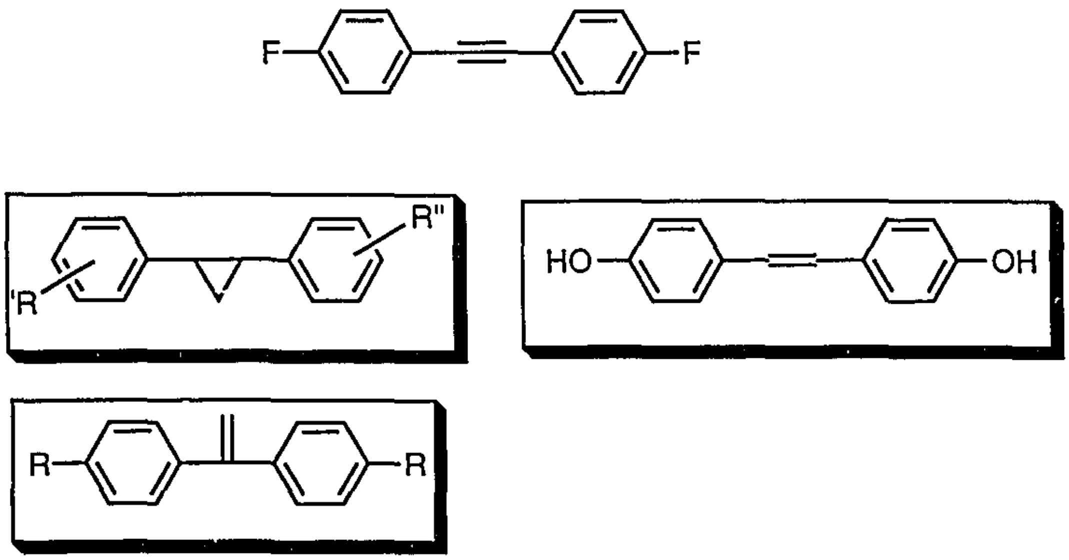
Scheme 2.1

poly(aryl ether ketone)s, which are very soluble in solvents such as chloroform and methylene chloride at room temperature and have glass transition temperatures ranging from 160 to 313°C.[9] The objective to attain reduced melting temperatures and hence melt processable thermoplastics was achieved by synthesizing fluoro substituted poly(2,6-diphenylphenylene ether)s from fluoro substituted 2,6-diphenylphenol monomers of structure **2.2.**[10] The polymers prepared from imidoaryl biphenols of general structure **2.3**[11] (polysulfones) and poly(ether ketone)s) and the new modified biphenols of structure **2.4**[12] containing 2,2'-disubstituents on the biphenyl groups exhibit considerably enhanced glass transition temperatures and are soluble in common organic solvents due to the noncoplanar biphenyl rings which increase the disorder along the polymer backbone thereby reducing interchain interactions.

The goal of this thesis is to synthesize high molecular weight processable polymers containing reactive groups which can undergo thermal chain extension to form cross-linked polymers. To fulfill the goal, new monomers have to be first designed and synthesized.

The monomers were designed with several criteria in mind. First, the monomer's reactivity was chosen such that it would not interfere with polymer synthesis and processing methods typically employed for poly(ether sulfone)s, polyformals and polyesters. This required a cross-linkable group that would be stable to alkali up to 200°C. Second, the functional group should be thermally stable up to Tg in order that cross-linking could be carried out in the melt. Third, cross-linking should occur without evolution of volatile byproducts and should involve a highly reactive intermediate in order to maximize conversion.

The new monomer bis(4-fluorophenyl)acetylene (**Scheme 2.2**) was designed and synthesized by a novel and simple method.[11a] It was demonstrated that reaction of bis(4-fluorophenyl)acetylene with bisphenols in the presence of potassium carbonate in a dipolar aprotic solvent at 160-180°C yields high molecular weight linear polymers which are thermally cross-linkable. We speculated that the similar monomers containing cyclopropane or ethylene groups (**Scheme 2.2**) might also be promising for the synthesis of thermally cross-linkable polymers.

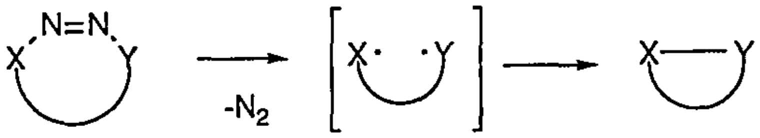


Scheme 2.2

2.2 Cyclopropane monomers

2.2.1 Thermal and photochemical cycloelimination of nitrogen

Cyclic azo compounds including heteroaromatics with a N=N bond with strong double-bond character can eliminate molecular nitrogen on addition of sufficient thermal energy or on electronic excitation. Some substrates decompose spontaneously, others are moderately or even extremely resistant to N_2-elimination.

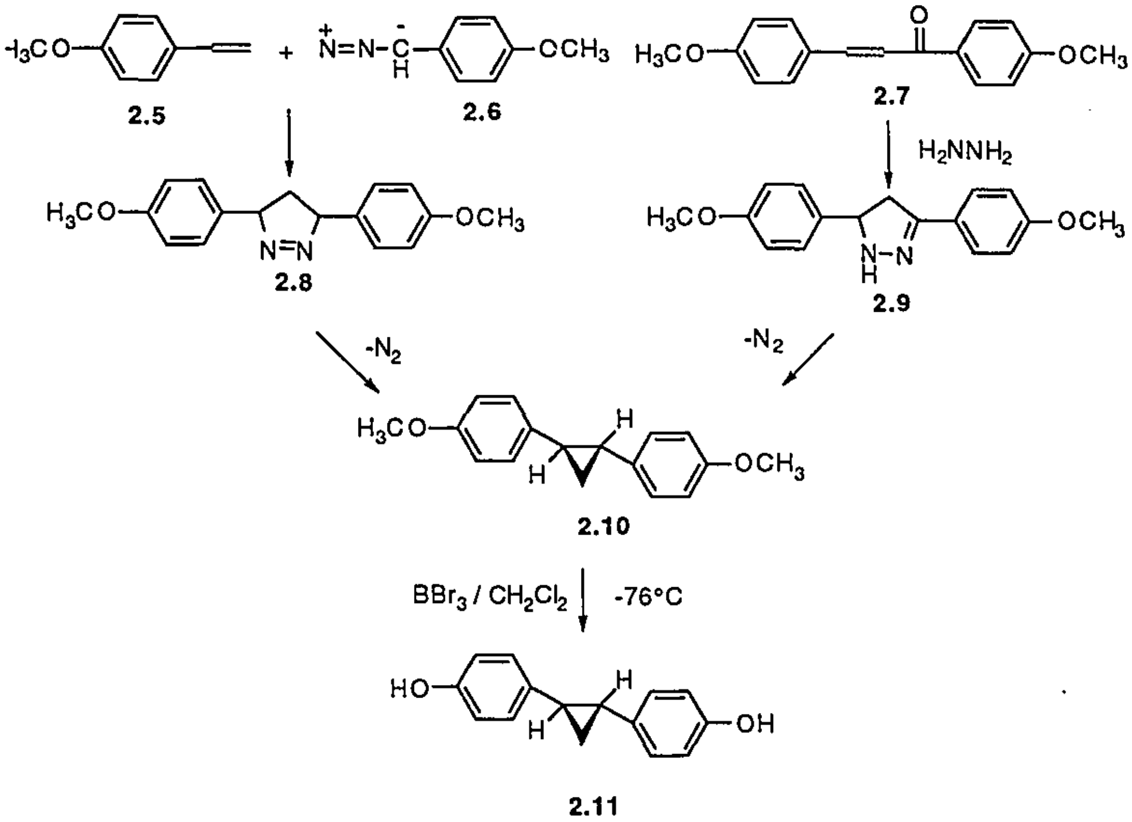


From a preparative point of view this type of reaction opens up a variety of interesting possibilities, e.g. the synthesis of small carbocycles or heterocycles, strained bi- and polycycles, as well as cage compounds. From a theoretical mechanistic viewpoint, current importance attaches to the primary fragments such as carbenes, diradicals, trimethylene, trimethylenemethane, dipoles, ylides, antiaromatic 4π-systems, unstable cycloalkynes, and arynes.[15-16]

The stereochemistry of product formation is particularly important. Depending on the substrate, method, and medium, all possible types of processes can be observed, from stereospecific through stereoselective to purely random. For example, the trans-isomer of 3,5-diphenyl-1-pyrazoline shows high stereoselectivity both photochemically and thermally, while the cis-isomer does not.

2.2.2 Results and discussion

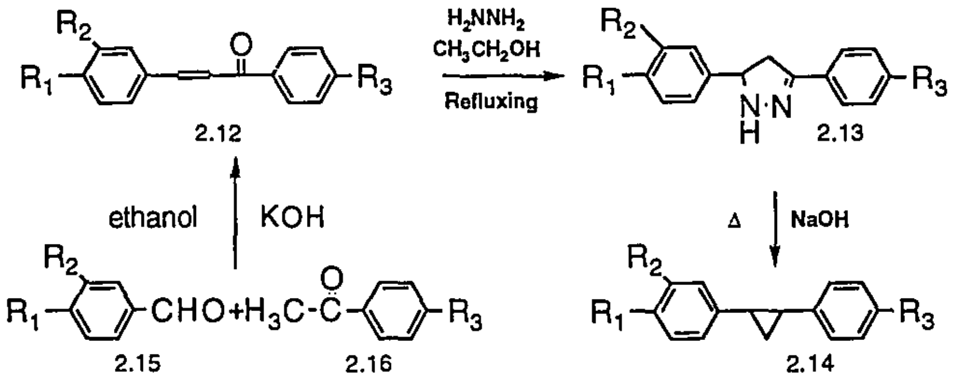
C. G. Overberger[17] reported a synthesis of trans-1,2-bis(4-methoxyphenyl)cyclopropane **2.10** (**Scheme 2.3**) by thermal and photolytic decomposition of 3,5-bis-(4-methoxyphenyl)-1-pyrazoline **2.8** which was made by the reaction of 4-methoxyphenyldiazomethane **2.6** with 4-methoxystyrene **2.5**. The yield of the reaction to make 3,5-bis-(4-methoxyphenyl)-1-pyrazoline **2.8** was only 35%. We found the method of Hamada[18] to be superior (**Scheme 2.3**).



Scheme 2.3

4,4'-Dimethoxybenzalacetophenone **2.8** reacts with hydrazine hydrate to afford 3,5-bis-(4-methoxyphenyl)-2-pyrazoline **2.9** which was converted to trans-1,2-bis(4-methoxyphenyl)cyclopropane **2.10** by base-catalyzed decomposition. Demethylation of **2.10** with BBr_3 in methylene chloride gave trans-1,2-bis(4-hydroxyphenyl)cyclopropane **2.11** in quantitative yield. The product was purified by recrystallization from acetic acid. The conversion of the reaction to synthesize trans-1,2-bis(4-hydroxyphenyl)cyclopropane **2.11** by demethylation of trans-1,2-bis(4-methoxyphenyl)cyclopropane **2.10** with BBr_3 is very high. However, the reaction mixture has to be cooled in a dry ice- acetone bath, water must be rigorously excluded and it takes more than 3 hours for the reaction to finish.

We have found that the method to synthesize trans-1,2-bis(4-methoxyphenyl)cyclopropane **2.10** from 3,5-bis-(4-methoxyphenyl)-2-pyrazoline **2.9** by base-catalyzed decomposition can be used directly on the hydroxychalcones, thus greatly simplifying the reaction. The following (**Scheme 2.4**) is the synthesis of hydroxysubstituted-3,5-diphenyl-2-pyrazolines **2.13** and 1,2-diphenylcyclopropanes **2.14** from the corresponding hydroxychalcones **2.12**. 4,4'-Dihydroxychalcone **2.12a** and 3, 4'-dihydroxychalcone **2.12b** were prepared by reaction of 4-hydroxybenzaldehyde **2.15a** or 3-hydroxybenzaldehyde **2.15b** with



Aldehyde	acetophenone	R_1	R_2	R_3	chalcone	pyrazoline	cyclopropane
2.15a	**2.16a**	OH	H	OH	**2.12a**	**2.13a**	**2.14a**
2.15b	**2.16a**	H	OH	OH	**2.12b**	**2.13b**	**2.14b**
2.15a	**2.16b**	OH	H	H	**2.12c**	**2.13c**	**2.14c**
2.15c	**2.16a**	H	H	OH	**2.12d**	**2.13d**	**2.14c**

Scheme 2.4

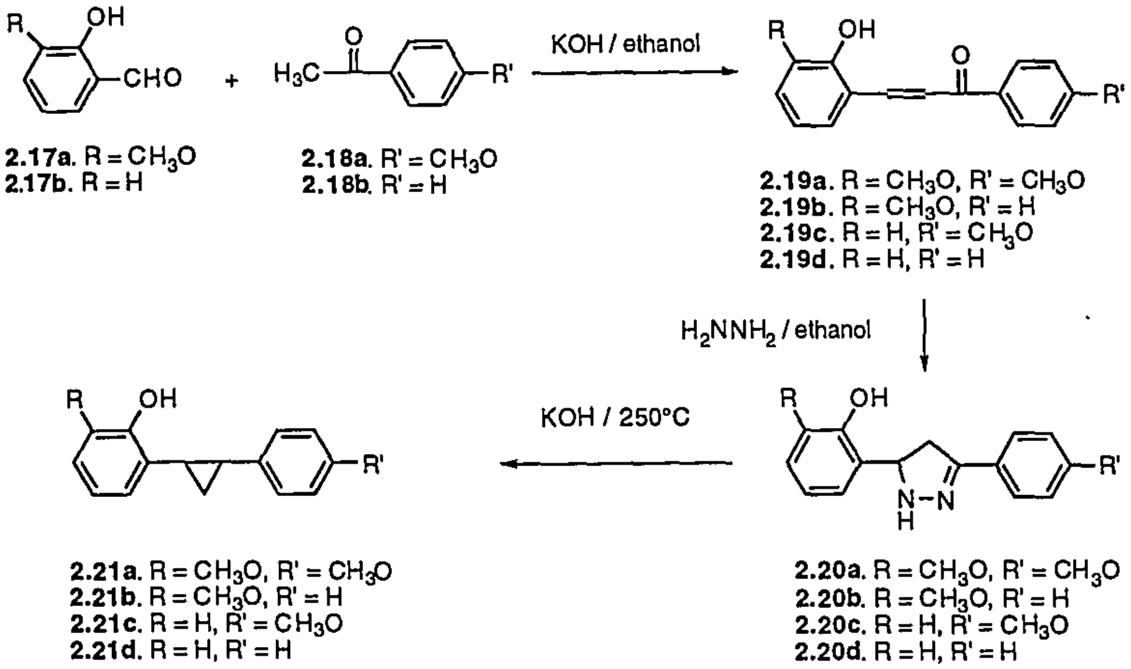
4'-hydroxyacetophenone **2.16a** by the hot condensation method.[19-20] The hydroxysubstituted-3,5-diphenyl-2-pyrazolines **2.13** were prepared by refluxing the ethanol solution of the hydroxychalcones **2.12** in the presence of a two fold excess of hydrazine monohydrate. The conversion in this step, as determined by HPLC, is quantitative. Only the trans isomer was obtained as indicated by proton NMR. A small amount of sodium hydroxide was mixed with the hydroxy substituted 3,5-diphenyl-2-pyrazolines, and the mixture was then heated to 250°C under nitrogen. The decomposition of the hydroxysubstituted-3,5-diphenyl-2-pyrazolines was finished in less than 30 minutes to give hydroxysubstituted-1,2-diphenylcyclpropanes in quantitative yield. The mixture obtained was shown to consist of 5-10% of the cis and 90-95% of the trans isomers. After recrystallization pure trans isomer was readily obtained.

The NMR spectra of trans-3,5-bis(4-hydroxyphenyl)-2-pyrazoline **2.13a** and trans-3(4-hydroxyphenyl)-5(3-hydroxyphenyl)-2-pyrazoline **2.13b** have a triplet at δ4.63-4.80 (benzylic protons) and an octet at δ2.71-3.42 (methylenic protons) while the NMR spectra of trans-3-phenyl-5(4-hydroxyphenyl)-2-pyrazoline **(2.13c)** and trans-3(4-hydroxyphenyl)-5-phenyl-2-pyrazoline **(2.13d)** have a sextet at δ4.66-4.81 and an octet at δ2.69-3.44. Compounds **2.13c** and **2.13d** are tautomers. The chemical shifts in the aromatic proton region of their ^{1}H NMR spectra are different for the two compounds **2.13c** and **2.13d.** We have seen no evidence of tautomerism. There are also significant difference in the fragmentation patterns in their mass spectra.

The NMR of trans-1,2-bis(p-hydroxyphenyl)cyclopropane **(2.14a)** has two triplets at δ1.16-1.22 and δ1.80-1.98 separately while trans-1-(3-hydroxyphenyl)-2-(4-hydroxyphenyl)cyclopropane **(2.14b)** and trans-1-(4-hydroxyphenyl)-2-

(phenyl)cyclopropane (**2.14c**) have a triplet at δ1.23-1.39 and a multiplet at δ2.04-2.10.

The method described here is a simple and high-yield procedure to synthesize hydroxy substituted 3,5-diphenyl-2-pyrazolines and 1,2-diphenylcyclopropanes, which are all new compounds.



Scheme 2.5

Four new hindered phenols **2.21a-d** containing the 1,2-diphenylcyclopropane group were synthesized according to the method described above (Scheme 2.5). 2-Hydroxychalcones **2.19a-c** were prepared by reaction of 2-hydroxybenzaldehydes **2.17a-b** with acetophenones **2.18a-b** by the hot condensation method. The hydroxysubstituted-3,5-diphenyl-2-pyrazolines **2.20a-d** were prepared by refluxing the ethanol solution of the hydroxychalcones **2.19a-d** in the presence of a two fold excess of hydrazine monohydrate. The conversion in this step, as determined by HPLC, is quantitative. Only the trans isomer was obtained as indicated by proton NMR. A small amount of sodium hydroxide was mixed with the hydroxy substituted 3,5-diphenyl-2-pyrazolines, and the mixture was then heated to 250°C under nitrogen. The decomposition of the hydroxysubstituted-3,5-diphenyl-2-pyrazolines was finished in less than 30 minutes to give hydroxy substituted-1,2-diphenylcyclpropanes **2.21a-d** in quantitative yield. The mixture obtained was shown to consist of 5-10% of the cis and 90-95% of the trans isomers. After recrystallization pure trans isomer was readily obtained.

2.3 Stilbene monomers

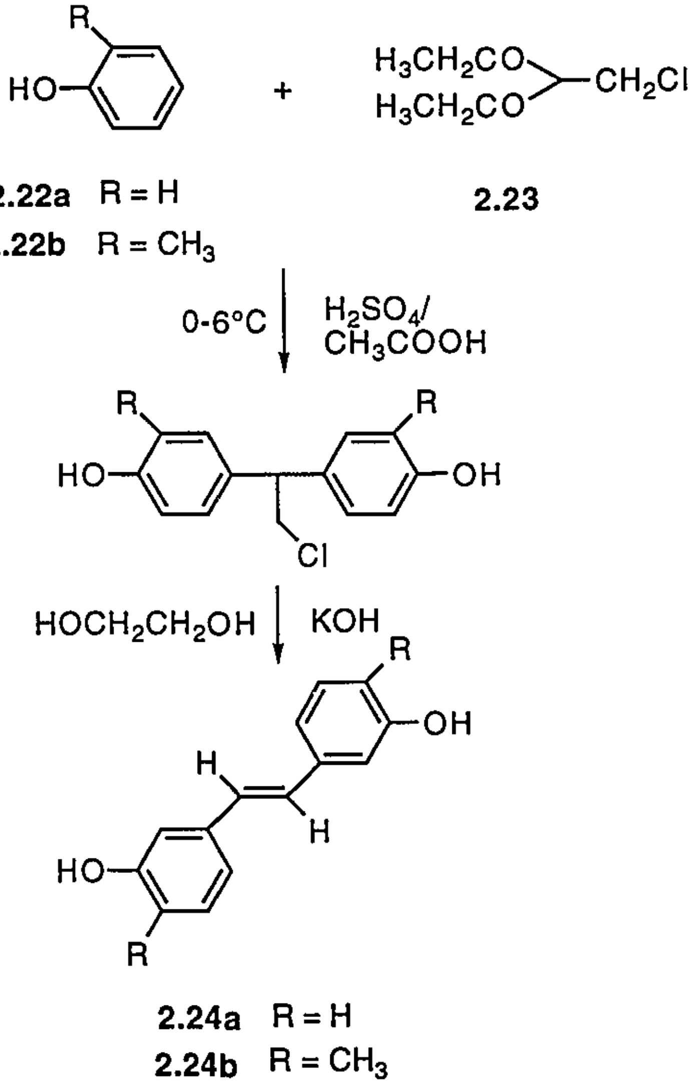
2.3.1 Stilbene forming reactions

Dehydrogenation of 1,2-diarylalkanes by SeO_2 is one of the methods used to synthesize stilbenes.[21] By condensation of chloroacetaldehyde with aromatic hydrocarbons, phenols, and phenol or thiophenol ethers, and rearrangement of the condensation products at higher temperature, 4,4'-disubstituted stilbene can be synthesized in a simple way with excellent yields.[22]

2.3.2 Isomerization of stilbene

Cis-stilbene can be converted to the trans isomer by photoisomerization.[23] The isomerization takes place because the excited states, both S_1 and T_{ii}, of many olefins have a perpendicular instead of a planar geometry, so that cis-trans isomerism disappears upon excitation. When the excited molecule drops back to the S_0 state, either isomer can be formed.

2.3.3 Results and discussion



2.22a R = H
2.22b $R = CH_3$

2.23

2.24a R = H
2.24b $R = CH_3$

Scheme 2.6

The monomers trans-4,4'-dihydroxystilbene **2.24a** and 3,3'-dimethyl-4,4'-dihydroxy-stilbene **2.24b** were synthesized according to the method described by Sieber[23] and Casanova[24] with minor modifications (**Scheme 2.6**). Chloroacetaldehyde diethyl acetal was used instead of chloroacetaldehyde which was used in Sieber's method. The dehydrohalogenation was carried out in one step in a refluxing solution of KOH and ethylene glycol instead of the two steps used in Casanova's method. Only a 40% yield was reported by Sieber while 80% yield was achieved by our modified method. Neither Sieber nor Casanova provided NMR spectra of the 4,4'-dihydroxystilbene.

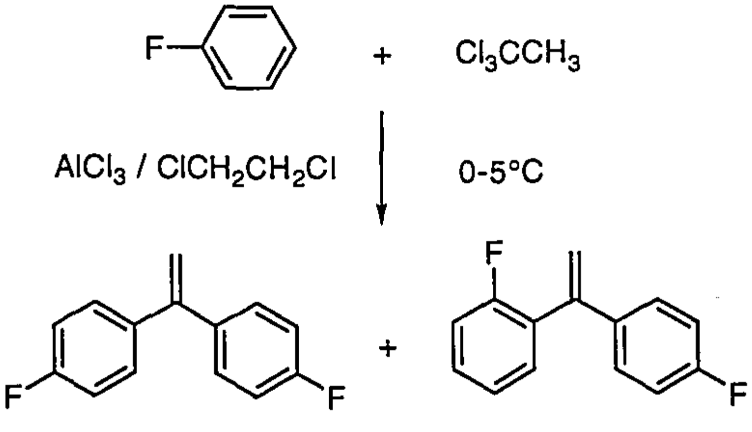
2.4 Diphenylethylene monomers

2.4.1 Ethylene forming reactions

As a class of organic intermediates, 1,1-diarylethylenes are known to undergo many synthetically useful reactions like cycloadditions,[25] dimerization,[26] photooxygenation[27] and polymerization.[28] The traditional methods employed in the preparation of 1,1-diarylethylene mainly rely upon the Grignard reaction[29] and Wittig olefination.[30]

2.4.2 Results and discussion

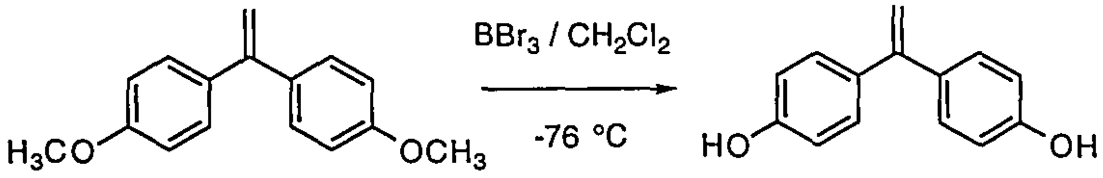
H.R. Sonawane and coworkers [31] described a new method for the synthesis of 1,1-diarylethylenes. 1,1,1-Trichloroethane, under Friedel-Crafts reaction conditions, reacts efficiently with aromatic compounds to afford 1,1-diarylethylenes in good yield. Compared to the traditional methods employed in the preparation of 1,1-diarylethylenes which mainly rely upon the Grignard reaction or Wittig olefination, Sonawane's method is a convenient and efficient method for the preparation of these compounds in excellent yield using a simple, inexpensive alkylating agent, 1,1,1-trichloroethane. In their work 1,1-bis(4-bromophenyl)ethylene and 1,1-bis(4-chlorophenyl)ethylene were synthesized in good yield and no isomers were formed. We attempted to make 1,1-bis(4-fluorophenyl)ethylene by this method. Two isomers, 1,1-bis(4-fluorophenyl)ethylene **2.25** and 1-(2-fluorophenyl)-1-(4-fluorophenyl)ethylene **2.26** (ratio: 7/3) were obtained (**Scheme 2.7**). Isomer formation and the ratio of the two isomers was confirmed by HPLC and NMR.



2.25 **2.26**

Scheme 2.7

1,1-Bis(4-hydroxyphenyl)ethylene **2.28** was synthesized by demethylation of 1,1-bis(4-methoxyphenyl)ethylene **2.27**, which was made by the method reported by Sonawane,[31] with BBr_3(**Scheme 2.8**). The yield in the reaction to 1,1-bis(4-hydroxyphenyl)ethylene **3** can be up to 80%. By HPLC it was found that the content of the monomethoxyl intermediate in the reaction mixture increased with reaction time in the earlier stages of reaction, reached a maximum, and then decreased in the later stages of reaction until it disappeared at the end of the reaction.



2.27 **2.28**

Scheme 2.8

2.5 Experimental

4,4'-Dihydroxychalcone (2.12a). It was synthesized according to the method described in references 3 and 4, mp 203-205°C (203.5 - 204.0°C[3]); ^{1}H NMR (DMSO-d_6) δ6.75-6.95 (two d, 4H), 7.60-7.75 (d, 2H), 7.70 (s, 2H), 7.98-8.06 (d,2H), 10.22 (s, 2H).

3,4'-Dihydroxychalcone (2.12b). It was synthesized according to the method described in references 3 and 4, mp 205-206°C (204 - 206°C[3]); ^{1}H NMR (DMSO-d_6) δ6.82-7.32 (m, 6H), 7.58-7.88 (q, 2H0, 8.10 (d, 2H), 10.00 (s, 2H).

5c and **5d** were bought from Aldrich.

Trans-3,5-bis (4-hydroxyphenyl) 2-pyrazoline (2.13a). To a solution of 30.7 g (128 mmol) of 4,4'-dihydroxychalcone in 300 mL of ethanol 30 mL (618 mmol) of hydrazine monohydrate was added. The resulting solution was refluxed for 1.5 h. Ice water was then added. The precipitate was collected, dried and crystallized from ethanol; yield > 90%; mp 183-185°C; ^{1}H NMR (CD_3OD) δ 2.90–3.45 (octet, 2H), 4.70-4.80 (t, 1H), 6.74-6.83 (two d, 4H), 7.18-7.22 (d, 2H), 7.51-7.56 (d, 2H). MS m/z 254 (M^+, 100), 161 (30), 134 (15), 120 (20). Calcd. for $C_{15}H_{14}N_2O_2$ (254.29): C, 70.85; H, 5.55. Found: C, 70.10; H, 5.75.

The following compounds were prepared using the same method.

Trans-3(4-hydroxyphenyl)-5(3-hydroxyphenyl)-2-pyrazoline (2.13b).

Yield > 90%; mp 234-235°C; ^{1}H NMR (CD_3OD) δ2.71-3.42 (octet, 2H), 4.63-4.75 (t, 1H), 6.62-7.18 (m, 6H), 7.45-7.50 (d,2H). MS m/z 254 (M^+, 100), 161 (66), 134 (14), 120(16). Calcd. for $C_{15}H_{14}N_2O_2$ (254.29): C, 70.85; H, 5.55. Found: C, 69.96; H, 5.59.

Trans-3-phenyl-5(4-hydroxyphenyl)-2-pyrazoline (2.13c). Yield > 90%; mp 139-140°C; ^{1}H NMR (DMSO) δ2.71-3.42 (octet, 2H), 4.66-4.78 (sextet, 1H), 6.69-6.72 (d, 2H), 7.12-7.46 (m, 5H), 7.59-7.62 (d, 2H). MS m/z 238 (M^+, 100), 145 (31), 129 (13), 120 (15). Calcd. for $C_{15}H_{14}N_2O$ (238.29): C, 75.63; H, 5.88. Found: C, 75.60; H, 6.00.

Trans-3(4-hydroxyphenyl)-5-phenyl-2-pyrazoline (2.13d). Yield > 90%; mp 105-109°C; ^{1}H NMR (DMSO) δ2.69-3.44 (octet, 2H), 4.70-4.81 (sextet, 1H), 6.74-6.78 (d, 2H), 7.24-7.38 (m, 5H), 7.43-7.47 (d, 2H); MS m/z 238 (M^+, 100), 161 (53), 134 (10), 129 (4), 120 (6), 119 (9). Calcd. for $C_{15}H_{14}N_2O$ (238.29): C, 75.63; H, 5.88. Found: C, 75.61; H, 6.02.

Trans-1,2-bis (p-hydroxyphenyl)cyclopropane (2.14a).

Method 1 5.08 g (20 mmol) of trans-1,2-bis(4-methoxyphenyl)cyclopropane **(1)** was dissolved in the specific quantity of methylene chloride. The resulting solution was cooled with an acetone-dry ice bath and 60 mL of a 1M solution of BBr_3 in CH_2Cl_2 was added carefully to the stirred solution. When the addition was complete, the acetone-dry ice bath was removed and stirring was continued until the reaction temperature reached room temperature. The reaction mixture was then hydrolyzed with water and the aqueous phase was extracted with ether. The organic layer was separated and extracted with 2N sodium hydroxide. The alkaline extract was neutralized with dilute hydrochloric acid, extracted with ether, and the ether extract was dried over anhydrous magnesium sulfate. On removal of the ether, the product was further purified by recrytallization from acetic acid, mp 190-191°C.

Method 2 1.0 g (3.9 mmol) of trans-3,5-bis(4-hydroxyphenyl)-2-pyrazoline **(2.14a)** was mixed with 1.0 g of powdered sodium hydroxide. The mixture was heated to 250°C under nitrogen and the decomposition proceeded for 30 min. The cooled reaction product was dissolved in water, neutralized with hydrochloric acid and extracted with ether. The ether layer was washed with water to remove the salt. Removal of the ether left the product which was crystallized from acetic acid; mp 190-191°C; ^{1}H NMR (DMSO-d_6) δ1.1.16-1.22 (t, 2H), 1.80-1.98 (t, 2H), 6.60-6.70 (d, 4H), 6.90-6.96 (d, 4H), 9.15 (s, 2H). MS m/z 226 (M$^+$, 100), 131 (15), 121 (45), 107 (20). Calcd. for $C_{15}H_{14}O_2$ (226.27): C, 79.62; H, 6.24. Found: C, 79.40; H, 6.24.

Trans-1-(3-hydroxyphenyl)-2-(4-hydroxyphenyl)cyclopropane (2.14b). mp 123-125°C; ^{1}H NMR (DMSO-d_6) δ1.23-1.30 (t, 2H), 1.94-2.07 (m, 2H), 6.50-7.06 (m, 8H), 9.16 (s, 1H), 9.25 (s, 1H). MS m/z 226 (M$^+$, 100), 131 (31), 120 (16), 107 (27). Calcd. for $C_{15}H_{14}O_2$ (226.27): C, 79.62; H, 6.24. Found: C, 79.08; H, 6.33.

Trans-1-(4-hydroxyphenyl)-2-phenylcyclopropane (2.14c) mp 78-79°C; 1H NMR (acetone-d_6) δ1.31-1.39 (t, 2H), 2.04-2.10 (m , 2H), 6.73-6.78 (d, 2H), 7.00-7.04 (d, 2H), 7.17-7.26 (m, 5H), 8.12 (s, 1H); MS m/z 210 (M$^+$, 100), 107 (20), 115 (30), 131 (17). Calcd. for $C_{15}H_{14}O$ (210.27): C, 85.71; H, 6.66. Found: C, 85.20; H, 6.58.

2-hydroxy-3,4'-dimethoxychalcone 2.19a 2-Hydroxy-3-methoxyphenol **2.17a** (3.00 g, 0.02 mol) and 4-methoxyacetophenone **2.18a** (3.0 g, 0.02 mol) were dissolved in 50 mL of boiling alcohol. To this solution at 55°C was added 13 mL. of 60% potassium hydroxide solution and the resulting solution was allowed to stand at room temperature for one week. The mixture set to a mass of solids; it was worked up by acidification in the cold and recrystallization of the product from alcohol.yield 80-85%. m.p. 100-102°C. ^{1}H NMR (200 MHz,CDCL$_3$) δ3.90 (s, 6H), 6.40 (s, 1H), 6.90 - 8.10 (m, 9H). MS (m/e, relative intensity %): 268 (M$^+$, 100).

The following compounds were prepared using the same method.

2-hydroxy-3-methoxychalcone 2.19b yield 80-85%. m.p. 135-138°C. ^{1}H NMR (200 MHz,CDCL$_3$) δ3.93 (s, 3H), 6.29 (s, 1H), 6.87-8.08 (m,10H). MS (m/e, relative intensity %): 254 (M$^+$, 100).

2-hydroxy-4'-methoxychalcone 2.19c yield 80-85%. m.p. 132-133°C. ^{1}H NMR (500 MHz,DMSO) δ3.81 (s, 3H), 6.62-8.10 (m, 11H), MS (m/e, relative intensity %): 254 (M$^+$, 100).

2-hydroxychalcone 2.19d purchased from Aldrich.

Trans-3(4-methoxyphenyl)-5(2-hydroxy-3-methoxyphenyl)-2-pyrazoline 2.20a To a solution of 30.7 g (128 mmol) of 4,4'-dihydroxychalcone in 300 mL of ethanol 30 mL (618 mmol) of hydrazine monohydrate was added. The resulting solution was refluxed for 1.5 h. Ice water was then added. The precipitate was collected, dried and crystallized from ethanol; yield > 90%; mp 115-117°C; ^{1}H NMR (200Mhz, CDCl$_3$) δ 2.99–3.50 (octet, 2H), 3.84 (s, 3H), 3.89 (s, 3H), 5.00-5.13 (sixtet, 1H), 6.03 (s, 1H), 6.82 (s, 3H), 6.89-7.64 (quatet, 4H). MS (m/e, relative intensity %): 298 (M$^+$, 100). Calcd. for $C_{17}H_{18}N_2O_3$ (298): C, 68.44; H, 6.08; N, 9.39. Found: C, 67.82; H, 5.96.

The following compounds were prepared using the same method.

Trans-3-phenyl-5(2-hydroxy-3-methoxyphenyl)-2-pyrazoline 2.20b

m.p. 118-119°C. ^{1}H NMR (200Mhz, $CDCl_3$) δ 3.10–3.53 (octet, 2H), 3.89 (s, 3H), 5.07-5.18 (triplet, 1H), 6.11 (s, 1H), 6.81-7.70 (m, 8H). MS (m/e, relative intensity %): 268 (M^+, 100). Calcd. for $C_{16}H_{16}N_2O_2$ (268): C, 71.62; H, 6.01; N, 10.44. Found: C, 71.43; H, 5.97; N, 10.22.

Trans-3(4-methoxyphenyl)-5(2-hydroxyphenyl)-2-pyrazoline 2.20c

m.p. 160-162°C. ^{1}H NMR (500Mhz, DMSO) δ 2.66–3.40 (octet, 2H), 3.75 (s, 3H), 4.93-4.97 (triplet, 1H), 6.73-8.03 (m, 9H). MS (m/e, relative intensity %): 268 (M^+, 100). Calcd. for $C_{16}H_{16}N_2O_2$ (268): C, 71.62; H, 6.01; N, 10.44. Found: C, 71.11; H, 6.05; N, 10.23.

Trans-3-phenyl-5(2-hydroxyphenyl)-2-pyrazoline 2.20d m.p. 196-197°C. ^{1}H NMR (500MHz, DMSO) δ 2.72-3.45 (octet, 2H), 5.02-5.06 (triplet, 1H), 6.74-7.63 (m, 9H), 9.64-9.65 (s, 1H). MS (m/e, relative intensity %): 238 (M^+, 100). Cald. for $C_{15}H_{14}N_2O$ (238): C, 75.61; H, 5.92; N, 11.76. Found: C, 75.41; H,6.02; N,11.82.

Trans-1-(4-methoxyphenyl)-2-(2'-hydroxy-3'-methoxyphenyl)cyclopropane 21a

4.8 g (16 mmol) of trans-3,5-bis(4-hydroxyphenyl)-2-pyrazoline **2.20a** was mixed with 1.1 g of powdered potassium hydroxide. The mixture was heated to 250°C under nitrogen and the decomposition proceeded for 30 min. The cooled reaction product was dissolved in water , neutralized with hydrochloric acid and extracted with ether. The ether layer was washed with water to remove the salt . Removal of the ether left the product which was crystallized from acetic acid. yield > 90%. m.p. 63-65°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.34-1.43 (sixtet, 2H), 2.14-2.40 (m, 2H), 3.81 (s, 3H), 3.90 (s, 3H), 6.59-7.15 (m, 7H). MS (m/e, relative intensity %): 270 (M^+, 77), 134 (100), 121 (47). Cald. for $C_{17}H_{18}O_3$ (270): C, 75.56; H, 6.71. Found: C, 75.60; H, 6.82.

The following compounds were prepared using the same method.

Trans-1-phenyl-2-(2'-hydroxy-3'-methoxyphenyl)cyclopropane 2.21b

m.p. 40-42°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ1.39- 1.48 (t, 2H), 2.18-2.48 (m, 2H), 3.90 (s, 3H), 5.75 (s, 1H), 6.60-7.34 (m, 8H). MS (m/e, relative intensity %): 240 (M+, 100). Cald. for $C_{16}H_{16}O_2$ (240): C, 79.97; H, 6.71. Found. C,79.36; H, 6.76.

Trans-1-(4-methoxyphenyl)-2-(2'-hydroxyphenyl)cyclopropane 2.21c

m.p. 55-56°C. ^{1}H NMR (200 MHz, DMSO) δ 1.26-1.43 (t, 2H), 2.10-2.20 (m, 2H), 3.82 (s, 3H), 6.88-7.18 (m, 8H). MS (m/e, relative intensity %): 240 (M+, 100). Cald. for $C_{16}H_{16}O_2$ (240): C, 79.97; H, 6.71. Found. C,79.15; H, 6.73.

Trans-1-phenyl-2-(2'-hydroxyphenyl)cyclopropane 2.21d ^{1}H NMR (200 MHz, $CDCl_3$) 1.28-1.41 (m, 2H), 2.04-2.42 (m, 2H), 4.89 (s, 1H), 6.74-7.27 (m, 9H). MS (m/e, relative intensity %): 210 (M+, 100). Cald. for $C_{15}H_{14}O$ (210): C, 85.68; H, 6.71. Found C, 84.94; H, 6.61.

trans-4,4'-dihydroxystilbene 2.24a To a solution of phenol (11.3 g, 0.12 mol) and chloroacetaldehyde diethyl acetal (9.16 g, 0.06 mol) in 22.5 mL of glacial acetic acid, which was cooled to 0°C (ice bath), there was added a solution of 13 mL of conc. sulfuric acid in 15 mL of glacial acetic acid dropwise with vigorous stirring. After addition, the reaction mixture was stirred for 40 min while maintaining the reaction temperature below 6°C. It was then poured into ice water with stirring and extracted with diethyl ether. The ether solution was washed with water and dried over $MgSO_4$. After removal of ether, the oily residue was heated to reflux in a solution of 22.5 g of KOH and 50 mL of ethylene glycol for one hour, then cooled to 60°C, poured it into ice water and acidified with dilute sulfuric acid. The aqueous mixture was extracted with ether, the ether layer was washed with water and then extracted with 20% KOH solution. The aqueous layer was washed with ether, the solution was acidified with dilute sulfuric acid and extracted with ether again. The organic phase was then washed with water, dried over $MgSO_4$ and evaporated by vacuum distillation. The residue was recrystalized from acetic acid to give white crystals (80% isolated yield), m.p. 293-294°C; MS(m/e, relative intensity%): 212(M^{+};100). ^{1}H-NMR (200 MHz, DMSO); δ9.55 (s, 2H), δ7.35(d, 4H), δ6.89(s, 2H),δ6.72(d,4H).

3,3'-Dimethyl-4,4'-dihydroxy-stilbene 2.24b To the solution of 13.96 g of 2-methylphenol and 9.16 g of chloroacetaldehyde diethyl acetal in 22.5 mL of glacial acetic acid, which was cooled to 0°C by using ice bath, then was added a solution of 13 mL of concentrated sulfuric acid in 15 mL of glacial acetic acid drop by drop with vigorous stirring. After the addition was finished the reaction mixture was stirred for another 40 minutes. The reaction temperature was kept below 6°C. The reaction mixture was poured into ice water while stirring and extracted with ether. The ether solution was washed with water and dried over $MgSO_4$. After removal of ether, the oily residue was added into the refluxing solution of 22.5 g of KOH and 50 ml of ethylene glycol after the ether was evaporated by vacuum distillation. The reaction mixture was kept at reflux for one hour, then cooled to 60°C, and poured into ice water, The solution was acidified with dilute sulfuric acid. The mixture was extracted with ether and the ether phase was washed with water, then extracted with 20% KOH solution and the aqueous phase was washed with ether, then the solution was acidified with dilute sulfuric acid and extracted with ether again, washed with water and dried over $MgSO_4$, the ether was evaporated by vacuum distillation and the product was recrystallized from acetic acid to give white crystals in 80% isolated yield. Melting point is 222-223°C. MS(m/e, relative intensity%): 240(M^{+}·100). ^{1}H-NMR (200 MHz, DMSO); δ9.55 (s, 2H), δ7.00(m, 6H), δ6.80(s, 2H),δ2.15(s,6H).

1,1-bis(4-fluorophenyl)ethylene 2.25 To a cooled solution of fluorobenzene (9.4 mL, 0.1 mol) and $AlCl_3$ (20 g, 0.15 mol) in 1,2-dichloroethane (50 mL), a solution of CH_3CCl_3 (8.0 g, 0.06 mol) in anhyd. 1,2-dichloroethane (10 mL) was added over 10 min with stirring. After 30 minutes the reaction mixture was poured into ice water and extracted with diethyl ether. The ether layer was washed with water and dried over anhydrous magnesium sulfate. On removal of the ether, two isomers (yield, 90% by HPLC): 1,1-bis(4-fluorophenyl)ethylene **1** and 1-(2-fluorophenyl)-1-(4-fluorophenyl)ethylene **2** (ratio: 7/3), which can be separated by column chromatography (SiO_2; hexane), were obtained. A 55% isolated yield of 1,1-bis(4-fluorophenyl)ethylene was achieved, m.p. 46.5-47.0°C (46-47°C[31]). ^{1}H-NMR (200MHz, $CDCl_3$) δ 7.31–7.22 (m, 4H), 7.05-6.97 (m, 4H), 5.40 (s, 2H); MS (EI, m/e, relative intensity %): 216 (M^+, 100).

1,1-bis(4-hydroxyphenyl)ethylene 2.28 1,1-Bis(4-methoxyphenyl)ethylene **3** (4.8g, 20 mmol) was dissolved in methylene chloride (10 mL). The resulting solution was cooled with an acetone-dry ice bath and 60 mL of a solution of 1M BBr_3 in CH_2Cl_2 was added carefully to the stirred solution. When the addition was complete, stirring was continued until the reaction temperature reached room temperature. The reaction mixture was then hydrolyzed with water and the aqueous phase was extracted with ether. The organic layer was separated and extracted with 2N sodium hydroxide solution. The alkaline extract was neutralized with dilute hydrochloric acid, extracted with ether, and the ether extract was dried over anhydrous magnesium sulfate. On removal of the ether, the product was further purified by recrystallization from acetic acid, m.p. 150-152°C. yield 70%. MS (m/e, relative intensity %): 212 (M^+, 100). ^{1}H-

NMR (200 MHz, DMSO); δ9.55 (s, 2H), δ7.15 (d, 4H), δ6.75 (d, 4H), δ5.20(s, 2H).

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Chapter 3

Cyclopropane Containing Polymers

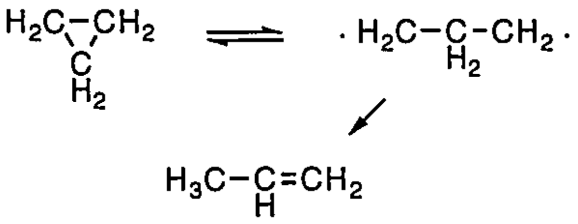
3.1 Introduction

3.1.1 Pyrolysis of small ring hydrocarbons

In the past decade the pyrolyses of small ring hydrocarbons have been very extensively investigated. Probably more work has been reported in this period than in the preceding hundred years. This development has resulted from several distinct causes. First, the discovery of many new synthetic procedures has made numerous strained ring systems relatively easily available. Second, the advent of gas chromatography has allowed the analysis of the reaction products (often of some. complexity) to be carried out with ease and high precision. Third, many of the pyrolyses appear to involve truly unimolecular reactions and have been studied in order to test the well-developed theories of such transformations.

The thermal isomerization of cyclopropane to propylene is perhaps the most important single example of a unimolecular reaction. This system has been studied by numerous workers. Following the work of Trautz and Winkler,[1-2] who showed that the reaction was first order and had an energy of activation of about 63,900 cal mole^{-1} measured in the temperature range 500-650°C, Chambers and Kistiakowsky[1,2] studied the reaction in greater detail and with higher precision from 469-519°C. They found that it was first order. Chambers and Kistiakowsky concluded that the isomerization was unimolecular and suggested two possible reaction paths.[1-2] One involved the rapture of carbon-carbon bond in the cyclopropane ring to yield trimethylene, followed by hydrogen migration to yield propylene. The other path involved hydrogen migration and carbon-carbon bond rupture occurring simultaneously, without the immediate formation of trimethylene.

Much of the recent work on the cyclopropane-propylene isomerization has had one of two objectives, either to try and determine which of the two reaction paths suggested by the early workers is involved, or to test the various theories of unimolecular reactions. Corner and Pease,[1,2] using catalytic hydrogenation to analyze their reaction product, but otherwise working under similar conditions to Chambers and Kistiakowsky, suggested that all the results obtained could be represented just as well by the reaction scheme as by the simple unimolecular path suggested earlier.



Since they found that "inert" gases did not increase the rate of reactions in the region where the rate constant was pressure-dependent, they argued against the reaction being unimolecular. Rabinovitch et al.[1,2] observed that trans- and cis-1,2-dideuteriocyclopropanes undergo a reversible geometrical isomerization at around 400°C. This geometrical isomerization appeared to be unimolecular, and was faster than the structural isomerization to propylene. The cis-trans isomerization of cyclopropanes is not restricted to the deuterium-substituted molecules. cis- and trans-1,2-Dimethylcyclopropane have been shown to undergo reversible geometrical isomerization as well as slower structural isomerization. All the processes are homogeneous and kinetically first order, and almost certainly unimolecular. In both cases geometrical isomerization is faster than the structural isomerization reactions to yield olefins.

A variety of substituted cyclopropanes have been shown to undergo thermal structural and geometrical isomerization.[3] The thermal, reversible cis-trans isomerization of 1,2-diphenylcyclopropane, proceeding without the accompanying structural isomerization noted in previous examples. Kinetic determinations in the liquid state over the temperature range 161°C - 220°C has been done. Pyrolysis of dimethoxyphenylcyclopropane has been studied. We found that cis-trans isomerization of 1,2-bis (anisyl) - cyclopropane proceeds at 350°C in nitrogen. 10% of trans-1,2-bis (anisyl) - cyclopropane was converted into cis isomer after heated at 350°C in nitrogen for 20 min. Only 17% of starting material trans-1,2-bis (anisyl) - cyclopropane left, and many new peaks appeared in the HPLC trace after trans-1,2-bis (anisyl) - cyclopropane was heated for 3 h at 350°C. It was indicated by GPC that most products of thermalysis of trans-1,2-bis (anisyl) - cyclopropane are higher molecular weight oligomers. NMR spectrum and Mass spectrum of the mixture tells that the products was resulted from the ring opening of cyclopropane. Most probably the singlet diradical is also the intermediate.

3.1.2 Cyclopropane containing polymers

A recent paper[4, 5] reported the synthesis of polymers derived from 1,1-bis-hydroxymethylcyclopropane. The polymerization and characterization of elastomeric polyethers containing the cyclopropane group were described. They found that the cyclopropane containing polymers show no exothermic reaction below 200°C and exhibit TGA stability characteristic of aliphatic hydrocarbon polymers with a break point of approximately 220°C under a nitrogen atmosphere.

3.1.3 Strategies and goals

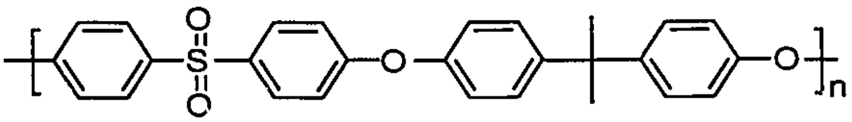
Our effort has been directed toward the synthesis of monomers containing reactive functionality which can be incorporated into high molecular weight linear polymers and copolymers which can then be cross-linked on heating or by photochemical means. The pyrolysis of small ring hydrocarbons has been very extensively investigated. The use of cyclopropane moieties in polymers for cross-linking which is the subject of the present chapter does not appear to have been studied up to now. We synthesized the reactive monomer trans-1,2-bis(4-hydroxyphenyl)cyclopropane **3.1**, (**2.11** in **Scheme 2.4** and **2.5**), designed to lie dormant throughout synthesis and processing but which can then be triggered to a reactive state at a later point. Poly(ether sulfone)s, polyformals and polyesters have been synthesized.

3.2 Results and discussion

3.2.1 Poly(ether sulfone)s containing the 1,2-diphenylcyclopropane moiety

3.2.1.1 Introduction

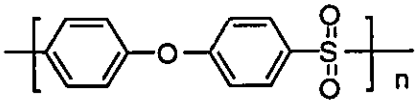
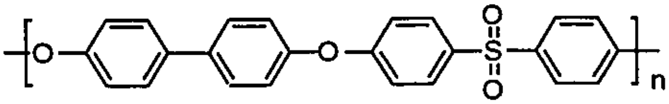
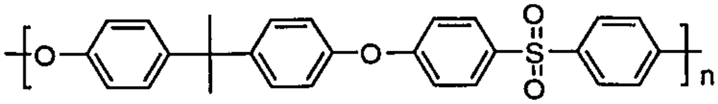
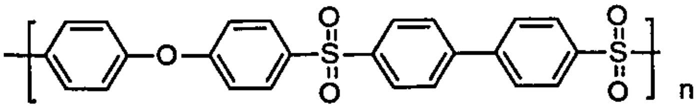
The polymeric sulfone shown below is thermoplastic and has glass-transition temperature ranging from 180°C to 250°C depending on the value of n (50-80). The polymer may be used continuously in the range of -100°C to 175°C.[6] The polymer rapidly degrades in air at temperatures above 460°C to give sulfur dioxide and other products.

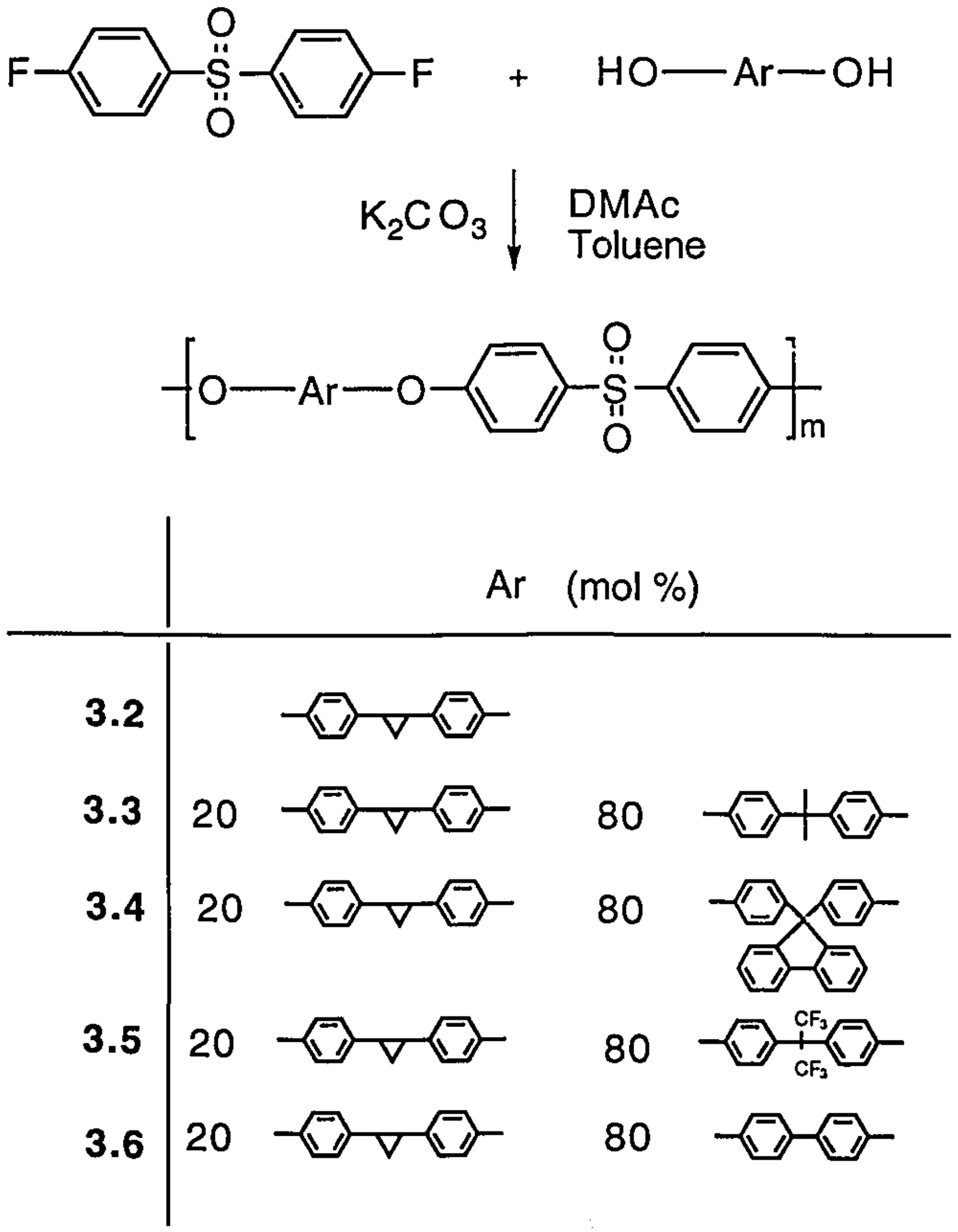


Poly(ether sulfone)s have been studied since the 1960's.[7-8] Two major methods have been developed for the synthesis of poly(ether sulfone)s. One method involves the base mediated nucleophilic displacement of aromatic bisphenols with activated aromatic bishalides. The second major method involves a Friedel-Crafts type polysulfonylation of aromatic substrates with aromatic bis(sulfonyl chlorides). For the first method, dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidinone (NMP) and tetramethylene sulfone have been used as solvent. NMP or tetramethylene sulfone are used if the polymerization needs to be carried out at higher temperature. In the present case polymer hydrolysis and bisphenate insolubility posed a problem in the synthesis when DMSO was used as solvent. The potassium carbonate/DMAc route is an alternate route. In this system, excess potassium carbonate, unlike aqueous caustic, does not prevent the synthesis of high molecular weight macromolecules.

In recent years, research has been directed towards the development of poly(arylether sulfones) that exhibit a high heat deflection or glass transition temperature and retain useful mechanical and physical properties at elevated temperatures and in harsh chemical environments. Current commercial applications for these poly(arylether sulfones) include electronic composites, and other articles that are exposed to thermal or mechanical stress. Some commercial polysulfones and their properties are listed in **Table 3.1.**

Table 3.1 Commercial Polysulfones[9-13]

Trade name/ Producer	Structure	Tg (°C)
Victrex (ICI)		230
Radel (Amoco Co)		232
Udel (Amoco Co)		190
720P (ICI)		250


F
O
S
O
F
+
HO—Ar—OH
K_2CO_3
DMAc
Toluene
O
Ar
O
O
S
O
m
Ar (mol %)
3.2
3.3
20
80
3.4
20
80
3.5
20
80
CF_3
CF_3
3.6
20
80

Scheme 3.1

3.2.1.2 Preparation

Trans-1,2-bis(4-hydroxyphenyl)cyclopropane **3.1** was polymerized with bis(4-fluorophenyl)sulfone to give a poly(ether sulfone) employing standard conditions in DMAc in the presence of excess (20%) anhydrous potassium carbonate. A series of copolymers was also synthesized from trans-1,2-bis(4-hydroxyphenyl)cyclopropane **3.1**, bisphenols and bis(4-fluorophenyl)sulfone (**Scheme 3.1**) under the same conditions. All polymers were characterized by ^{1}H NMR. In the ^{1}H NMR spectrum of polymer **3.2,** two triplets at 2.23 ppm and 1.45 ppm were observed for the benzylic protons and the methylene protons in cyclopropane, a doublet at 7.89 ppm for protons ortho to the sulphone group, a doublet at 7.22 ppm for protons ortho to the cyclopropane group, a multiplet for protons ortho to the ether linkage. It can be concluded from these results that monomer **3.1** is stable under the polymerization conditions.

3.2.1.3 Characterization and properties

The properties of the poly(ether sulfone)s are listed in **Table 3.2**. All the uncured polymers are soluble in chloroform. Flexible and transparent films can be obtained by casting from chloroform solution at room temperature. When films of these polymers are heated they maintain good mechanical properties above 200 °C. Poly(ether sulfone)s with inherent viscosities in the 0.35-0.62 range and with Tgs in the range from 189 to 261°C were prepared. The Tg of poly(ether sulfone) **3.2** is 189 °C which is almost the same as that of the poly(ether sulfone) from Bisphenol A. The molecular weight distribution of the polymers was determined by GPC based on polystyrene standards. GPC results are consistent with their inherent viscosities. Polydispersities of these polymers are less than three suggesting that the polymerization reaction proceeds without any unusual termination reactions that

Table 3.2
Properties of Polysulfones

Polymers	Tg(uncured) °C DSC/tanδ [a]	Tg (cured)[b] °C	η_{inh}[c] dL/g	TGA[d], °C N_2 (-5%)	Mw/Mn[e]
3.2	189/180	ND	0.35	450	40000/20000
3.3	184/148	207	0.41	438	63000/22000
3.4	261/248	293	0.56	449	88000/44000
3.5	183/152	222	0.60	428	96000/45000
3.6	230/216	246	0.62	451	92000/47000

[a] DSC, heating at 10°C/min. TMA, temperatures were recorded where tanδ curve shows a maximum.[b] After curing for 2 hr at 350°C under nitrogen. [c] 5 g/dL in $CHCl_3$ at 25°C.[d] TGA, heating at 10°C/min. ND means that no Tg was detected in DSC. [e] GPC, based on polystyrene standards.

might be ascribed to the cyclopropane moiety. Thermogravimetric analyses of these polymers show no significant weight loss (-5%) occurs before 430°C, which is similar to the poly(ether sulfone) from BPA.

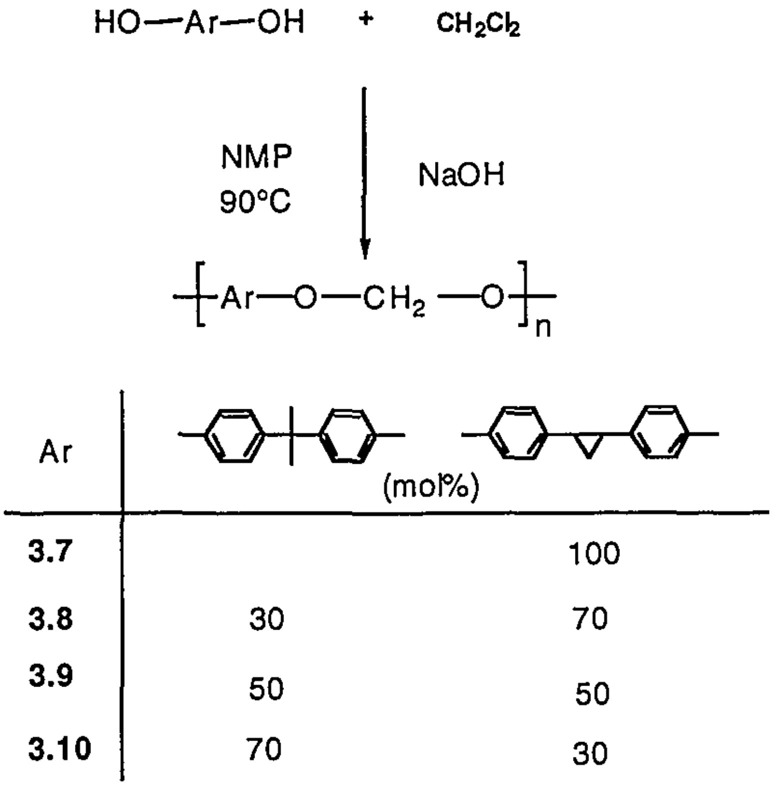
3.2.2 Polyformals containing the trans-1,2-diphenylcyclopropane moiety

3.2.2.1 Introduction

Hay previously developed a very simple method for the synthesis of polyformals by the reaction of bisphenols, such as bisphenol-A (BPA), and methylene chloride or methylene bromide in the presence of a phase transfer catalyst or in an aprotic dipolar solvent.[14] For this method one does not need to control the stoichiometry of the starting monomers as in the usual nucleophilic displacement polymerization reactions because the first intermediate formed in the reaction between the phenoxide anion and methylene chloride is much more reactive than methylene chloride. When a phase-transfer catalyst was used, methylene chloride can be both solvent and reactant. The Tg of the polyformal from BPA is only 96 °C which limits its usefulness.

3.2.2.2 Preparation

Reaction of trans-1,2-bis(4-hydroxyphenyl)cyclopropane **3.1** in a 60:40 NMP / methylene chloride mixture in the presence of NaOH gave a high molecular weight polymer. It was found that there were some cyclics formed if the reaction temperature is maintained below 70 °C. The sodium or potassium salts of BPA are quite insoluble at lower temperatures, therefore, the reaction proceeds as if it were being carried out under high dilution conditions as a result of the slow dissolution of the salt. At 90°C the salts are more soluble and the reaction is rapid and cyclic formation is minimized. 4-tert-Butylphenol is used as end-capping agent to avoid formation of extremely high molecular weight polymer. A series of copolymers from **3.1**, BPA and methylene chloride were prepared under similar conditions **(Scheme 3.2)**.



Ar	(mol%)	
3.7		100
3.8	30	70
3.9	50	50
3.10	70	30

Scheme 3.2

The polymers were characterized by ^{1}H NMR. In the ^{1}H NMR spectrum of polymer **8** two triplets at 2.00 ppm and 1.30 ppm were observed for the benzylic protons and methylene protons in the cyclopropane group, a singlet for the formal protons and a singlet for the aromatic protons.

3.2.2.3 Characterization and properties

Properties of the polyformals are summarized in **Table 3.3**. The polyformal homopolymer **3.7** with inherent viscosity 0.58 dissolves with difficulty in chloroform and is very soluble in DMAc at higher temperatures, while all the copolymers are soluble in chloroform at room temperature. The Tg of the polyformal **3.7** from trans-1,2-bis(4-hydroxyphenyl)cyclopropane **2** is 98.9°C which is slightly higher than that of the polyformal from BPA. Films can be readily cast from chloroform which are all very tough and flexible. Molecular weights of these polymers obtained by GPC relative to polystyrene standards are consistent with their inherent viscosities in chloroform solution. There is no significant weight loss (-5%) by TGA before 430°C in nitrogen which is similar to the homopolyformal from BPA which is very thermally stable both in nitrogen and air.

Table 3.3

Properties of polyformals

polymers	n/m	η_{inh}[a] dL/g	Tg(°C)[b] DSC/tanδ	Tg(°C)[c] (cured)	TGA[d] N_2/Air	Solubility
3.7	0	0.58	98.5/85.0	ND	433/411	DMAc
3.8	3/7	0.40	92.9/76.0	ND	438/416	$CHCl_3$
3.9	1/1	0.45	95.0/75.0	128.0	444/405	$CHCl_3$
3.10	7/3	0.40	95.3/78.0	116.0	433/411	$CHCl_3$

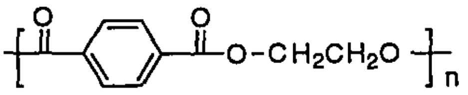
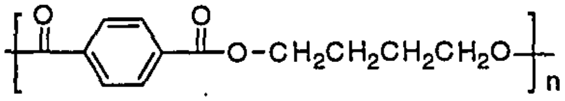
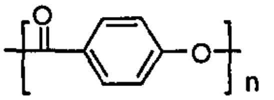
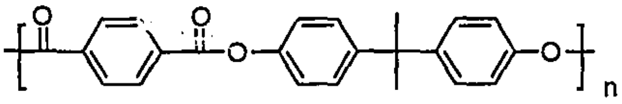
a 0.5 g/dL in $CHCl_3$ at 25°C or in DMAc at 50°C. b DSC heating at 10°C / min. c After curing for 2 h at 350°C under nitrogen. d TGA, heating at 10°C / min.

3.2.3 Polyesters containing the trans-1,2-diphenylcyclopropane moiety

3.2.3.1 Introduction

Polyesters[15-17] are among the more versatile synthetic polymers in that they find wide commercial use as fibers, plastics, and coating. Some commercial polyesters are listed in Table 3.4. Polyarylesters are an emerging class of new class of engineering polymers which show high impact strength, good flexural recovery, good surface hardness and high dimensional stability. They also have good mechanical properties, electrical insulation properties, resistance to degradation to ultraviolet light, and are self-extinguishing.

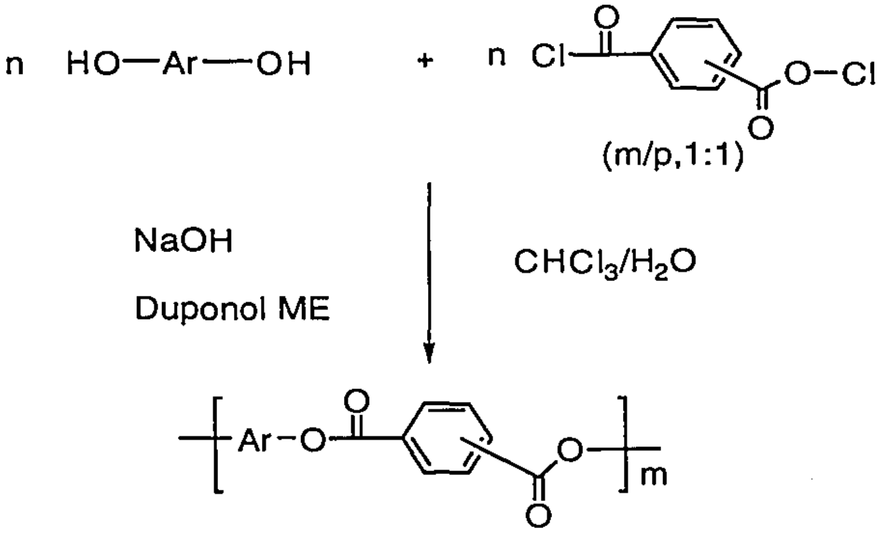
Table 3.4 Commercial Polyesters

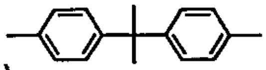
Trade name Producer	Structure	Tg(°C)	Tm(°C)
PET/du Pont, ICI		69	265
Fortrel/ Fiber Industries		80	232
Carborundum			610
ARDEL/Union Carbide		250	350

The usual technique of polyesterification, such as direct reaction of dibasic acid and glycol,[18] ester exchange,[19] and the reaction in the melt between an acid chloride and glycol,[20] are not readily adaptable to the preparation of poly(phenyl ester)s. Several patents[21] issued after 1945 describe acid exchange reactions in which the acetate ester of the bisphenol reacts with a dibasic acid to yield the polyphenyl ester and acetic acid.This reaction yielded only highly colored products. It was discovered that interfacial polycondensation at or near room temperature is an excellent laboratory method for preparing high molecular weight poly(phenyl ester)s of excellent color.[22]

3.2.3.2 Preparation

Interfacial polycondensation was used to synthesize the poly(aryl ester)s. Homopolymer and high molecular weight copolymers were prepared from **3.1**, BPA, isophthaloyl and terephthaloyl chloride by interfacial polycondensation using typical conditions as described in the literature (**Scheme 3.3**).[22]



Ar		
	(mol%)	
3.11	100	
3.12	50	50
3.13	20	20

Scheme 3.3

The properties of the polyesters are listed in **Table 3.5** . The polyester homopolymer precipitates from the reaction mixture during the polymerization and is infusible and insoluble in all organic solvents tried. High molecular weight copolymers **3.12** and **3.13** which are soluble in DMAc at higher temperatures can be readily prepared. Polymers **3.12** and **3.13** are amorphous with a glass transition at 208°C and no melting points are observable in the DSC scans. No significant weight losses (-5%) are observed by TGA for the polyesters before 426 °C in nitrogen.

Table 3.5

Properties of polyesters

polymers	m/n	$\eta_{inh}{}^{a}$ dL/g	Tg(°C)^{b} (uncured)	Tg(°C)^{c} (Cured)	TGA(°C) N_2/Air^{d}	Solubility
3.11	o	-	-	-	435/420	-
3.12	1/1	1.38	208.2	ND	426/421	DMAC
3.13	4/1	1.51	208.0	236	464/430	DMAc

a 0.5 g/dL in DMAC at 50°C. b DSC, heating at 10°C / min. c after curing for 2 h at 350°C under nitrogen. d TGA, heating at 10°C / min.

3.2.4 Cross-linking studies.

3.2.4.1 DSC scans

The DSC scans of homopolymer **3.2**, **3.7** and **3.11** are shown in **Figure 3.1**. For poly(ether sulfone) **3.2** and polyformal **3.7** a Tg was observed while no Tg was found in the DSC scan of polyester **3.11**. Exotherms which are associated with the cross-linking reaction begin at 300°C and reach a maxima at 415°C for all of the polymers. The cross-linking reaction proceeds readily at 350°C. In the DSC scans of the homopolymers, **3.2**, **3.7** and **3.11** no Tg is detected if they are cured at 350°C under nitrogen for longer than 30 minutes .

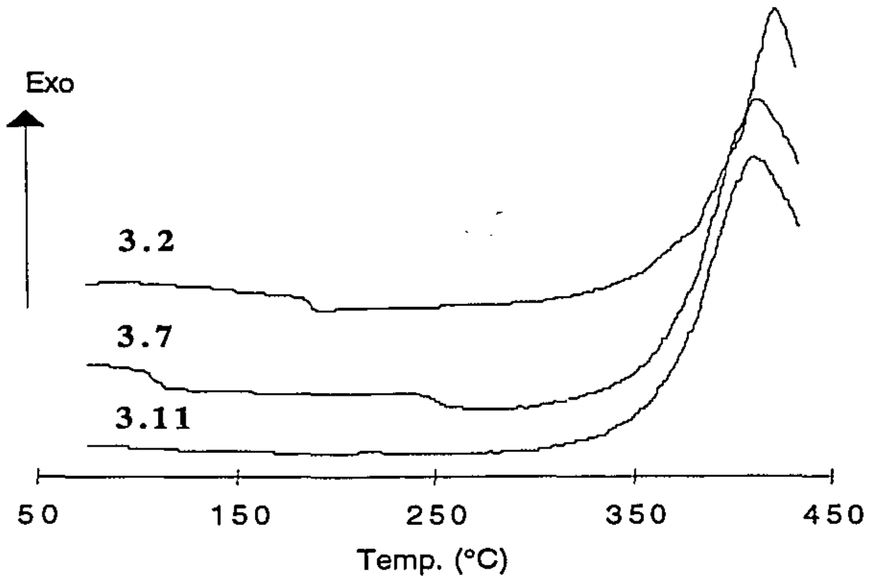


Figure 3.1 DSC thermograms of polymers **3.2, 3.7, 3.11**

3.2.4.2 Effect of curing time on Tg and ΔCp

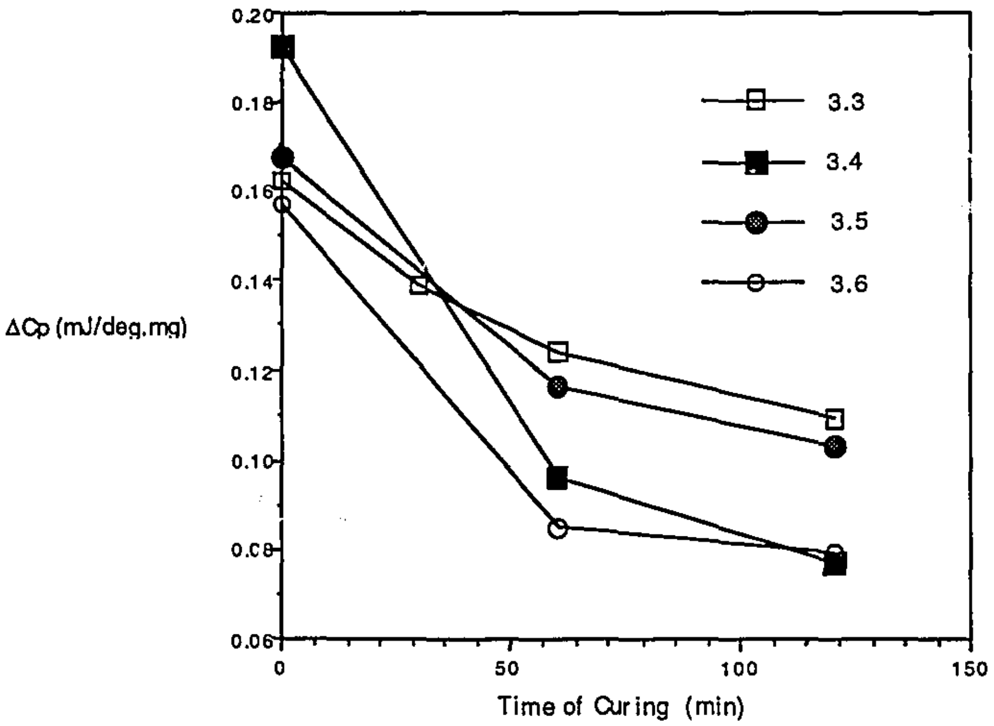


Figure 3.2 Effect of curing time on ΔCp at Tg (at 350°C) under N_2, ΔCp at Tg was obtained in a DSC

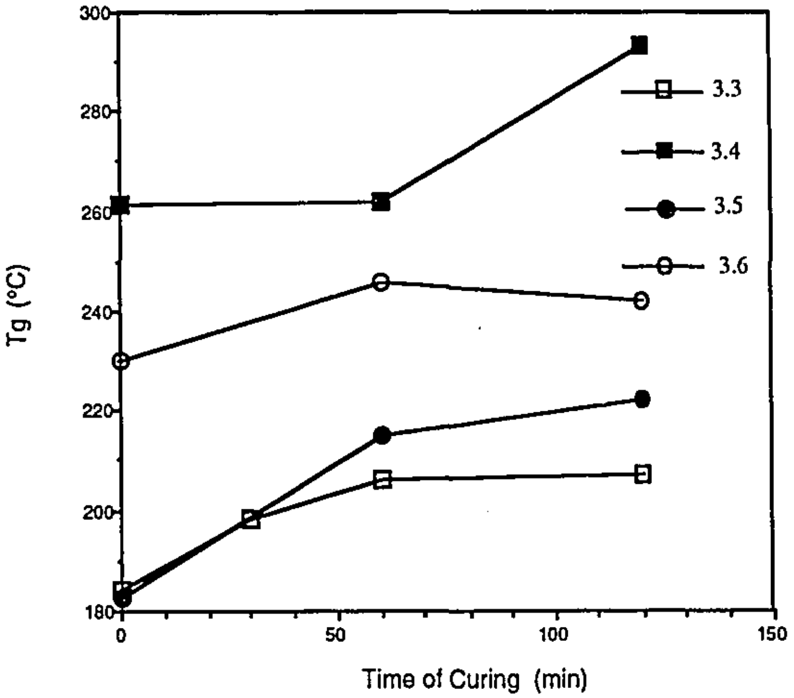


Figure 3.3 Effect of curing time on Tg (at 350°C) under N_2, heating rate 10°C / min.)

Thermal analysis is frequently used to characterize cross-linked polymers. It is well known that the Tg rises while the difference in specific heat capacity (ΔCp) at Tg decreases with increasing numbers of cross-links. The effect of curing time on the difference in specific heat capacity (ΔCp) at Tg (**Figure 3.2**) and on the Tg (**Figure 3.3**) of the poly(ether sulfone) copolymers containing 20 mole per cent of cyclopropane moieties has been studied. After copolymers **3.3, 3.4, 3.5** and **3.6** were cured at 350°C under nitrogen in TGA for different time periods the cured polymers were examined in the DSC to determine the Tg increase and ΔCp decrease. It was found that ΔCp decreased rapidly and Tg increased as curing time increased as a result of the cross-linking of the polymers. Among the copolymers **3.3, 3.4, 3.5** and **3.6**, ΔCp of copolymer **3.4** decreased most and its Tg increased most with increased curing time. After one hour the changes in ΔCp and Tg slowed down significantly.

The effect of curing time on ΔCp and Tg of polyformals and polyesters containing different amounts of cyclopropane groups was also studied, and results were listed in Table 3.6 and 3.7. As expected, for the same curing time the higher the content of cyclopropane group in the polymers, the larger the change in Tg and ΔCp. No Tg is detected by DSC after 2 hours curing at 350°C in nitrogen when the content of cyclopropane group in polyformals is higher than 70 % and that in the polyesters is higher than 50 %.

Table 3.6 Cross-linking of polyformals

polymers	n/m	Curing Time (min)	Tg (°C)	ΔCp mJ/deg.mg
3.7	0	0	98.5	0.205
		30	166.9	0.026
		120	ND	-
3.8	3/7	0	92.9	0.275
		60	138.0	0.015
		120	ND	-
3.9	1/1	0	95.0	0.222
		60	126.0	0.104
		120	128.0	0.061
3.10	7/3	0	95.3	0.334
		60	115.0	0.168
		120	116.0	0.084

Table 3.7 Crosslinking of polyesters

polymers	m/n	Curing time (min)	Tg (°C)	ΔCp mJ/deg.mg
3.12	1/1	0	208.2	0.191
		60	230.o	0.011
		120	ND	ND
3.13	4/1	0	208	0.104
		60	220	0.082
		120	236	0.031

Tg and ΔCp were measured in DSC with heating rate 10°C / min. ND means that no Tg was detected in DSC.

3.2.4.3 Solvent resistance of cross-linked polymers

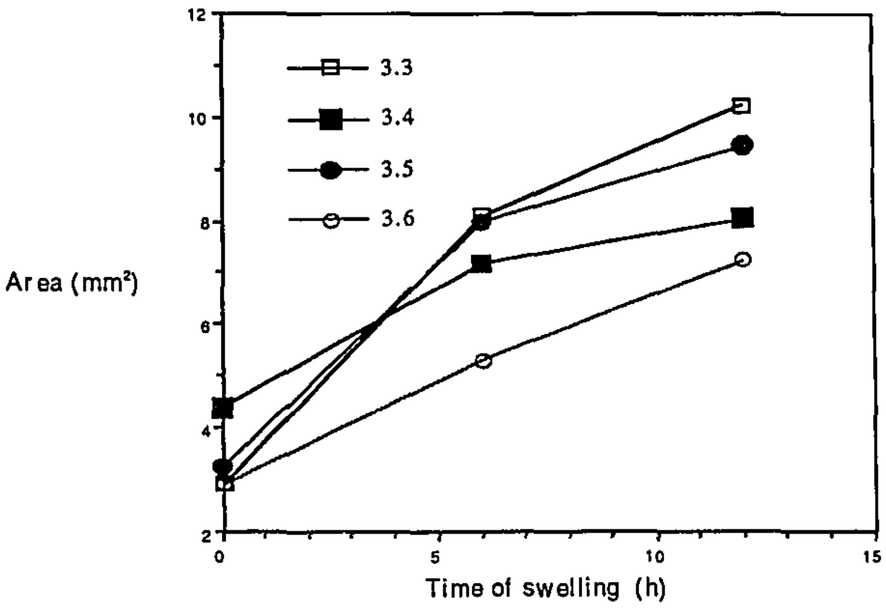


Figure 3.4 Swelling of polymers in chloroform (25°C after curing for 2 h at 340°C under N_2)

The cured polymers were insoluble in chloroform. The polymer films which were cured at 350°C for 2 hours were placed in chloroform at room temperature to test solubility and swelling. Homopolymers **3.2**, **3.7** and **3.11** show no observable swelling over 24 hours in chloroform while all the copolymers swell to a certain degree. The swelling of polymers **3.3**, **3.4**, **3.5** and **3.6** in chloroform is shown in **Figure 3.4.** The area of their films rises with time of swelling. After swelling for 6 hours the area of the polymer films increases by 16-47%. Polymer **5** swells least among them. Swelling studies of polymer **3.8**, **3.9**, **3.10**, **3.12** and **3.13** show that the greater content of diphenylcyclopropane moiety contained in its backbone, the less the polymer swells after cross-linking.

3.2.4.4 CP-MAS ^{13}C-NMR studies.

In an attempt to better understand the cross-linking chemistry of the polymers, CP-MAS ^{13}C-NMR spectra were taken for noncross-linked and cross-linked polymers **3.2**, **3.7** and **3.8**. Typical spectra for noncross-linked and cross-linked polymers **3.2** are presented in **Figure 3.5**.

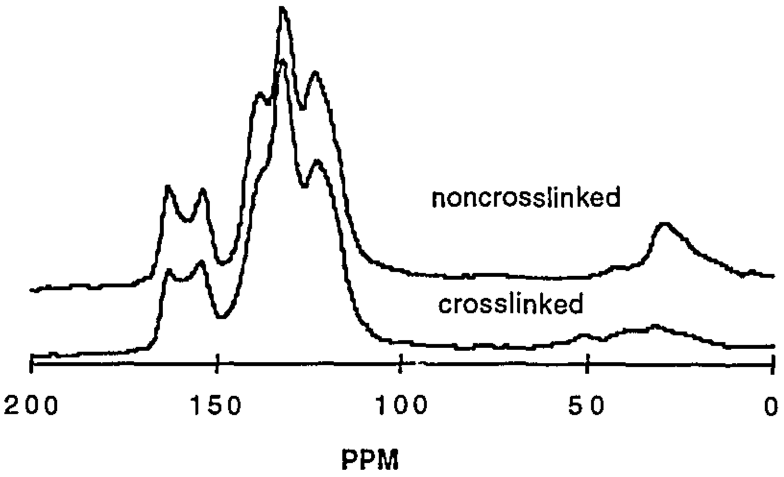


Figure 3.5 CP-MAS ^{13}C-NMR spectra of noncross-linked and cross-linked polymers 3.2. Cross-linking reaction at 350°C for 2 h under N_2.

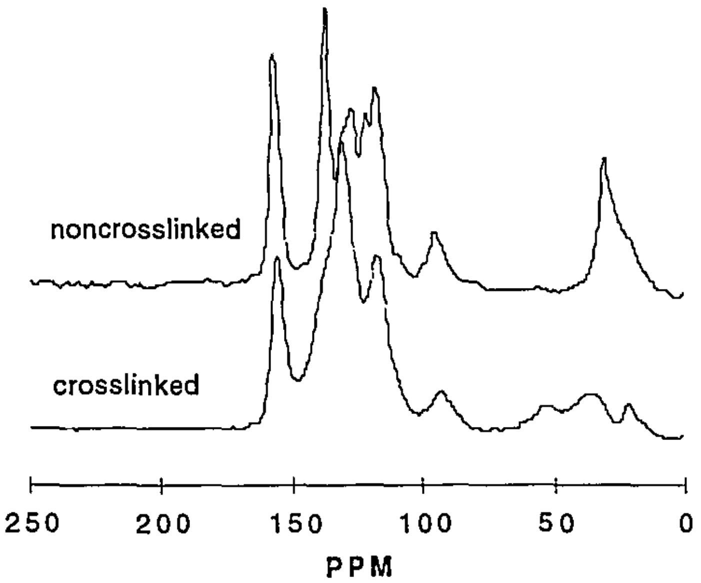


Figure 3.6 CP-MAS ^{13}C-NMR spectra of noncross-linked and cross-linked polymers 3.7. Cross-linking reaction at 350°C for 2 h under N_2.

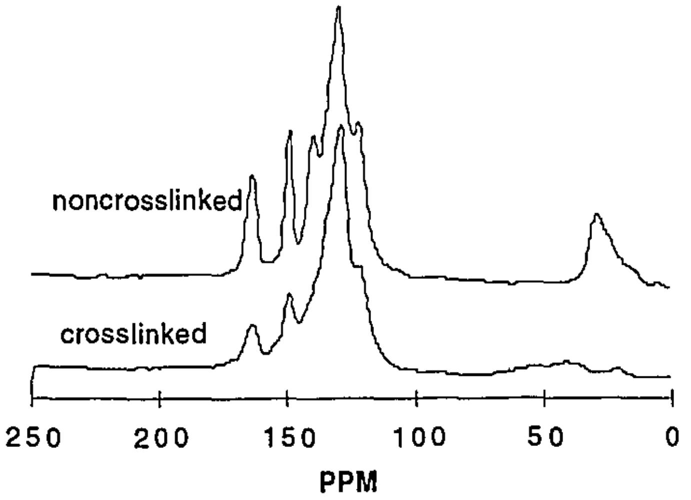


Figure 3.7 CP-MAS ^{13}C-NMR spectra of noncross-linked and cross-linked polymers 3.11. Cross-linking reaction at 350°C for 2 h under N_2.

We also obtained dipolar dephasing magic angle spin (DP-MAS) ^{13}C solid state NMR spectra of noncross-linked and cross-linked polymers **3.2, 3.7** and **3.11** to use as an assignment tool. Typically, after a 60 μsecond delay, most of the methylene and methine carbon signals disappear from the spectrum, only nonprotonated carbons and methyl carbons remain in the DP-MAS ^{13}C solid state NMR spectra since they are weakly coupled to the protons. By a combination of dipolar dephasing and cross polarized-MAS ^{13}C solid NMR the assignments for the solid state NMR spectra of the polymers was possible.

Peaks at 162.69, 152.91 and 136.90 ppm, which were the signals of nonprotonated carbons, were observed in the DP-MAS ^{13}C NMR spectrum of polymer **3.2**. The peak at 162.69 ppm is assigned to the aromatic carbons bonded to the sulfonyl groups, the peak at 152.91 ppm is the signal of the aromatic carbons connected to the oxygen atoms and the peak at 136.90 ppm is due to the aromatic carbons bonded with the cyclopropane group. The other protonated carbon signals overlap together to give peaks at 130.25 ppm, 121.66 ppm and 116.97 ppm. The peak at 28.68 ppm is assigned to the aliphatic cyclopropane carbons.

Assignments for the solid state NMR spectrum of polymer **3.7 (Figure 3.6)** is as follows. The peak at 156.77 ppm and peak at 136.85 ppm are assigned to the aromatic carbons bonded with oxygen atoms and cyclopropane carbons respectively. The peak at 30.19 ppm is for the signals of the aliphatic cyclopropane carbons while the peak at 94.65 ppm is due to the methylene groups in the formal linkage. The other peaks correspond to the other protonated aromatic carbons.

The peak at 163.80 ppm is assigned to the carbonyl carbon in the ester linkage in the solid state NMR spectra of polymer **3.11 (Figure 3,7)**. The peak at 149.35 ppm and peak at 139.00 ppm correspond to aromatic carbons bonded with oxygen and cyclopropane ring, respectively. The peak at 28.63 ppm is due to the cyclopropane aliphatic carbons. The remaining carbon signals overlap to give a peak at 130.59 ppm and a peak at 122.00 ppm.

After cross-linking the signals of the cyclopropane aliphatic carbons peaks at 26.68 ppm for polymer **3.2** disappear and three new aliphatic peaks are generated. The peak at 136.90 ppm for polymer **3.2** corresponds to the aromatic carbons bonded with the cyclopropane ring which are shifted to high field. Similar changes are observed for the polyformals and polyesters. These are believed to be the result of opening of cyclopropane rings in the polymers at 350°C and formation of aliphatic chains.

3.3 Conclusions

High molecular weight poly(ether sulfone)s, polyformals and polyesters prepared from trans-1,2-bis(4-hydroxyphenyl)cyclopropane have been synthesized by solution polycondensation. The polymers can be cross-linked well above their glass transition temperature by treatment in nitrogen at 350°C. The glass transition temperatures increase and the differences in specific heat capacity (ΔCp) at Tg decrease after cross-linking. The resulting cured polymers were insoluble in all solvents. It was confirmed by MAS-^{13}C NMR that the cyclopropane rings were opened on heating. Thermogravimetric analysis shows that no significant weight loss accompanies the cross-linking reaction.

3.4 Experimental Section

Homopolymer 3.2. A mixture of trans-1,2-bis(4-hydroxyphenyl)cyclopropane (**3.1**; 3.0 mmol, 0.6788 g), K_2CO_3 (5.6 mmol, 0.774 g) and bis(4-fluorphenyl)sulphone (3.0 mmol, 0.7628 g) in toluene (4 mL) and N,N'-dimethylacetamide (8 mL, freshly purified) was heated with stirring under nitrogen atmosphere with azeotropic removal of water for 3 h. Some toluene was bled continuously from the Dean-Stark trap until the temperature rose to 155°C. The reaction mixture was lightly colored and was maintained at this temperature for 2 h. At this time the reaction was assumed to be complete. The reaction mixture was cooled to 100°C and diluted with DMAc (5 mL) and filtered. The filtrate was neutralized with acetic acid and coagulated into methanol. The precipitate was filtered and washed with methanolic water and finally with water. It was then boiled in distilled water for 1 h to remove any trapped salts, filtered and dried in a vacuum oven at 80°C; yield > 90%. ^{1}H-NMR (200 MHz, DMSO) δ7.89 (d, 4H); 7.22 (d, 4H); 7.04 (m, 8H); 2.23 (t, 2H), 1.45(t, 2H).

Copolymers 3.3, 3.4, 3.5, 3.6. A mixture of trans-1,2-bis(4-hydroxyphenyl)cyclopropane (**3.1**; 0.6 mmol, 0.1359 g), the other bisphenol (2.4 mmol), K_2CO_3 (0.774 g) and bis(4-fluorophenyl)sulphone (3.0 mmol, 0.7628 g), toluene (4 mL) and DMAc (8 mL, freshly purified) was treated as described for the synthesis of the homopolymer.

Homopolymer 3.7. A mixture of trans-1,2-bis(4-hydroxyphenyl)cyclopropane (**3.1**; 10.0 mmol, 2.26 g), 4-tert-butylphenol (0.15 mmol, 0.0225 g), reagent grade methylene chloride (3.09 mL), and NMP (5 mL) was stirred under nitrogen until a homogeneous solution was obtained. At this point 0.849 g of NaOH pellets was added and the mixture exothermed to 37°C. The mixture was placed in a 90°C oil bath and the solution was refluxed for 2 h, after which the solution was cooled and diluted with NMP. The mixture was allowed to cool to room temperature and the white solid (NaCl) was removed by filtration. The polymer was isolated by a reverse precipitation. This procedure involved the addition of 50:50 (v/v) MeOH:acetone mixture to the polymer solution while stirring. The resulting solid was filtered and dried in a 75°C vacuum oven; yield >90%. ^{1}H-NMR ($CDCl_3$). δ7.00 (s, 8H), 5.65 (s, 2H), 2.00 (t, 2H), 1.30 (t, 2H).

Copolymer 3.8, 3.9, 3.10. The copolymers were made by the procedure as described for the synthesis of the homopolymer using 2,2-bis(4-hydroxyphenyl)propane (BPA) and trans-1,2-bis(4-hydroxyphenyl)cyclopropane.

Polyesters 3.11, 3.12, 3.13. A solution of bisphenol(s) (2.5 mmol) and sodium hydroxide (0.2 g) in water (15 mL) was prepared in a blender. A second solution containing acid chloride(s) (2.5 mmol) in chloroform (7.5 mL) was prepared in a beaker. A solution of Duponol ME (sodium lauryl sulfate, 0.15 g) detergent in water (1.5 mL) was added to the slowly stirred aqueous solution in the blender, and the blender was run at maximum speed. The acid chloride solution was added as rapidly as possible and the emulsion so formed was stirred for five minutes. The reaction mixture was filtered, the polymer was washed well with methanol and dried.

Characterization of Polymers. Glass transition temperatures of the polymers were obtained using a Seiko 220 DSC instrument at a heating rate of 10°C/min in N_2 (50 mL/min) and Seiko 220 TMA instrument at a heating rate of 3°C/min. When recording Tg values samples were never heated above 300°C, to avoid cross-linking, and the values recorded are from the second scan. The Tg was taken from the midpoint of the change in slope of the baseline. The weight loss data were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 10°C/min in nitrogen and air. Polymer samples were cured at 350°C under nitrogen in the TGA instrument. A DSC was then employed to determine the Tg increase. Inherent viscosity data were obtained with a calibrated Ubbelohde viscometer. The measurements were performed in $CHCl_3$ at 25°C or in DMAc at 50°C with a

1B(205) instrument. Molecular weights were obtained by gel permeation chromatography (GPC) relative to polystyrene standards in chloroform solution using a Waters 510 HPLC instrument equipped with μ–Styragel columns (500 Å) arranged in series and a UV detector. ^{1}H-NMR spectra were recorded at 200 MHz using a Varian XL-200 spectrometer in $CDCl_3$ with $(CH_3)_4Si$ as the internal standard.

Solid State NMR. CP-MAS ^{13}C-NMR spectra and DP-MAS ^{13}C-NMR spectra were obtained in zirconium rotors on a Chemagnetics CMX-300 spectrometer at 75 MHz with spinning speeds of 5 KHz. All experiments were performed with a contact time of 1 ms and recycle delays of 1 s. The ^{1}H p/2 pulse width was 4 ms. The number of transients varied from 60,000-80,000. A sensitivity enhancement of 50 Hz was applied to the FID prior to Fourier transformation.

Swelling. Film strips with dimensions of ca. 0.1 x 3 x 10 mm were cured at 320°C in a vacuum oven. The cured film strips were put into chloroform and the change in area of the films measured at specific time intervals.

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Chapter 4
Stilbene containing polymers

4.1 Introduction

4.1.1 Stilbene containing polymers

Reported synthesis of stilbene containing polymer have been mainly based on 4,4'-dihydroxystilbene. 4,4'-Dihydroxystilbene was used to synthesize polyesters by reaction with terephthaloyl chloride in toluene.[1] The polycondensation, in the absence of stirring, gave thin transparent films which could be converted to thick fibers. The polycondensation with stirring gave a product resembling paper pulp. 4,4'-Dihydroxystilbene also has been previously used to synthesize mesogenic polyesters which are liquid crystalline polymers.[2] Griffith synthesized epoxy resins based on epichlorohydrin and 4,4'-dihydroxystilbene. The double bonds in the resin can be cleaved by an oxidizing agent such as ozone.[3]

4.1.2 Preparation of epoxides

Epoxidation of unsaturated polymers is a well studied reaction and has been reviewed[4]. Peracids have been most commonly employed for the epoxidation reaction and the oxirane group has been utilized as a site for grafting or conversion to other functionalities on polymers. Udipi[5-6] epoxidized styrene-butadiene block copolymers with peroxyformic acid generated in situ. The resulting polymers exhibit greatly improved solvent resistance. At conversion above 50% the oxirane ring undergoes significant amounts of ring opening to give formate esters and alcohols. The epoxidation of block copolymers with molecular weights in excess of 60,000 invariably led to gelation. Davies[7] has epoxidised cis-1,4-polyisoprene to produce random copolymers with enhanced resistance to swelling by hydrocarbons while maintaining their high strength. Dreyfuss and Kennedy[8-9] used m-chlorobenzoic acid for the introduction of small amounts of oxirane groups into butyl rubbers and EPDM rubbers as sites for introducing polytetrahydrofuran grafts. Cameron[10-11] studied the epoxidation of polybutadienes with m-chlorobenzoic acid. The resulting polymers, which were epoxidised to low levels, were converted to the chlorohydrins or used directly for the preparation of graft copolymers with polytetrahydrofuran. The reaction of epoxidised 1,4-polyisoprene with 4-anilinoaniline has been used to synthesize a macromolecular antioxidant.[12] Recently, a new method, which utilizes a methyltrioctylammonium tetrakis (diperoxotungsto) phosphate (3-) catalyst in conjunction with hydrogen peroxide, for conversion of a ethylene group into an epoxide ring, was described.[13-15]

4.1.3 Goals and strategy

The objective of this thesis is to synthesize high molecular weight polymers containing reactive groups on the polymer backbone which can be cross-linked by heating to a high temperature (above Tg) or by heating in the presence of a curing agent. The specific goal herein was to synthesize stilbene containing polymers based on 4,4'-dihydroxystilbene **4.1**, and to convert those polymers to their corresponding epoxidized polymers utilizing the method described above.[13-15] The resulting oxirane containing polymers should be readily cross-linkable.

4.2 Results and discussion

4.2.1 Monomer synthesis

The monomer trans-4,4'-dihydroxystilbene **4.1** was synthesized according to the method described by Sieber[17] and Casanova[18] with minor modifications (Chapter 2). Chloroacetaldehyde diethyl acetal was used instead of chloroacetaldehyde which was used in Sieber's method. The dehydrohalogenation was carried out in one step in a refluxing solution of KOH and ethylene glycol instead of the two steps used in Casanova's method. Only a 40% yield was reported by Sieber while 80% yield was achieved by our modified method. Neither Sieber nor Casanova provided NMR spectra of the 4,4'-dihydroxystilbene.

4.2.2 Polymer syntheses

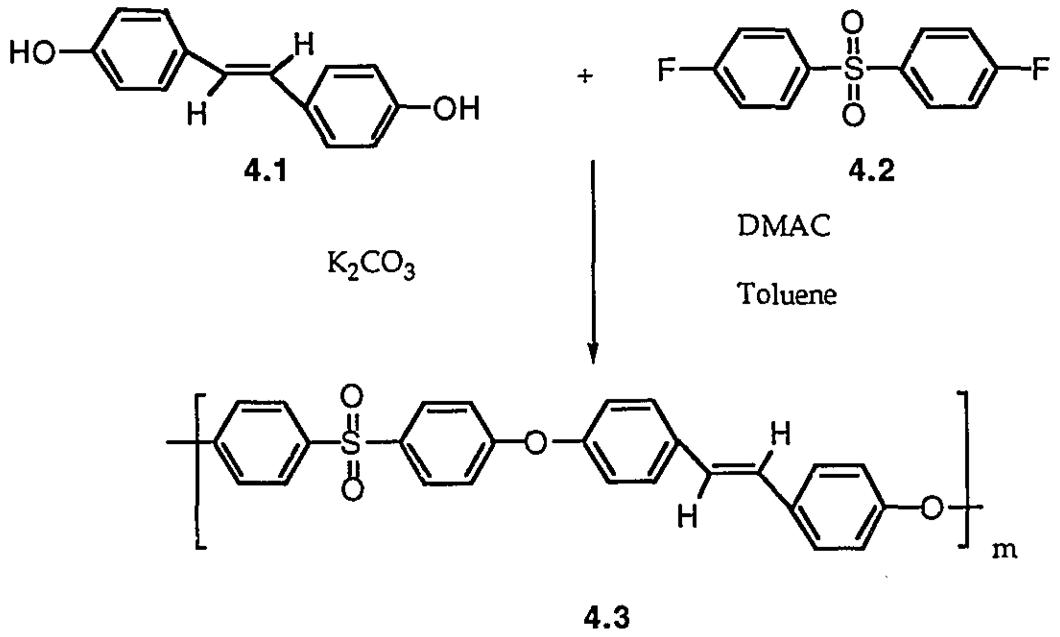
4,4'-Dihydroxystilbene **4.1** was polymerized with 4,4'-difluorodiphenylsulphone **4.2** (**Scheme 4.1**) to give polymer **4.3** employing standard conditions in DMAc as solvent in the presence of excess (20%) anhydrous potassium carbonate.[19] A series of copolymers **4.4, 4.5, 4.6, 4.7, 4.8** also were synthesized from 4,4'-dihydroxystilbene, bisphenols and 4,4'-difluorodiphenylsulphone **4.2** (Scheme 4.2) under the same condition as described above.

4.2.3 Properties of polymers

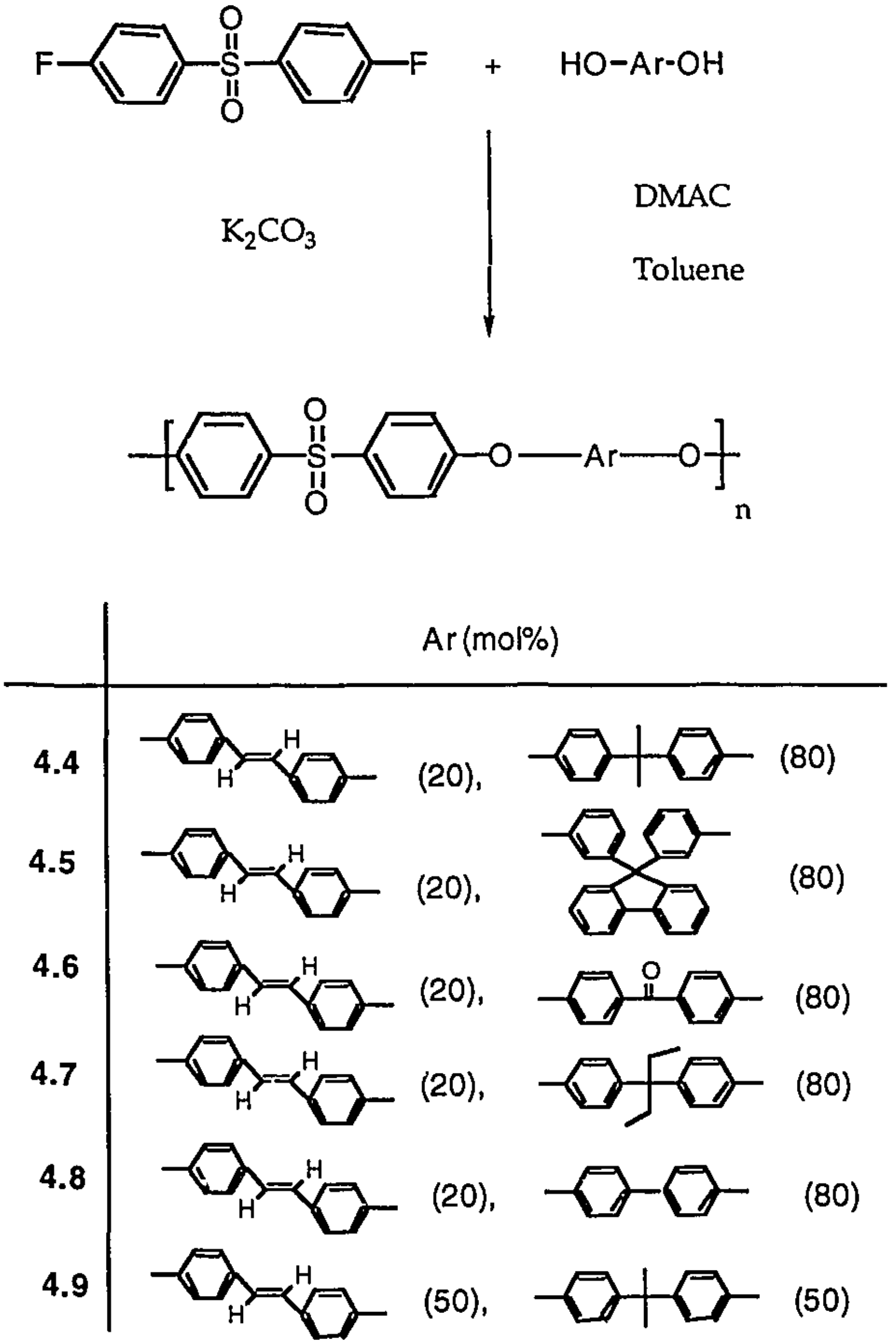
Some important properties of the polymers such as inherent viscosity, glass transition temperature, TGA results and polydispersity are listed in Table 4.1.

4.2.3.1 Homopolymer 4.3

High molecular weight polymer **4.3** is soluble in DMAc and less soluble in chloroform. Thermogravimetric analysis of the polymer shows no significant weight loss (-5%) in nitrogen before 450°C. The film cast from DMAc solution is not transparent and somewhat brittle. The DSC scans of polymer **4.3** are shown in Figure 4.1. Curve **a** is the DSC thermogram of the film of polymer **4.3** cast from DMAc solution at 90°C. Curve **b** is the DSC thermogram of the coagulated polymer **4.3** which was dried for 24 h under vacuum at 70°C. In the curve **a** two peaks are observed, an exotherm at 204°C and an endotherm at 320°C. In the curve **b** only a glass transition temperature at 214°C and an exotherm starting from 320°C are observed. This suggests that during the casting process the polymer **4.3** partially



Scheme 4.1


F
O
S
O
F
+
HO-Ar-OH
K2CO3
DMAC
Toluene
O
S
O
O
Ar
O
n
Ar (mol%)
4.4
H
H
(20),
(80)
4.5
H
H
(20),
(80)
4.6
H
H
(20),
O
(80)
4.7
H
H
(20),
(80)
4.8
H
H
(20),
(80)
4.9
H
H
(50),
(50)

Scheme 4.2.

crystallizes. The peak at 214°C in curve **a** corresponds to the heat of crystallization while the second peak at 320°C corresponds to the heat of fusion. The melting point of polymer **4.3** is 320°C.

Table 4.1 Properties of polymers from 4,4'-dihydroxystilbene

polymer	Tg(°C)[a] uncured	Tg(°C)[b] cured	η_{inh}[c]	TGA(°C)[d] N_2/Air(-5%)	Polydispersity[e]
4.3	214	255	0.41	500/450	5
4.4	180	204	0.53	440/410	4
4.5	266	281	0.36	528/510	5
4.6	204	226		431/412	
4.7	183	198	0.50	460/435	3
4.8	227	243	0.37	463/450	

[a] DSC, Heating at 10°C/min.

[b] After curing in TGA(N_2) for 2h at 350°C(sample **4.3**, **4.5**, **4.6**) or at 300°C (sample **4.4**,**4.7**,**4.8**)

[c] 5 g/dL in $CHCl_3$ at 25°C (Sample **4.3**, **4.5**, **4.7**) or in DMAC at 50°C(Sample **4.4**, **4.8**).

[d] TGA, Heating at 10°C/min.

[e] GPC, based on polystyrene standards.

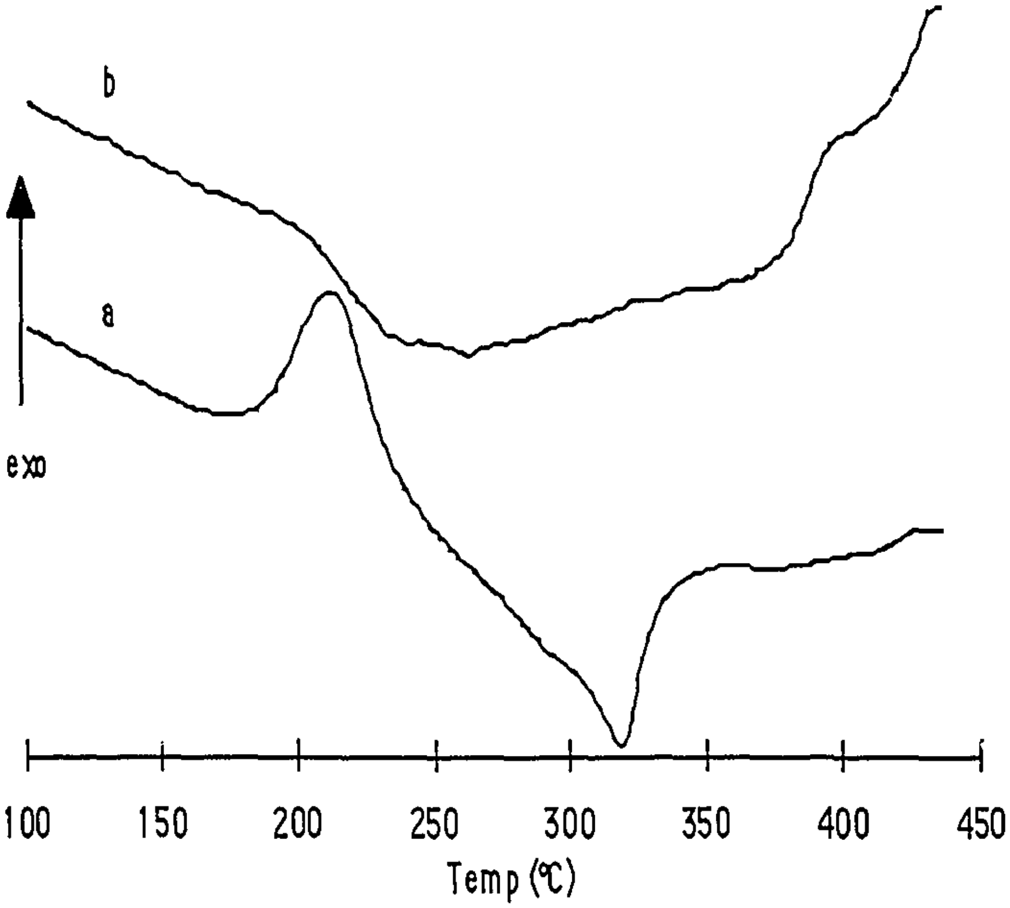


Figure 4.1 DSC thermograms of polymer **4.3**, a: film , b: coagulated, heating rate: 10°C / min.

The X-ray diffraction pattern of the film of polymer **4.3**, which is shown in Figure 4.2, shows a series of sharply defined rings superimposed on a diffuse background, indicating considerable crystallinity in the polymer sample.

4.2.3.2 Copolymers

Copolymers **4.4, 4.5, 4.7** are very soluble in chloroform while copolymer **4.8,** synthesized from 4,4'-biphenol, is not soluble in chloroform and is soluble in DMAc and DMSO. The copolymer **4.6** from 4,4'dihydroxybenzophenone is not soluble in chloroform, DMAc, NMP or DMSO.

The properties of the copolymers, glass transition temperatures, viscosity, thermo-oxidative stability and polydispersity are listed in the Table 4.1. The Tgs range from 180°C to 266°C. The inherent viscosities of all copolymers are above 0.30 dl/g.. All the copolymers are quite thermally and oxidatively stable as indicated by the weight loss measurements in TGA (5% weight loss: in nitrogen at 431-528°C, in air at 410-510°C).

The mechanical properties of copolymers are listed in the Table 4.2. Young's moduli of copolymers range from 1.82 to 2.44 GPa at 25°C, and from 1.06 to 1.52 GPa at 100°C. After cross-linking the Young's moduli of the copolymers at 25°C decreases slightly. The Tgs recorded from tanδ curves are slightly lower than those recorded by DSC.

4.2.4 Cross-linking study of stilbene containing polymers

It was found in the DSC scan of the coagulated polymer **4.3** (Figure 4.1) that the exotherm associated with the cross-linking reaction begins at 320°C.

The effect of curing temperature on the Tg of polymer **4.3** (Figure 4.3) and the effect of curing time on the Tg of polymer **4.3** (Figure 4.4) were examined using TGA and DSC.

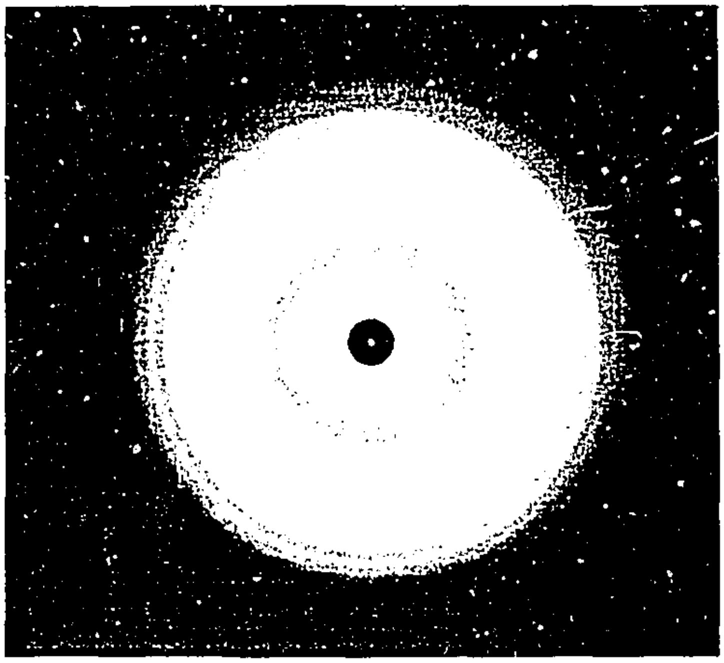


Figure 4.2 X-ray photograph of film of polymer **4.3**

Table 4.2 Mechanical properties of polymers from 4,4'-dihydroxystilbene

Polymers	E' (uncured)[a] 25°C/100°C, GPa	E' (cured)[b] 25°C/100°C, GPa	Tanδ (uncured)[c] (TMA/SS), °C	Tanδ (cured)[d] (TMA/SS), °C
4.2	2.44/1.52	2.13/1.83	161	195
4.3	1.82/1.06	1.56/1.41	263	263/267
4.5	2.22/1.39	2.03/1.76	149/170	193
4.6	1.84/1.28	1.52/1.38	225	238

[a] E' is Young's modulus measured by TMA. [b] After curing for 2 hrs at 300°C under vacuum [c] Temperatures were recorded where the tanδ curve shows a maximum. [d] After curing for 2 hrs at 300°C under vacuum

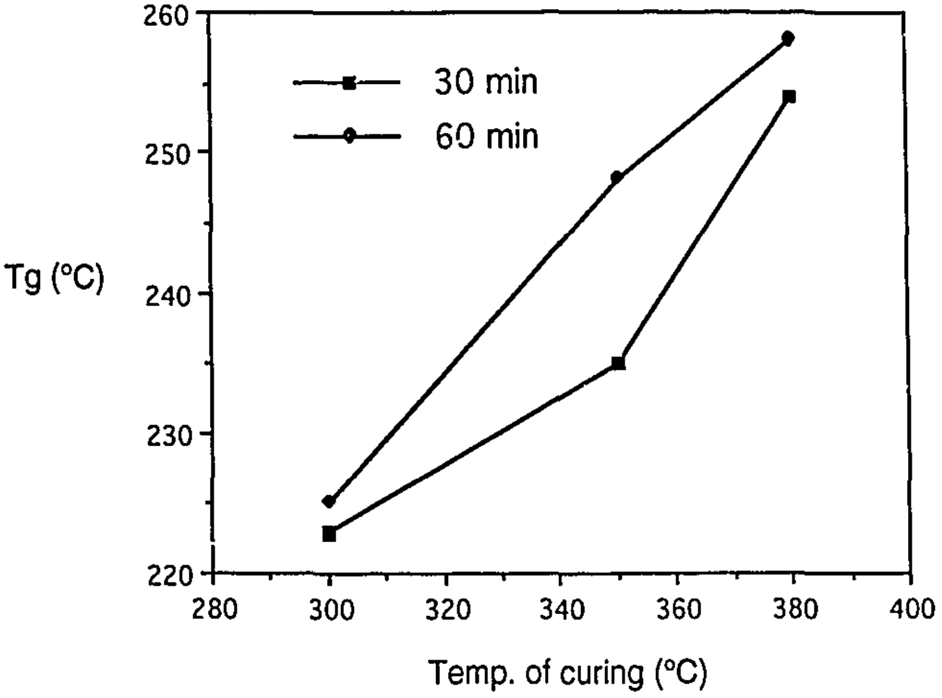


Figure 4.3 Effect of curing temperature on Tg of polymer **4.3**

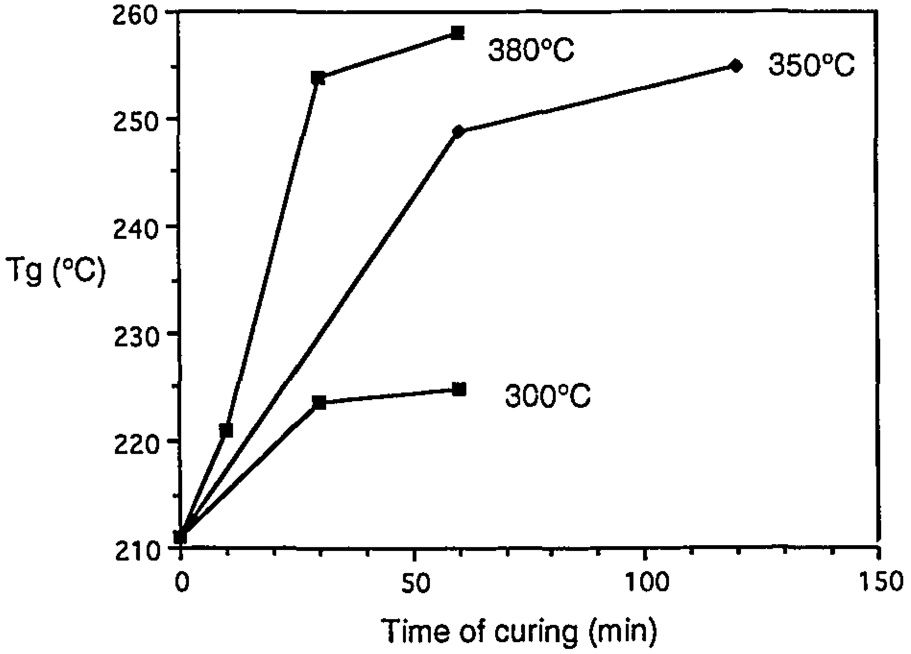


Figure 4.4 Effect of curing time on Tg of polymer **4.3.**

For the same curing time, the higher the curing temperature is, the higher the Tg is after cross-linking under nitrogen atmosphere. However, temperatures higher than 350°C may cause degradation reactions, so a curing temperature below 350°C was chosen. For the same curing temperature, the longer the curing time is, the higher the Tg is after cross-linking. When polymer **4.3** was cured at 350°C for 2 hours, it was found that the Tg is increased by about 50°C. After cross-linking the polymers are insoluble in DMAc, DMSO and NMP.

In order to understand the cross-linking chemistry of the polymer, solid state NMR was utilized. A typical solid state NMR spectra of a noncross-linked and cross-linked polymer **4.3** are presented in Figure 4.5. The dipolar dephasing solid state NMR spectra were obtained for use as an assignment tool. Typically after ca. a 60 µs delay, most of the methylene and methine carbon signals disappear from the spectra. Nonprotonated carbons remain because they are weakly coupled to protons. The peak at 162 ppm is assigned to carbon **c**, the peak at 154 ppm is assigned to carbon **b** and the peak at 135 ppm is assigned to carbon **d** in the double bond. The peaks for carbon **a** and other protonated aromatic carbons overlap together to give peaks at 129 ppm and 122 ppm. From the solid state NMR spectra it was found that the intensity of the peak at 135 ppm, which corresponds to the carbon in the double bond, decreases after curing at 320°C for 2 h.

For the copolymers from 4,4'-dihydroxystilbene **4.1**, bisphenols and bis(4-fluorophenyl)sulfone **4.2**, it was found that the Tgs of copolymers increase (Table 4.1 and 4.2) after curing at 350°C or 300°C under nitrogen or under vacuum due to the cross-linking. After cross-linking the Young's modulus of the copolymers decreases slightly, but the cross-linked films still maintain flexibility. Copolymers become insoluble in chloroform after cross-linking.

4.2.5 Epoxidation

In the presence of methyltrioctyl ammonium tetrakis(diperoxotungsto) phosphate (3-) as the catalyst, homopolymer **4.3** and copolymer **4.7** can be epoxidized with 30% hydrogen peroxide (scheme 4.3). High selectivities to the epoxides based on both hydrogen peroxide and olefinic double bonds are attained after relatively short reaction times and under mild conditions. The results are summarized in Table 4.3 and Table 4.4.

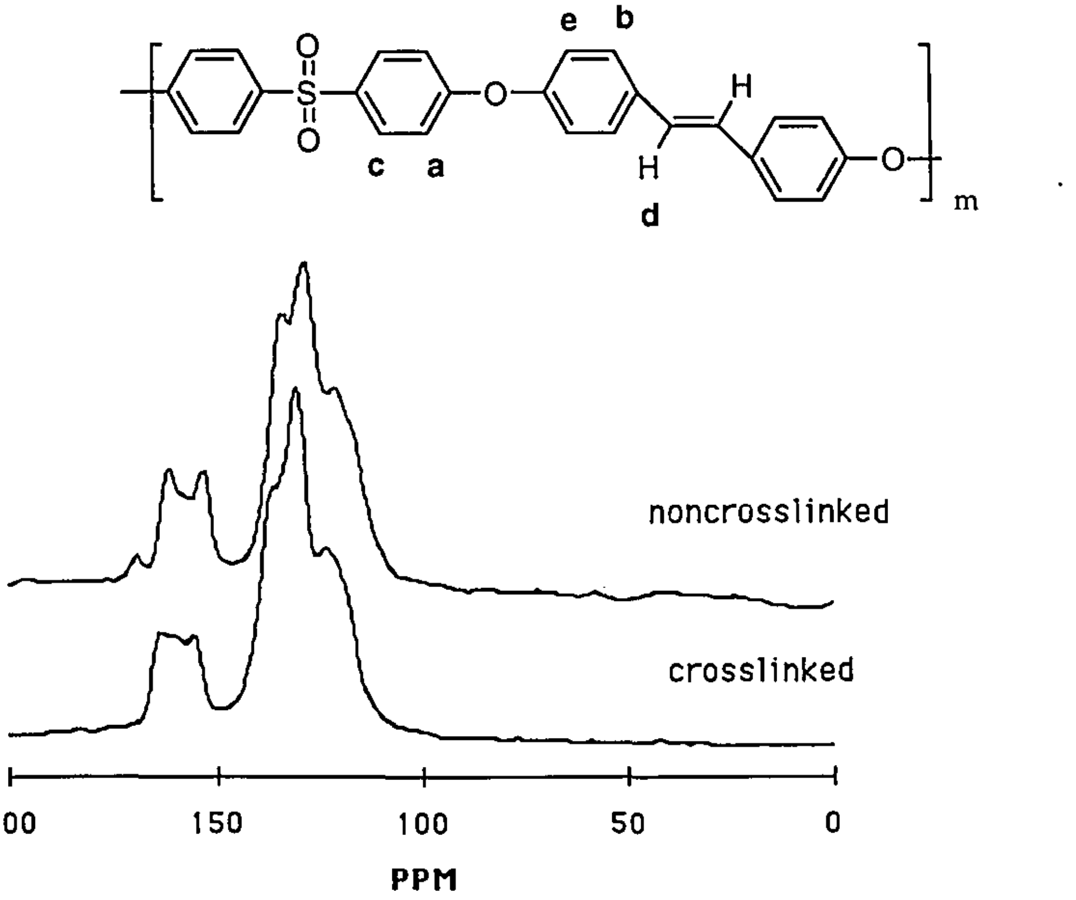
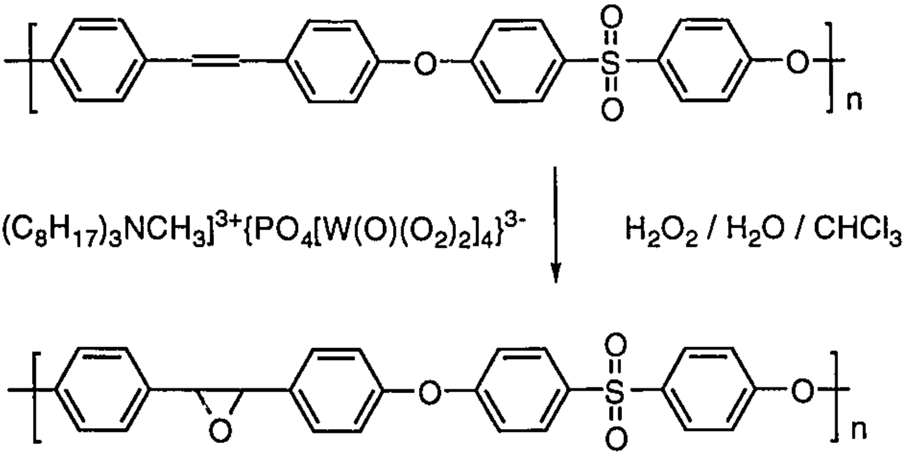


Figure 4.5 CP-MAS ^{13}C-NMR spectra of noncross-linked and cross-linked polymer **4.3**, cross-linking reaction at 320°C for 2 hours in nitrogen.

Typical ^{1}H-NMR spectra of the poly(ether sulfone) **4.3** from 4,4'-dihydroxystilbene **4.1** and partly and completely epoxidized copolymers are shown in Figure 4.6. In the ^{1}H-NMR spectrum of the parent polymer **4.3** there are peaks at δ7.25 ppm derived from the protons of the double bonds of the ethylene moieties in the polymer and another doublet at δ7.45 ppm derived from the aromatic protons adjacent to the double bond in the stilbene moieties. In the ^{1}H-NMR spectra of the epoxidized polymers a new peak at δ4.12 ppm and another new doublet at δ7.65 ppm appear. During the course of the reaction there is a decrease in the intensity of the peaks at δ7.25 ppm and δ7.45 ppm and a corresponding increase in the intensity of the peaks at δ4.12 ppm and δ7.65 ppm. In the ^{1}H-NMR spectrum of completely epoxidized polymer, the peaks at δ7.25 ppm and δ7.45 ppm disappear while peaks at δ4.12 ppm and δ7.65 ppm reach their maximum.

For the epoxidation of homopolymer **4.3** and copolymer **4.9**, excess hydrogen peroxide was employed. As the concentration of catalyst increases, the conversion of double bonds increases and then levels off. The reaction is relatively fast and is complete in 2 hours at 60°C. The solubility of the epoxidized polymers varies with the conversion of the double bonds. When the conversion of double bonds is lower the resultant polymer is soluble in nonpolar solvents such as chloroform. When the conversion of double bonds is higher the solubility of the resultant polymer decreases. Because homopolymer **4.3** and copolymer **4.9** are not soluble in toluene and methylene chloride but are soluble in chloroform, chloroform was used as solvent. The conversion is independent of the volume ratio of organic phase to hydrogen peroxide phase. In conclusion, we demonstrated that the complex methyltrioctylammonium tetrakis (diperoxotungsto) phosphate (3-) used as a catalyst in conjunction with hydrogen peroxide provides an efficient and simple route for the epoxidation of olefinic polymers.



4.10 : completely epoxidized polymer, **4.11**: 55% conversion

Scheme 4.3

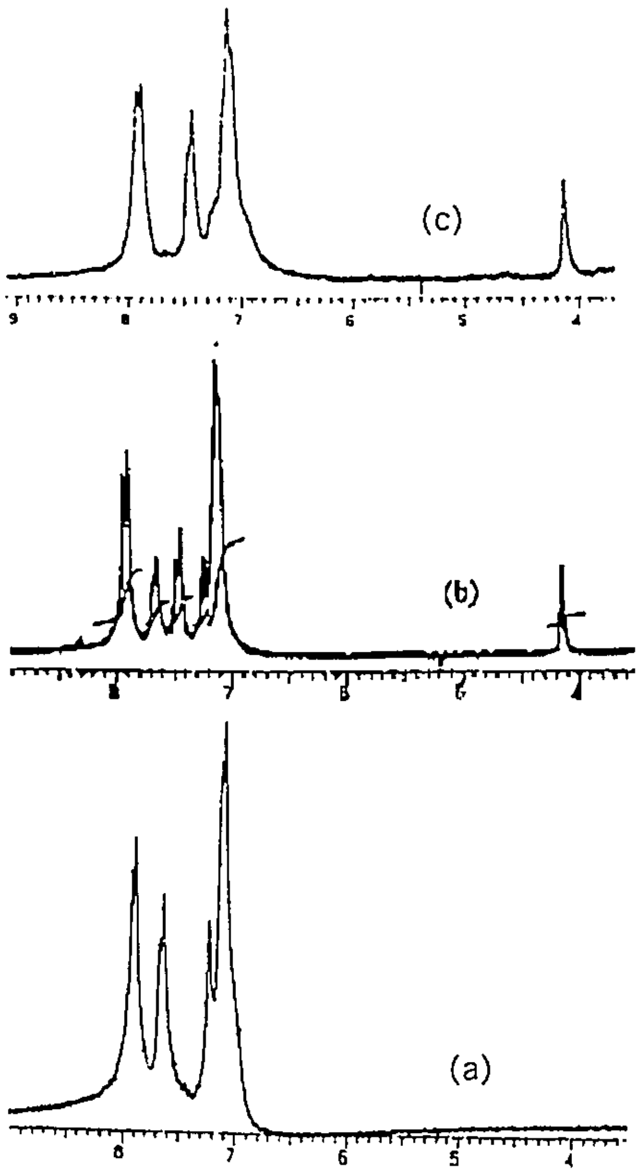


Figure 4.6 ^{1}H NMR spectra of polymer **4.3** (a); and partly epoxidized polymer : (b) 55%, **4.11**, (c) completely epoxidized polymer **4.10**.

Table 4.3 Epoxidation of polymer **4.3** with H_2O_2 catalyzed by methyltrioctyl ammonium tetrakis(diperoxotungsto)phosphate(3-)

H_2O_2(30%) (mL)	Catalyst (g)	$CHCl_3$ (mL)	$CHCl_3/H_2O$ (V/V)	Time (min)	Conversion (%)
10	0.2	10	1/1	120	55
10	0.1	10	1/1	120	45
5	1.8	10	2/2	60	100
5	1.8	10	1/1	120	100
10	1.2	10	1/1	60	100
10	1.2	10	1/1	120	100

* 100 mg polymer was used, reaction temperature was 60°C.

Table 4.4 Epoxidation of copolymer **4.8** with H_2O_2 catalyzed by methyltrioctyl ammonium tetrakis(diperoxotungsto)phosphate(3-)

H_2O_2(30%) (mL)	Catalyst (mg)	$CHCl_3$ (mL)	$CHCl_3/H_2O$ (V/V)	Time (min)	Conversion (%)
60	500	10	1/6	120	40
60	200	10	1/6	120	34
30	500	10	1/3	120	34
30	200	10	1/3	120	32
30	200	5	1/6	120	26
10	100	10	1/1	120	18
10	100	10	1/1	180	19
10	200	10	1/1	120	26

*100 mg polymer was used, reaction temperature was 60°C.

4.2.6 Properties and cross-linking study of epoxidized polymers

The DSC thermogram of the completely epoxidized polymer **4.10** is shown in Figure 4.7. A glass transition at 144°C was observed. An exothermic reaction commenced at 320°C. After curing at 350°C for one half hour under nitrogen, no Tg was observed in the DSC scan and the cured polymer was no longer soluble and did not swell in organic solvents. Thermogravimetric analysis of completely epoxidized polymer **4.10** showed no significant weight loss at 350°C under nitrogen and a 5% weight loss at 390°C. All the results from DSC and TGA suggest that the completely epoxidized polymer **4.10** can be thermally cross-linked more efficiently than the precursor stilbene containing polymers .

The DSC thermograms of partly epoxidized polymer **4.11** (55% conversion) are shown in Figure 4.8. Curve **a** is the first scan that shows a Tg at 205 °C, an exotherm at 275°C and another exotherm with onset at 330°C. Scan **b** is partly epoxidized polymer **4.11** after annealing for 30 min. An endotherm at 294°C was detected, which suggested that the exotherm at 275°C in curve **a** was due to crystallization of the copolymer with a Tm at 294°C. After the copolymer was cured at 350°C under nitrogen for 30 min, the Tg increase to 234°C. No Tg was detected in the DSC after being cured for one hour under nitrogen. The copolymer became insoluble and swelled in organic solvents. Thermogravimetric analysis of partly epoxidized polymer **4.11** showed no significant weight loss at 350°C and a 5% weight loss at 435°C. Compared to the homopolymer **4.3**, the partly epoxidized polymer **4.11** (55% conversion) can be thermally cross-linked more efficiently.

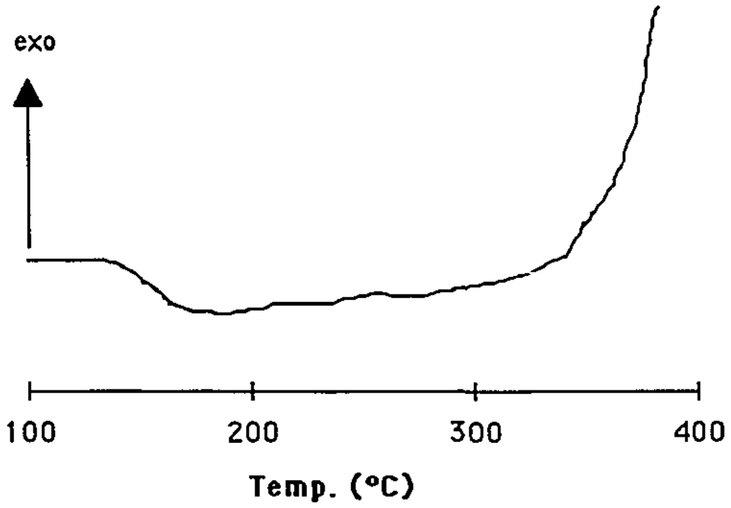


Figure 4.7 DSC thermogram of completely epoxidized polymer **4.10**, heating rate: 10°C / min.

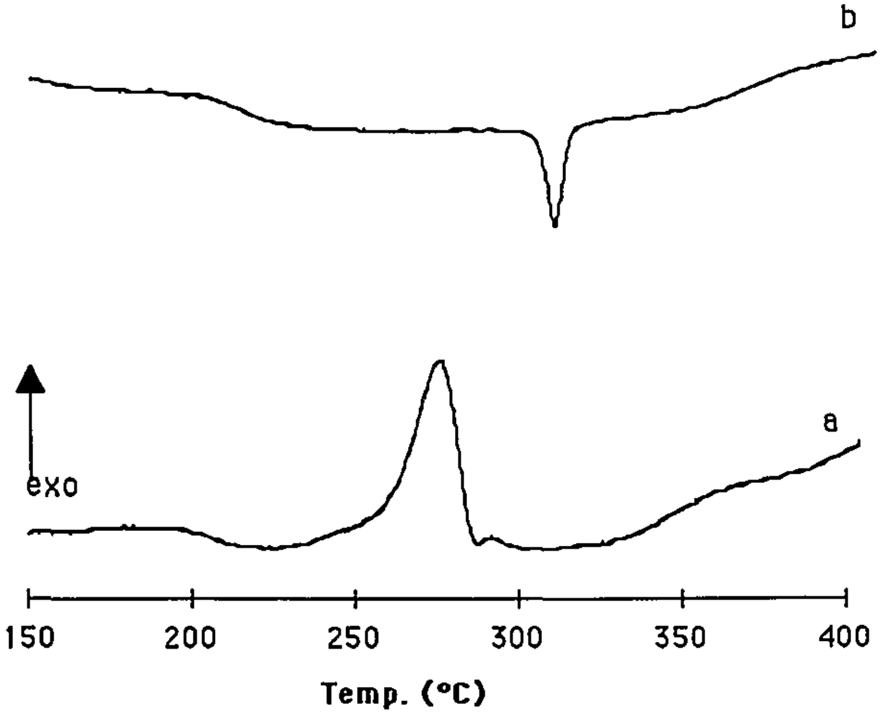


Figure 4.8 DSC thermograms of partly epoxidized polymer (55%) **4.11**, a: first scan, b: after annealing for 30 min at 275°C, heating rate 10°C / min.

4.3 Conclusions

The homopolymer from trans-4,4'-dihydroxystilbene and bis(4-fluorophenyl)sulfone crystallizes easily from solution. The poly(ether sulfone)s containing the diphenylethylene moiety can be cross-linked on heating to 350°C. The films of the cross-linked polymers still maintain flexibility and become insoluble. In the presence of methyltrioctylammonium tetrakis (diperoxotungsto)phosphate (3-) as catalyst, homopolymer **4.3** and copolymer **4.9** can be epoxidized with 30% hydrogen peroxide. The epoxidized polymers are thermally cross-linkable.

4.4 Experimental

Monomer synthesis

Trans-4,4'-dihydroxystilbene 4.1 To a solution of phenol (11.3 g, 0.12 mol) and chloroacetaldehyde diethyl acetal (9.16 g, 0.06 mol) in 22.5 mL of glacial acetic acid, which was cooled to 0°C (ice bath), there was added a solution of 13 mL of conc. sulfuric acid in 15 mL of glacial acetic acid dropwise with vigorous stirring. After addition, the reaction mixture was stirred for 40 min while maintaining the reaction temperature below 6°C. It was then poured into ice water with stirring and extracted with diethyl ether. The ether solution was washed with water and dried over $MgSO_4$. The oily residue was heated to reflux in a solution of 22.5 g of KOH and 50 mL of ethylene glycol for one hour, then cooled to 60°C, poured into ice water and acidified with dilute sulfuric acid. The aqueous mixture was extracted with ether, the ether layer was washed with water and then extracted with 20% KOH solution. The aqueous layer was washed with ether, the solution was acidified with dilute sulfuric acid and extracted with ether again. The organic phase was then washed with water, dried over $MgSO_4$ and evaporated by vacuum distillation. The residue was recrystallized from acetic acid to give white crystals (80% isolated yield), mp 293-294°C; MS(m/e, relative intensity%): 212($M^{+\cdot}$100). ^{1}H-NMR (200 MHz, DMSO); δ9.55 (s, 2H), δ7.35(d, 4H), δ6.89(s, 2H),δ6.72(d,4H).

Polymer synthesis

Homopolymer: A mixture of 4,4'-dihydroxystilbene **4.1** (0.6368 g, 0.003 mol), 0.774 g of K_2CO_3 and bis(4-fluorophenyl)sulphone **4.2** (0.7628 g, 0.003 mol) in 4 mL of toluene and 8 mL of N,N'-dimethylacetamide (freshly purified) was heated with stirring under nitrogen atmosphere with azeotropic removal of water for 3 h. Toluene was bled continuously from the Dean-Stark trap until the reaction temperature rose to about 155°C. The reaction mixture appeared lightly colored and was maintained at this temperature for 2 h. The reaction mixture was cooled to about 100°C and diluted with 5 mL of DMAc and filtered through celite. The filtrate was neutralized with acetic acid and coagulated into methanol. The precipitate was filtered and washed with methanolic water and finally with water. It was then boiled in distilled water for 1 h to remove any trapped salts, filtered and dried in a vacuum oven at 80°C; yield > 90%.

Copolymer: A mixture of 4,4'-dihydroxystilbene (0.1274 g, 0.0006 mol), 0.0024 mol of a bisphenol, 0.774 g of K_2CO_3 and bis(4-fluorophenyl)sulphone (0.7628 g, 0.003 mol) in 4 mL of toluene and 8 mL of N,N'-dimethylacetamide (freshly purified) was treated as described in the synthesis of the homopolymer.

Preparation of the catalyst

$[(C_8H_{17})_3NCH_3]_3^+\{PO_4[W(O)(O_2)_2]_4\}^{3-}$

The catalyst used for the epoxidation in this work was prepared by the method described by Venturello[16] who obtained a syrup whereas in our hands a white crystalline material with melting point 43°C was obtained.

Epoxidation procedure

In a typical epoxidation run, 100 mg of polymer was dissolved in 10 mL of chloroform in a 100 mL three-necked flask equipped with a thermometer, a reflux condenser, and a mechanical stirrer. The polymer solution was heated to, and maintained at, the desired temperature with the aid of a hot-oil bath equipped with a temperature controller. The required weight of the catalyst was introduced, followed by the addition of a measured volume of 30% hydrogen peroxide. The resulting biphasic reaction mixture was vigorously stirred for a predetermined time. After completion of the reaction, the organic layer was separated from the water layer and washed with a large amount of distilled water to remove the residual traces of unreacted H_2O_2. The polymer was precipitated into 250 mL of methanol. The coagulated polymer was then dried at 70°C under vacuum for at least 24 h.

Analysis of the epoxidized products

The ^{1}H-NMR spectra of the epoxidized products were obtained on a VARIAN XL-200 spectrometer with $CDCl_3$ or DMSO as solvent. The conversion of double bonds was calculated from the intensity ratio of the peak at $\delta 7.25$ derived from the protons of double bonds in the ethylene moieties and the peak at $\delta 4.12$ ppm which is attributed to the protons attached to the epoxy groups.

Characterization

Glass transition temperatures (Tg) of the polymers were obtained using a Seiko 220 DSC instrument at a heating rate of 10°C/min in N_2 (50 mL/min). When recording Tg values samples were never heated above 300°C, to prevent cross-linking, and the values recorded are from a second scan. The Tg was taken from the midpoint of the change in slope of the baseline. The weight loss data were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 10°C/min in N_2 and air. The TGA was used to cure polymer sample at 350°C for 2 h. The DSC was then employed to determine the

Tg increase. Inherent viscosity data were obtained with a calibrated Ubbelohde viscometer. The measurements were done in $CHCl_3$ at 25°C with a 1B(205). Mw/Mn was obtained relative to polystyrene standards in chloroform solution using a Waters 510 HPLC equipped with µStyragel columns arranged in series and a UV detector. ^{1}H-NMR was recorded at 200 MHz using a Varian XL-200 spectrometer in $CDCl_3$ with $(CH_3)_4Si$ as the internal standard.

Solid State NMR CP-MAS ^{13}C-NMR spectra were obtained using zirconium rotors on a Chemagnetics CMX-300 spectrometer at 75 MHz with spinning speeds of 5 KHz. All experiments were performed with a contact time of 1 ms and recycle delays of 1 s. The ^{1}H p/2 pulse width was 4 ms. The number of transients varied from 60,000-80,000. A sensitivity enhancement of 50 Hz was applied to the FID prior to Fourier transformation.

X-Ray diffraction spectra Cu radiation was used. Cast polymer films were used.

Mechanical Properties Mechanical properties were measured on cast films. A typical procedure to obtain Young's Modulus at 25°C and to determine how it varies with temperature was performed as follows: a stamp was used to cut out a film strip (length = 5-10 mm, width = 2 mm, thickness = 0.09 mm) which was mounted between two chucks in a Seiko TMA/SS 120 instrument. For Young's modulus at 25°C, the parameters were set as: offset = 20-30 g, amplitude = 5-10 g and cycling frequency = 0.05-0.1 Hz. After these data were collected, the same film was used without changing the parameters to measure Young's modulus variation with temperature by heating to 300°C at a ramp rate of 3°C/min in static air. To obtain an accurate tan delta (δ) value, the film was also heated in the same manner as above, however, the offset and amplitude values were reduced to 2 g and 1 g respectively. This load reduction was necessary to obtain a symmetrical curve at δ. If a higher load was employed (offset =

20-30 g, amplitude = 5-10 g) the film distorted too much when the temperature approached Tg (δ m).

4.5 References

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Chapter 5

Poly(aryl ether)s Containing the 1,1-Diphenylethylene Moiety

5.1 Introduction

5.1.2 Chemistry of ethylene containing polymers

The chemical modification of polymers has taken its place alongside copolymerization and blending as a common means of altering and optimizing the physical and mechanical properties of macromolecules. Chemical reactions on unsaturated polymers are of particular interest because of the technological importance of the parent materials and the reactivity of the available double bonds.[1]

Early work on the photoinduced microstructural changes in various unsaturated hydrocarbon polymers has been reviewed.[2, 3] In polymers with internal double bonds, e.g., 1,4-PBD (polybutadiene) and 1,4-PIP (polyisopropene), the major changes which take place, all with rather low quantum yields, are cis-trans isomerization and loss of 1,4 double bonds, accompanied by formation of cyclopropane groups and the appearance of new external double bonds. In polymers with external double bonds, e.g., 1,2-PBD and 3,4-PIP, the dominant photoinduced process is loss of 1,2 or 3,4 unsaturation, which was believed to involve mainly [2 + 2] cycloaddition of double bonds in a 1,6-diene arrangement.

The thermal rearrangements of unsaturated hydrocarbon polymers under pyrolytic and nonpyrolytic conditions have been reviewed.[4] Three types of thermal cyclization reactions have been delineated: one under pyrolytic conditions, and the other two under nonpyrolytic conditions. Type I cyclization is a radical reaction, following chain rupture which gives rise to six-membered rings. This occurs in the anaerobic pyrolysis of polymers with double bonds in the 1,5- or 1,6-diene configuration. Type II cyclization is a [2+2] thermal cycloaddition of double bonds in certain polymers with a 1,6-diene configuration which yields bicycloheptane structures, presumably by a biradical process. This cyclization was invoked for 1,2-PBD and 3,4-PIP to account for their pronounced loss of unsaturation when heated anaerobically under nonpyrolytic conditions. Type III cyclization, the first unambiguous example of the type III process in a polymer, was a thermal anaerobic cyclization, under nonpyrolytic conditions, of TPD. Type III reaction is the macromolecular counterpart of the thermal cyclization of trans-1,6-octadiene to 1-methyl-2-vinylcyclopentane which was shown to involve an intramolecular ene process[5].

A wide variety of catalytic, photochemical methods for the cis-trans isomerization of unsaturated hydrocarbon polymers have been known for some time[6,7,8]. Several examples of thermal uncatalyzed cis-trans isomerization of such polymers have also been investigated.[5] Cis-trans isomerization of an unsaturated macromolecule, 1,4-polybutadiene, was first achieved in 1957 when Golub[9] reported that a high cis-1,4-PBD was converted to a high-trans structure by means of UV irradiation in dilute benzene solution in the presence of a suitable sensitizer, such as elemental bromine or an organic bromine, sulfide, disulfide, or mercaptan. The mechanism depicted for the photo- or radiation-sensitized cis-trans isomerization of 1,4-PBD involves a free-radical chain reaction proceeding through a freely rotating radical adduct formed from the double bond, and the bromine atom or thiyl radical generated in the photolysis or radiolysis of the sensitizer. On release of the attached radical the double bonds are reestablished, but with the thermodynamically more stable trans configuration predominating. In the course of work on the pyrolytic changes in 1,4-PBD, it was found to undergo thermal uncatalyzed cis-trans isomerization even under nonpyrolytic conditions. The results implied that the mechanism for isomerization of 1,4-PBD was more complex than just thermal excitation of the individual double bonds.

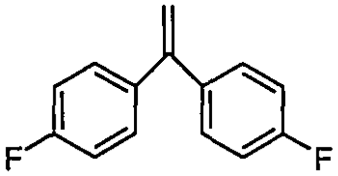
Not only chemical functionalization or structural modification, but also cross-linking, grafting, oxidation and degradation can be achieved if a polymer contains ethylene groups. The olefin functionality is a useful target for various purposes because of its varied reactivity. Besides the cyclization and cis-trans isomerization discussed above, unsaturated polymers can undergo many other reactions such as hydrogenation, halogenation, hydrohalogenation, epoxidation, ene and other cycloaddition reactions, sulfonation, carboxylation, phosphonylation, carbene addition, metalation, silylation etc..

5.1.2. Oligomers containing ethylene end groups

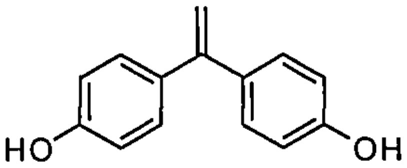
Substituted ethylenes is the reactive end groups in oligomers such as bismaleimide, allyl or ethylene end-capped oligomers[10-20] which can be thermally chain extended to produce a highly cross-linked polymer matrix. The oligomers with reactive end groups exhibit good solubility and wetting, and have lower melt and softening temperature allowing for facile processing. The cured materials generally have very good solvent and moisture resistance. In addition, the initial mechanical properties at elevated temperature are superior to those of noncross-linked long chain polymers due to the high degree of cross-linking. However, the cured materials have lower toughness than the thermoplastics, and the long term thermo-oxidative stability is also lower than that of the high molecular weight linear polymers, due to the unstable linkages which are formed during cross-linking reactions.

5.1.3 Goals and strategies

Our aim was to synthesize high molecular weight, thermally stable and processable polymers containing reactive groups in the polymer backbone which can be cross-linked by heating above the Tg. This chapter reports the syntheses and cross-linking of poly(aryl ether)s containing the 1,1-diphenylethylene moiety. Two monomers, 1,1-bis(4-fluorophenyl)ethylene **5.1** and 1,1-bis(4-hydroxyphenyl)ethylene **5.2** were synthesized (Chapter 2) to prepare ethylene containing polymers by condensation polymerization reactions.



5.1

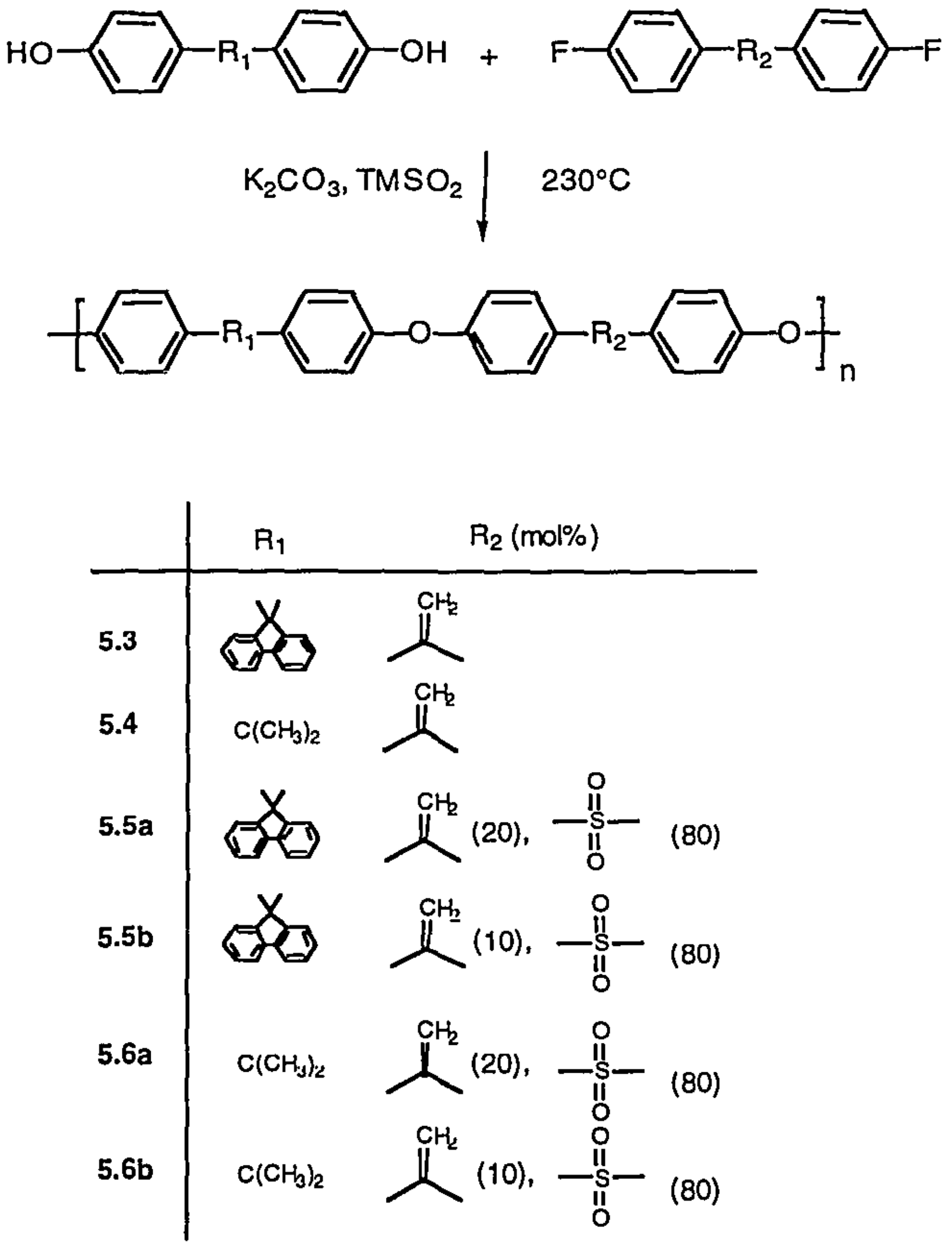


5.2

5.2 Results and discussion

5.2.1 Polymer synthesis

1,1-bis(4-fluorophenyl)ethylene **5.1** has low reactivity as a monomer in a nucleophilic displacement polymerization reaction, compared to bis(4-fluorophenyl)acetylene from which high molecular weight polymers can be made by reaction with bisphenols.[21] Utilizing the method reported by Andrews,[22] oligomers **5.3** and **5.4** were synthesized by the base mediated polycondensation reaction between 1,1-bis(4-fluorophenyl)ethylene and bisphenols in tetramethylene sulfone solvent. Novel copolymers **5.5a**, **5.5b**, **5.6a** and **5.6b** from 1,1-bis(4-fluorophenyl)ethylene **5.1**, bis(4-chlorophenyl)sulfone and bisphenols were


HO
R1
OH
+
F
R2
F
K2CO3, TMSO2
230°C
O
n
R1
R2 (mol%)
5.3
CH2
5.4
C(CH3)2
CH2
5.5a
CH2
(20),
O
S
O
(80)
5.5b
CH2
(10),
(80)
5.6a
C(CH3)2
CH2
(20),
(80)
5.6b
C(CH3)2
CH2
(10),
(80)

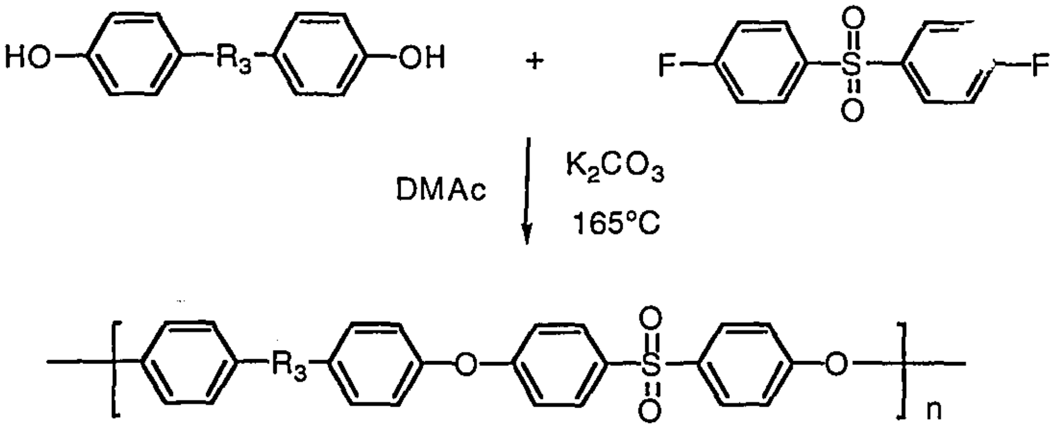
Scheme 5.1

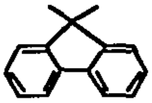
synthesized using sulfolane as solvent. The molar ratio of 1,1-bis(4-fluorophenyl)ethylene **5.1** and bis(4-chlorophenyl)sulfone in the copolymers synthesized was 1/9 and 2/8 (**Scheme 5.1**). It was found that a reaction temperature of at least 235 ℃ and 40% solids concentration was required in order to obtain high molecular weight copolymer because of the low reactivity of 1,1-bis(4-fluorophenyl)ethylene. Copolymers were made by the reaction of phenoxide end-capped oligomers, which were formed from the reaction of excess bisphenols and 1,1-bis(4-fuorophenyl)ethylene, followed by the addition of bis(4-chlorophenyl)sulfone to the reaction mixture after 6 hours reaction of excess bisphenol with 1,1-bis(4-fluorophenyl)ethylene **5.1**.

Because of the low reactivity of 1,1-bis(4-fluorophenyl)ethylene **5.1**, we were not able to obtain high molecular weight homopolymer by nucleophilic displacement polymerization. Therefore, we synthesized 1,1-bis(4-hydroxyphenyl)ethylene **5.2** and this bisphenol was used to make random copolymers of any composition by co-reacting with other commercially available bisphenols. Homopolymer **5.7** and four copolymers **5.8**, **5.9**, **5.10** and **5.11** were synthesized using DMAc as solvent under standard conditions from 1,1-bis(4-hydroxyphenyl)ethylene, bis(4-fluorophenyl)sulfone and bisphenols (**Scheme 5.2**).

5.2.2 Properties of polymers

The properties of the polymers from 1-bis(4-fluorophenyl)ethylene **5.1** are listed in Table 5.1. All oligomers and copolymers are soluble in chloroform. The molecular weight distribution of the polymers was determined by gel permeation chromatography (GPC) based on polystyrene standards. The inherent viscosities were also measured and are consistent with their GPC results. Copolymers with inherent viscosities in the 0.35-0.50 dl/g range and with Tg's in the



	R_3 (mol%)			
5.7				
5.8		(20),	$C(CH_3)_2$	(80)
5.9		(20),	$C(CF_3)_2$	(80)
5.10		(20),		(80)
5.11		(20),	—	(80)

Scheme 5.2

range from 170 to 230°C were prepared. The inherent viscosities of homopolymers **5.3** and **5.4** are only 0.21 and 0.25 dl/g. The glass transition temperature decreases slightly when 1,1-bis(4-fluorophenyl)ethylene **5.1** was incorporated into the polysulfone backbone. Thermogravimetric analyses of these copolymers show that no significant weight loss (-10%) occurs below 420°C.

The general properties of polymers from 1,1-bis(4-hydroxyphenyl)ethylene **5.2** are summarized in **Table 5.2.** Polymers with inherent viscosities in the 0.35-0.62 dl/g range and with Tgs in the range from 167 to 258°C were prepared. All polymers are high molecular weight, thermally very stable and soluble in chloroform solution. Flexible and transparent films can be cast from chloroform solution at room temperature. The Tg's of the poly(aryl ether sulfone) from 1,1-bis(4-hydroxyphenyl)ethylene **5.2** and bis(4-fluorophenyl)sulfone is lower than that of the poly(aryl ether sulfone) from BPA and bis(4-chlorophenyl)sulfone.

5.2.3 Curing of oligomers and polymers

Polymers containing the diphenylethylene moiety are cured through the ethylene functionality by heating at 320°C. A catalyst was not required for this cross-linking reaction. No volatile byproducts evolved during the curing reaction. This behavior is crucial for the preparation of "void free" polymer structures, since volatiles may cause voids which decrease the strength of the molded component. When the oligomer **5.3** was heated from 30°C to 300°C in the DSC under nitrogen a Tg was observable at 202°C. When it was reheated from 30°C to 300°C after cooling down its Tg increased to 207°C. In a third scan the sample was heated from 30°C to 350°C and a Tg was observable at 207°C, followed by an exotherm at 330°C. After cooling down if it was heated from 30°C to 300°C the Tg increased by 10°C. A complete DSC scan of oligomer **5.3** is shown in **Figure 5.1**. In addition to a Tg at 207°C and an exotherm at 330°C, another exotherm starting at 345 °C was observed.

It was found that Tg's of the cured polymers are dependent on the curing time. Tg increased as the curing time was increased (**Figure 5.2**). For the oligomers **5.3** and **5.4** after heating at 320°C for 30 min, their Tg's were not observable in the DSC,. The Tg's of the copolymers **5.5a** and **5.6a,** after heating at 320°C for 30 min, were shown no further increase with increased curing time.

All polymers from 1,1-bis(4-fluorophenyl)ethylene became insoluble in chloroform after cross-linking. The cross-linked oligomers **5.3** and **5.4** did not swell at all in chloroform over 24 hours while other cross-linked polymers **5.5a, 5.5b, 5.6a** and **5.6b** swelled in chloroform.

In the DSC scan of homopolymer **5.7** (shown in **Figure 5.3**), an apparent Tg at 167°C and an exotherm starting at 300°C and reaching maximum at 446°C were observed. The Tg of polymer **5.7** increased to 195°C and it became insoluble and swelled very slowly in chloroform after being cured at 320°C in nitrogen for 2 hours. The Tg's of all copolymers from 1,1-bis(4-hydroxyphenyl)ethylene increased by more than 13° after being cured at 320°C in nitrogen for 2 hours and the cured copolymers swelled more than cured homopolymer **5.7**.

5.3 Conclusions

Poly(aryl ether)s containing the 1,1'-diphenylethylene moiety, synthesized from 1,1-bis(4-fluorophenyl)ethylene **5.1** or 1,1-bis(4-hydroxyphenyl)ethylene **5.2** are thermally cross-linkable. Characterization and cross-linking studies of these polymers were carried out by GPC, DSC, TGA and NMR. The solvent resistance and Tg's of the resulting cross-linked networks increase after cross-linking. Thermogravimetric analysis shows that no significant mass loss accompanies the cross-linking reaction.

Table 5.1. Properties of Polymers from 1,1-Bis(4-fluorophenyl)ethylene

polymer	Tg (°C)[a] uncured	Tg (°C)[b] cured	η_{inh} dl / g	[c]TGA (°C) N_2/Air (-10%)	[d]Mw/Mn (x10^{-4}) [f]
5	202	ND[e]	0.25	420 /405	4.3/0.8
6	80	ND	0.21	380 /350	4.2/0.6
7a	214	270	0.50	500 /480	9.2/2.9
7b	230	254	0.43	510 /500	8.8/3.8
8a	170	230	0.41	450 /420	8.5/2.1
8b	180	240	0.35	480 /470	8.1/1.9

[a] DSC. heating at 10°C / min.
[b] after being cured at 320°C for 2 h.
[c] 0.5 g/ dl in chloroform at 25°C.
[d] TGA. heating at 10°C / min.
[e] ND means that no Tg was detected.
[f] GPC, based on polystyrene standards

Table 5.2 Properties of polymers from 1,1'-bis(4-hydroxyphenyl)ethylene

polymer	Tg (°C) [a] uncured	Tg (°C) [b] cured	η_{inh} [c] dl / g	TGA (°C) [d] N_2/Air (-10%)	Mw/Mn [e] ($x10^4$)
9	167	195	0.35	488	4.2/1.
10	174	193	0.46	508	7.1/2.
11	175	188	0.38	507	6.6/2.
12	258	285	0.41	502	6.7/2.
13	203	238	0.62	520	9.1/4.

[a] DSC. heating at 10°C / min.
[b] after being cured at 320°C for 2 hs.
[c] 0.5 g/ dl in chloroform at 25°C.
[d] TGA. heating at 10°C / min.
[e] GPC, based on polystyrene standards.

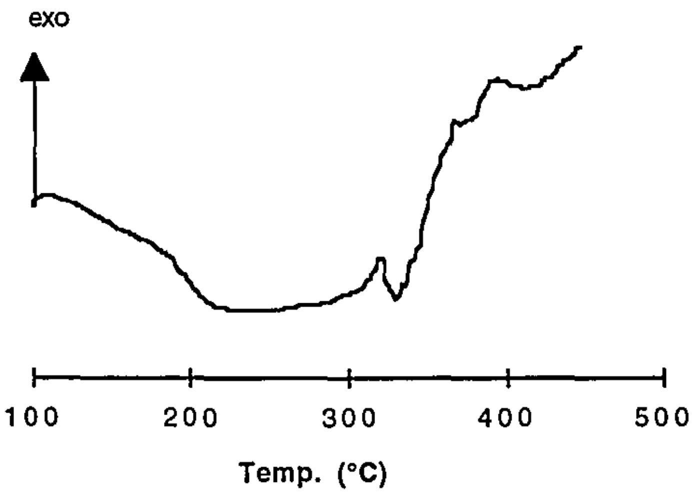


Figure 5.1. DSC thermogram of oligomer **5.3**, heating rate : 10°C / min.

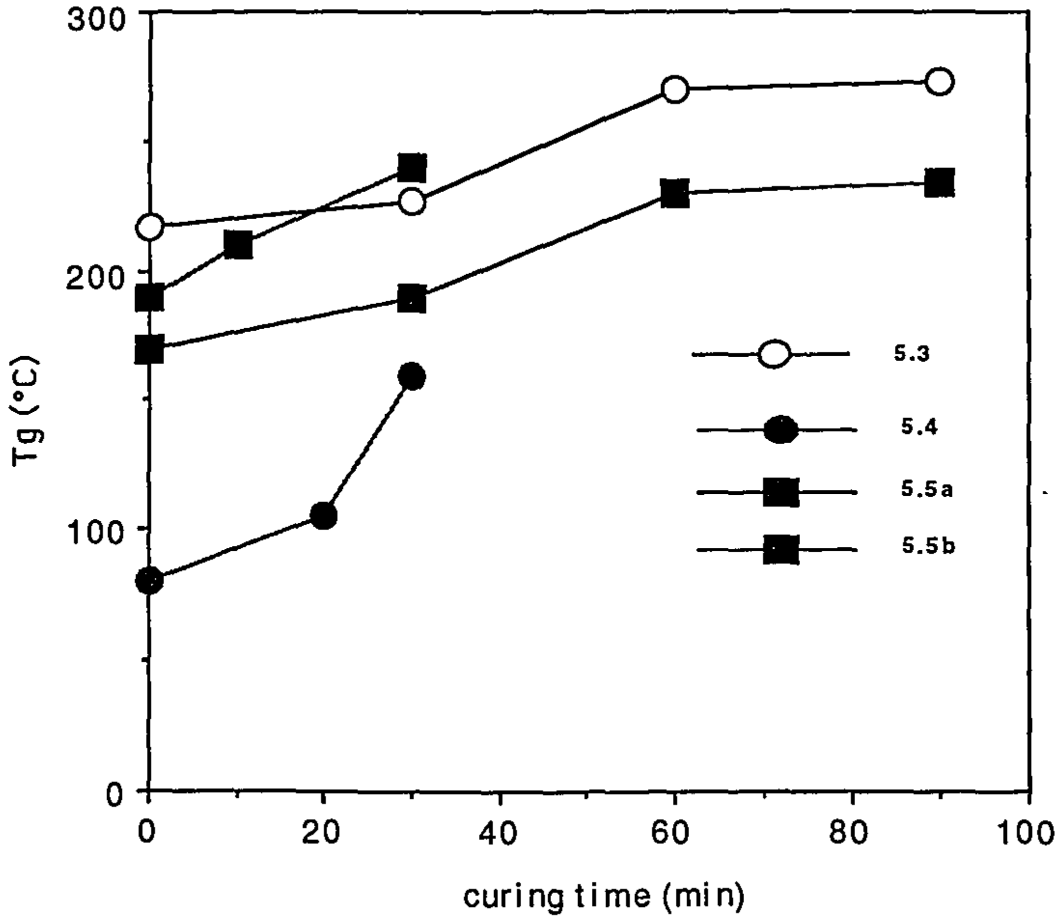


Figure 5.2. Effect of curing time on Tg's of polymers, curing is at 320°C in nitrogen.

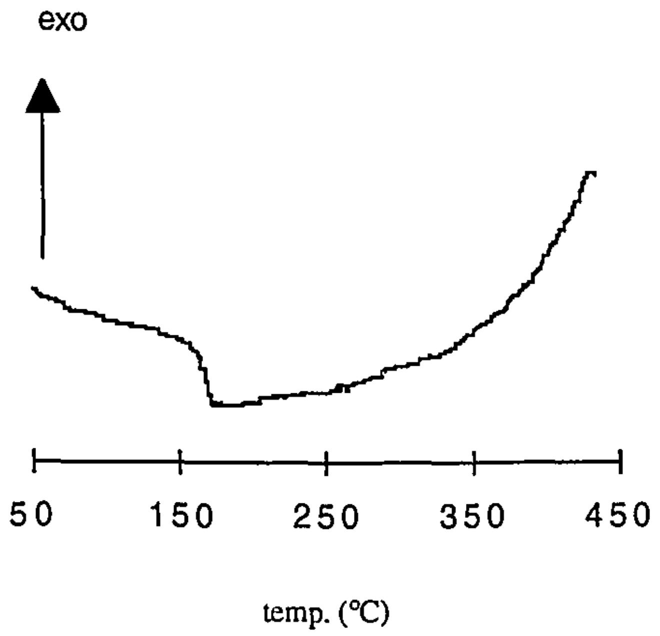


Figure 5.3. DSC thermograms of polymer **5.7**, heating rate : 10°C / min.

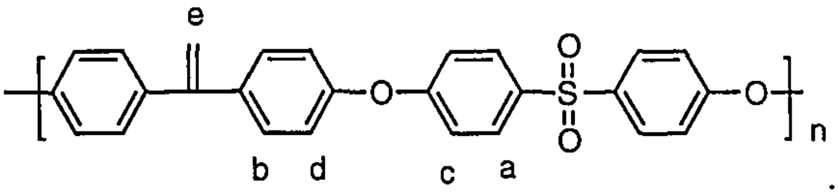
5.4 Experimental

5.4.1 Polymer Synthesis

Homopolymers from 1,1-bis(4-fluorophenyl)ethylene: To a dry 50 mL 3-neck flask equipped with a Dean-Stark trap, cold water condenser, thermometer and nitrogen inlet was added 0.02 mol of bisphenol (BPA or 9,9'-bis(4-hydroxyphenyl)fluorene) and 1,1-bis(4-fluorophenyl)ethylene **5.1** (4.324 g, 0.02 mol). Chlorobenzene (10 mL) and sulfolane (20 mL) were then added. The reaction was purged with nitrogen for 15 minutes, then heated with stirring directly to 235°C using a silicone oil bath. Water and chlorobenzene codistilled from the reaction mixture during heatup starting at 135°C. After a reaction time of 6 h at 235°C, the reaction mixture was diluted to 20% solids with sulfolane and cooled to 180°C. The polymer was isolated by coagulating into methanol (1 to 4 parts, Vol/Vol), filtered, and reslurried in fresh methanol. The coagulated polymer was washed in boiling deionized water with stirring for 6 h, and filtered. After drying in the vacuum oven for 24 h, the yield was 95%. ^{1}H NMR of oligomer 5.3 (200 MHz, $CDCl_3$), δ7.90-6.70 (m, 24 H), 5.35 (s, 2H).

Copolymers from 1,1-bis(4-fluorophenyl)ethylene: To a dry 50 mL 3-neck flask equipped with a Dean-Stark trap, cold water condenser, thermometer and nitrogen inlet was added 0.02 mol of bisphenol (BPA or 9,9'-bis(4-hydroxyphenyl)fluorene) and 1,1-bis(4-fluorophenyl)ethylene **5.1** (0.432g, 0.004 mol). Chlorobenzene (10 mL) and sulfolane (20 mL) were added. The reaction was purged with nitrogen for 15 minutes, then heated with stirring directly to 235°C using a silicone oil bath. Water and chlorobenzene codistilled during heatup starting at 135°C. After a reaction time of 6 h at 235°C, bis(4-chlorophenyl)sulfone (4.595g, 0.016 mol) was added. After a further 4 h, the reaction mixture was diluted to 20% solids with sulfolane and cooled to 180°C. The polymer was isolated by coagulating into methanol (1 to 4 parts), filtered, and reslurried in fresh methanol. The coagulated polymer was washed in boiling deionized water with stirring for 6 h, and filtered. After drying in a vacuum oven for 24 h, the yield was 98%.

Homopolymer 5.7 from 1,1-bis(4-hydroxyphenyl)ethylene A mixture of 1,1-bis(4-hydroxyphenyl)ethylene **5.2** (0.6368 g, 0.003 mol), K_2CO_3 (0.774 g) and bis(4-fluorophenyl)sulfone (0.7628 g, 0.003 mol) in 4 mL of toluene and 8 mL of N,N'-dimethylacetamide (freshly purified) was heated with stirring under nitrogen atmosphere with azeotropic removal of water for 3 h. Toluene was bled continuously from the Dean-Stark trap until the temperature rose to about 155°C. The reaction mixture then appeared lightly colored and was maintained at the temperature for 2 hs. At this time the reaction was assumed to be complete. The reaction mixture was cooled to about 100°C and diluted with 5 ml of N,N'-dimethylacetamide and filtered. The filtrate was neutralized with acetic acid and coagulated into methanol. The precipitate was filtered and washed with methanol and finally with water. It was boiled in distilled water for 1 h to remove any trapped salts, filtered and dried in a vacuum oven at 80°C; yield > 90%. ^{1}H-NMR (200 MHz, DMSO); a: δ7.92–7.83 (d, 4H); b: δ7.42-7.31 (d, 4H), c and d: δ7.10-6.90 (m, 8H); e: δ4.55 (s, 2H)



Copolymers from 1,1-bis(4-hydroxyphenyl)ethylene A mixture of 1,1-bis(4-hydroxyphenyl)ethylene **5.1** (0.1274 g, 0.0006 mol), 0.0024 mole of the other bisphenol, K_2CO_3 (0.774 g) and bis(4-fluorophenyl)sulfone (0.7628 g, 0.003 mol) in toluene (4 mL) and N,N'-dimethylacetamide (8 mL) (freshly purified) was treated as described for the synthesis of the homopolymer.

5.4.2 Characterization: Glass transition temperatures (Tg) of the polymers were obtained using a Seiko 220 DSC instrument at a heating rate of 10°C/min in N_2 (50 mL/min). When recording Tg values the samples never were heated above 300°C, to prevent cross-linking, and the values were recorded from the second scan. The Tg was taken from the midpoint of the change in slope of the baseline. The weight loss data were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 10°C/min in N_2 and air. The TGA was used to cure polymer sample at 320°C for two hs. DSC was then employed to determine the Tg increase. Inherent viscosity data were obtained with a calibrated Ubbelohde viscometer. The measurements were done in $CHCl_3$ at 25°C with a 1B(205). Mw/Mn was obtained relative to polystyrene standards in chloroform solution using a Waters 510 HPLC equipped with mStyragel columns arranged in series and a UV detector. ^{1}H-NMR was recorded at 200 MHz using a Varian XL-200 spectrometer in $CDCl_3$ with $(CH_3)_4Si$ as the internal standard.

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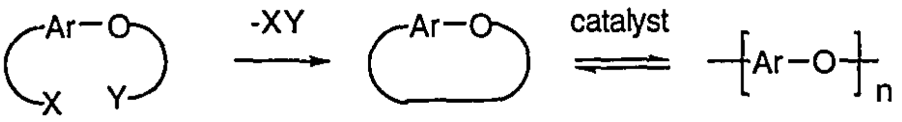
Chapter 6

New Cross-linkable Cyclic Aryl Ether Ketones Containing the trans-1,2-Diphenylcyclopropane Moiety

6.1 Introduction

In the fabrication of thermoplastic composites starting with high molecular weight linear polymers, problems like poor fiber wetting and breakage of the fibers are difficult to avoid. These problems are a direct result of the extremely high viscosity typical of thermoplastics in the melt. The attractiveness of using cyclooligomers to prepare linear polymers results from the unique combination of low melt viscosity for processing and polymerization in the melt without the liberation of volatile byproducts.[1-5]

The overall concept is shown here:

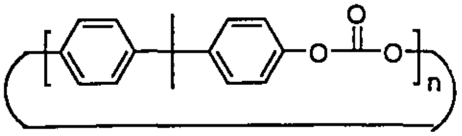


Ar represents an aromatic group, X an electrophile, and Y an anionic leaving group. The starting materials for the first step are conventional monomers. The key is selecting process conditions in which the reactive end-groups are present in low concentrations, resulting in the macrocycles being the kinectically favored products. A distribution of ring sizes is obtained. The second step, ring-opening polymerization, is conducted in the melt at high concentrations at elevated temperatures where the thermodynamically favored product is high molecular weight linear polymer.[6]

6.1.1 Preparation of cyclic oligomers

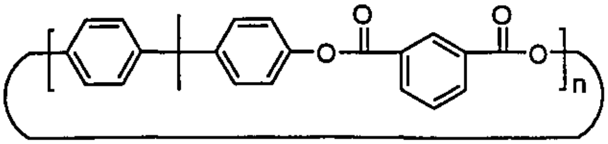
Workers at General Electric have developed low molecular weight aromatic carbonate cyclooligomers (Scheme 6.1).[7-9] The procedure selectively affords a mixture of oligomeric aromatic carbonates, ranging from cyclic dimer to about docosamer (predominantly dimer to decamer), with almost total exclusion of linear oligomeric materials: typical levels of linear oligomers in the crude reaction products are 0.01 to 0.05%. Minimization of low molecular weight linear oligomers is critical for subsequent ring-opening polymerization reactions, because linear materials will limit the polymer's final molecular weight. The procedure utilizes a pseudo-high dilution reaction, in which a solution of bischloroformate in methylene chloride (about 1.0 M) is added to a rapidly stirred mixture of triethylamine, methylene chloride, and aqueous base. The addition takes 20-60 min; unlike typical macrocyclization reactions, little effect of addition time on yield of product is evident, except at very short reaction times. This hydrolysis / condensation reaction is a novel example of a pseudo-high dilution reaction. Although this new technology may become useful for several applications, polycarbonates typically have limited solvent resistance which may restrict the utility of composites based on such polymers.

Poly(aryl ethers), which have superior thermooxidative stability,[4] have been synthesized by the ring-opening polymerization of macrocyclic ethers. Mullins found that, with a proper choice of process conditions, aryl ether cyclooligomers (Scheme 6.1) are surprisingly easy to prepare on a lab scale. Even membered cyclooligomers with 4 or more repeat units were obtained with starting materials like bis(4-fluorophenyl)sulfone and bis(4-hydroxyphenyl)sulfone.

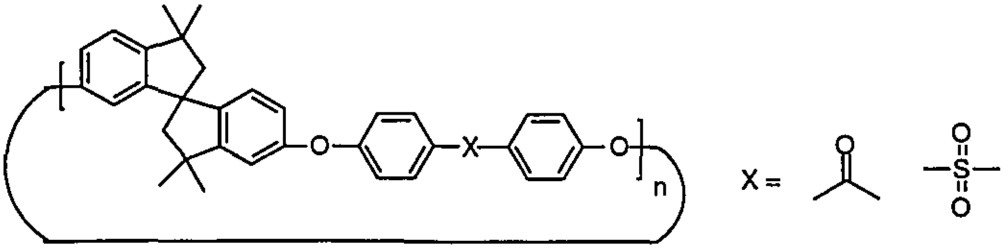


n = 2-20

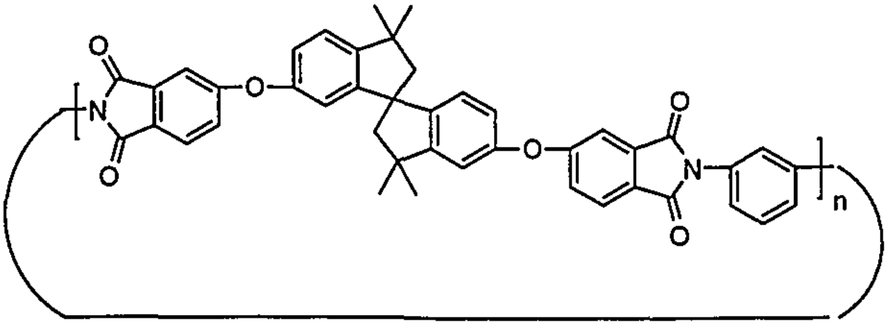
Cyclic BPA Carbonate



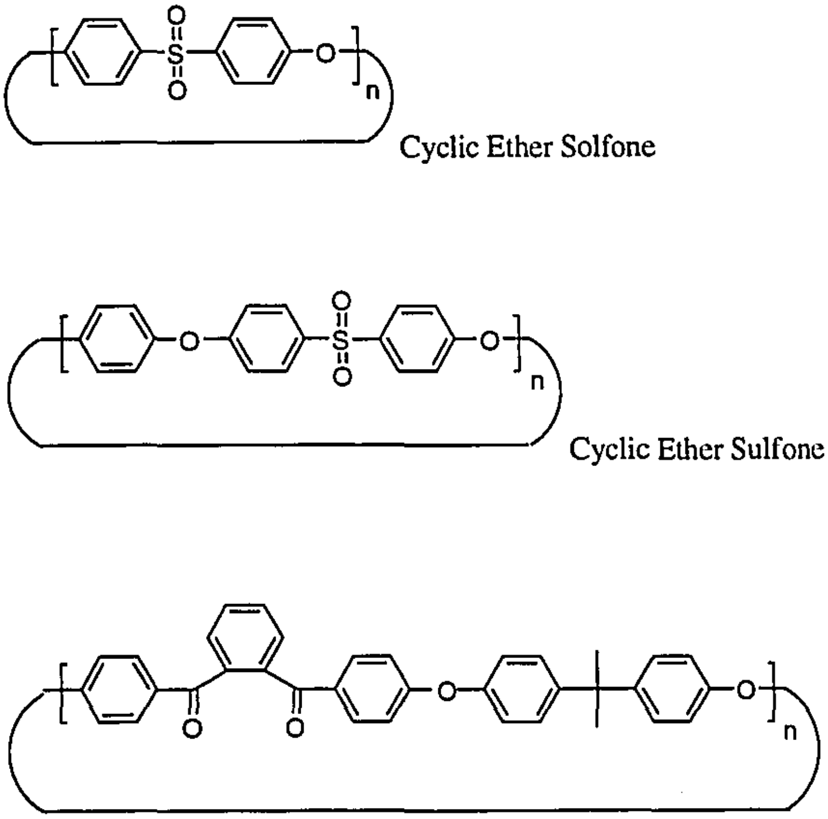
Cyclic Ester



Cyclic Ether Sulfone and Ketone



Cyclic Ether Imide



Cyclic Ether Solfone

Cyclic Ether Sulfone

Cyclic Ether Ketone

Scheme 6.1

In a typical experiment, solutions of bis(4-fluorophenyl)sulfone (60 mL 1M in DMSO) and KOH (60 mL, 2M in water) were simultaneously added at 1 mL/hour to a refluxing solution of 750 mL DMSO and 225 mL of toluene. Some cross-linkable cyclic oligomers were prepared from 2,4-difluorobenzonitrile and 1,3-dihydroxybenzene. The product mixture polymerized readily to give a cross-linked polymer.

A cyclic oligomeric arylate (Scheme 6.1) was prepared by the interfacial polymerization reaction of bisphenol A (BPA) disodium salt in water and iso- or terephthaloyl dichloride in methylene chloride in the presence of a phase transfer catalyst (PTC) under pseudo-high dilution conditions.[10] Fukuyama[1] used a spirobiindanediol (2,2',3,3'-tetrahydro-3,3,3',3'-tetramethyl-1,1'-spiro[1H-indene]-6,6'diol) which has a 'bent' conformation that promotes cyclic oligomers formation. However, these materials show incomplete polymerization with a large amount of cyclics remaining. Cyclic ether imide (Scheme 6.1) was also prepared from a spirobiindanediol. Gibson[5] employed a 4-step synthetic sequence with protection/deprotection and isolated single sized cyclic materials rather than a mixture of cyclic oligomers. Overall yields ranged from 16% to 45%.

6.1.2 Ring opening

The ring-opening polymerization of the cyclic carbonate ring systems occurs in solution and in the melt.[9] Effective reaction solvents include o-dichlorobenzene, 2,4-dichlorotoluene, tetrahydrofuran, dimethoxyethane and N,N-dimethylformamide. Only anionic initiator systems lead to polymerization, but a wide range of anionic systems were effective. These included very reactive anions such as phenyllithium as well as considerably less active systems such as lithium phenoxide.

The ring-opening reaction of cyclic bisphenol-A carbonate oligomers possesses the characteristics of a "living" addition polymerization. No significant ring-chain equilibrium is observed in solution or in the melt, but chain-chain equilibration occurs very rapidly leading to average dispersities near 2. Very high molecular weight polycarbonate can be obtained by the use of low initiator levels.

The individual ether sulfone or ketone cyclooligomers are extremely high melting solids. Despite this, the crude mixture can be induced to polymerize in the melt in the presence of catalysts which reversibly cleave the activated carbon-oxygen bonds joining the rings. A variety of phenoxides and alkali metal fluorides are effective catalysts. The cyclooligomers are typically contaminated with small amounts of linear oligomers terminated with phenolic groups. These residual phenolics can be titrated with alkali metal hydroxides, converting them to oligomeric phenoxides which are also excellent catalysts.

6.1.3 Goals and strategies

An efficient synthesis for cyclic aryl ether oligomers which proceeds in high yield by reaction of 1,2-bis(4-fluorobenzoyl)benzene with a number of bisphenols has been described.[11] These oligomers undergo melt polymerization readily at 340°C, in the presence of an anionic catalyst, to give high molecular weight polymers with high Tgs (up to 260°C). However, these polymers typically have limited solvent resistance which may restrict the utility of composites based on such polymers. One way we are investigating to overcome this problem is to synthesize cyclic aryl ether oligomers which polymerize readily to give cross-linked polymers. For many composite applications some cross-linking is desirable. Cross-linking systems are often used in these applications when resistance to solvents, resistance to high temperatures, and high mechanical performance are required.

Recently we have developed new types of cross-linkable polymers containing the trans-1,2-diphenylcyclopropane moiety.[12] The polymers, which have been synthesized from the monomer trans-1,2-bis(4-hydroxyphenyl)cyclopropane by solution polycondensation, can be thermally cross-linked when heated above the glass transition temperature without producing volatile byproducts. The resulting cross-linked networks are insoluble in all solvents tried.

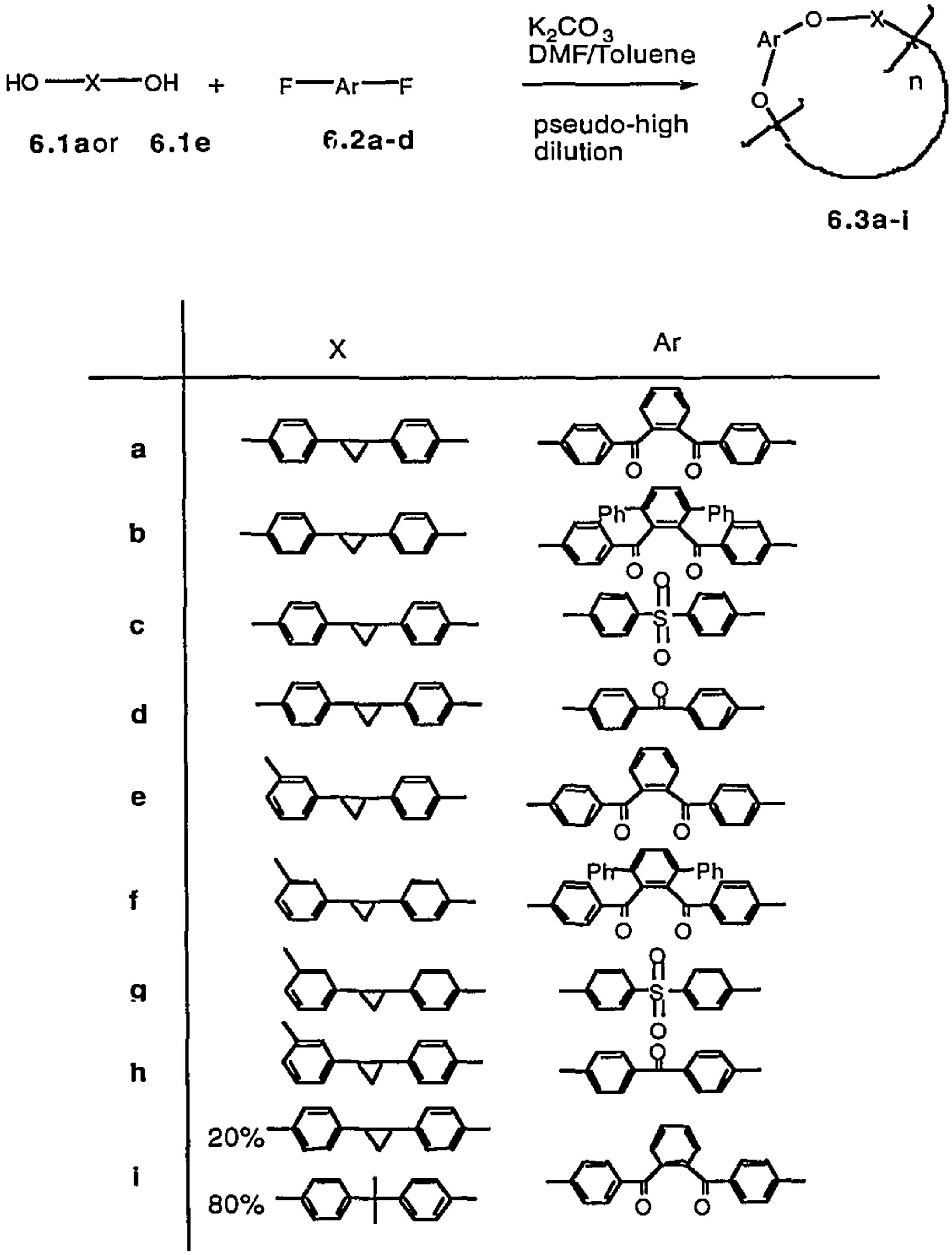
Herein, we report the synthesis, ring opening polymerization, and cross-linking of cyclic aryl ethers containing the trans-1,2-diphenylcyclopropane moiety.

6.2 Results and discussion

6.2.1 Preparation of cyclic oligomers

The monomers 1,2-bis(4-hydroxyphenyl)cyclopropane **6.1a** and 1-(3-hydroxyphenyl)-2-(4'-hydroxyphenyl)cyclopropane **6.1e** were synthesized by catalytic decomposition of the corresponding hydroxyl substituted 3,5-diphenyl-2-pyrazolines which were the products of the reaction between hydroxychalcones and hydrazine monohydrate according to the simple method we reported recently[13]. Linear high molecular weight poly(ether sulfone)s, polyformals and polyesters have been synthesized from 1,2-bis(4-hydroxyphenyl)cyclopropane **6.1a.**[12]

1,2-bis(4-fluorobenzoyl)benzene **6.2a** and 1,2-di(4-fluorobenzoyl)-3,6-diphenylbenzene **6.2b** were synthesized utilizing the method recently described[14]. The monomers were isolated in very high yield. These fluoro substituted monomers undergo reactions with bisphenols in the presence of excess anhydrous potassium carbonate in an aprotic dipolar solvent (N,N-dimethylacetamide) to give high molecular weight amorphous poly(aryl ether ketone)s with high glass transition temperatures which are very soluble in solvents such as chloroform and toluene at room temperature.


HO—X—OH + F—Ar—F
6.1a or 6.1e
6.2a-d
K2CO3
DMF/Toluene
pseudo-high dilution
Ar
O
X
n
6.3a-i
X
Ar
a
b
c
d
e
f
g
h
i
Ph
S
20%
80%

Scheme 6.2

Cyclic aryl ether oligomers **6.3a, 6.3b, 6.3e, 6.3f** and **6.3i** containing the trans-1,2-diphenylcyclopropane moiety were synthesized in high yield from 1,2-bis(4-hydroxyphenyl)cyclopropane **6.1a** and 1-(3-hydroxyphenyl)-2-(4'-hydroxyphenyl)cyclopropane **6.1b** by reaction with 1,2-bis(4-fluorobenzoyl)benzene **6.2a** or 1,2-bis(4-fluorobenzoyl)-3,6-diphenylbenzene **6.2b** (Scheme 6.2). An efficient pseudo-high dilution method[11] was used to achieve a high yield of cyclic oligomers. Thus, a concentrated DMF solution of reactants (0.6M) is pumped into the reaction vessel containing solvent (DMF) and base (K_2CO_3) over a period of 8 hours. Toluene is used for continuous azeotropic removal of water generated during the reaction. Following the addition of the reactants, it takes another 8 hours at the temperature of reflux to ensure a complete reaction. In this way, the concentrations of reactants in solution were maintained at high dilution by slow addition of starting materials, in the correct stoichiometry, and using conditions where the displacement reaction is as fast as possible. In this manner, cyclic aryl ether oligomers **6.3c, 6.3d, 6.3g** and **6.3h** containing the trans-1,2-diphenylcyclopropane moiety were also synthesized from 1,2-bis(4-hydroxyphenyl)cyclopropane **6.1a** and 1-(3-hydroxyphenyl)-2-(4'-hydroxyphenyl)cyclopropane **6.1e** by reaction with bis(4-fluorophenyl)sulfone **6.2c** and 4,4'-difluorobenzophenone **6.2d** (Scheme 6.2).

6.2.2 Characterization of cyclic oligomers

The cyclic oligomers were characterized by the combination of GPC and matrix assisted laser desorption ionization mass spectrometry (MALDI-MS) which indicates that the range of oligomerization of 1,2-bis(4-hydroxyphenyl)cyclopropane **6.1a** with the activated aromatic bisfluorides **6.2a** and **6.2b** is from 2 up to about 9. MALDI-MS spectra of cyclic oligomers **6.3a** and **6.3b** are shown in Figure 6.1. All cyclic oligomers with degree of polymerization from 2 to 9 can be seen clearly in the MALDI-

MS spectra of **6.3a** and **6.3b.** Potassium chloride in 2,5-dihydroxybenzoic acid was used as the matrix material in the analyses and the mass numbers in the MALDI-MS spectrum correspond to oligomer ions with K^+ attachment. The largest peak in both cases corresponds to a cyclic dimer, and is a doublet with the peak at lower mass corresponding to the free cyclic oligomer. It also can be seen that the content of linear oligomers in the mixture is not significant. The molecular weight of cyclic oligomers **6.3a** and **6.3b** determined by MALDI-MS are listed in Table 6.1.

The composition of cyclic oligomers determined by GPC are summarized in Table 6.2. A GPC trace of cyclic oligomers **6.3a** is shown in Figure 6.2 which indicates along with MALDI-MS data that the smallest ring is the easiest formed.

Attempts to make cyclic oligomers from 1,2-bis(4-hydroxyphenyl)cyclopropane **6.1a** and bis(4-fluorophenyl)sulfone **6.2c** or 4,4'-difluorobenzophenone **6.2d** using the same method were not as successful. GPC traces of those oligomers show that the mixture contains significant amounts of linear polymers along with the desired cyclic oligomers. As expected from a study of molecular models, bis(4-fluorophenyl)sulfone **6.2c** or 4,4'-difluorobenzophenone **6.2d** are less prone to cyclooligomer formation than 1,2-bis(4-fluorobenzoyl)benzene **6.2a** or 1,2-bis(4-fluorobenzoyl)-3,6-diphenylbenzene **6.2b.**

In the oligomerization of 1-(3-hydroxyphenyl)-2-(4'-hydroxyphenyl)cyclopropane **6.1e** and activated aromatic bisfluorides **6.2a** and **6.2b,** 22% of the monocyclic (n = 1) and no cyclic aryl ether oligomers with degree of polymerization higher than 5 were formed. A GPC trace of cyclic oligomers **6.3c** is shown in Figure 6.2. Cyclic oligomers were synthesized from 1-(3-hydroxyphenyl)-2-(4'-hydroxyphenyl)cyclopropane **6.1e** and bis(4-fluorophenyl)sulfone **6.2c** or 4,4'-difluorobenzophenone **6.2d** under the same conditions. It was found that no cyclic oligomers with degree of polymerization higher than 5 were formed. The cyclic aryl ether oligomers from 1-(3-hydroxyphenyl)-2-(4'-hydroxyphenyl)cyclopropane have high melting points.

Cocyclic oligomers **6.3i** were also prepared by reaction of 20 mol% of 1,2-bis(4-hydroxyphenyl)cyclopropane, 80 mol% of 2,2-bis(4-hydroxyphenyl)propane (BPA) with bis-1,2-(4-fluorobenzoyl)benzene **6.2a**.

All the cyclic oligomers are readily soluble in chloroform. The residual potassium salts in the cyclics were removed by twice precipitating a DMF solution into a large excess of aqueous 0.2 M HCl.

6.2.3 Thermal analysis of cyclic oligomers

The results of the thermal analysis of the cyclic oligomers are summarized in Table 6.3. The cyclic oligomers **6.3a**, **6.3c**, **6.3d** and **6.3i** exhibit no observable melting endotherm along with the Tg while **6.3b** shows a moderate melting endotherm at 325°C after a Tg at 179°C. In the DSC scan of the cyclic oligomers **6.3e**, **6.3f**, **6.3g** and **6.3h** only melting endotherms and no Tg's were observed. An exotherm at about 400°C, which is associated with the cross-linking reaction, was observed in the DSC scans of all cyclic oligomers. The exotherms of cyclic oligomers are consistent with those of linear polymers described previously.[12]

The DSC scans of cyclic oligomers **6.3a** are shown in Figure 6.3. Curve **a** is the DSC thermogram of cyclic oligomers **6.3a**, curve **b** is DSC scan of cyclic oligomers **6.3a** after being heated at 300°C for 30 minutes in nitrogen and the curve **c** is the result after being heated at 350°C for 30 minutes in nitrogen. A Tg at 154°C and an exotherm at 401°C were observed in scan a. A Tg at 188°C and an exotherm at 406°C were shown in scan **b**. Only an exotherm, starting from 360°C, appears in curve **c**. These results suggest that curing at 350°C for 30 minutes can provide efficient cross-linking while 300°C is not high enough temperature to achieve significant cross-linking in 30 minutes.

Ring opening polymerization of the cyclic oligomers can be initiated with a phenolate catalyst. Since the aryl ether linkage is activated by an electron-withdrawing group, it will undergo ether exchange reaction readily.[15] The potassium salt of 4,4'-biphenol has been shown to be an effective catalyst for the polymerization of cyclic oligomers from 1,2-bis(4-fluorobenzoyl)benzene and BPA.[6]

It was found that ring opening polymerization and cross-linking occurred simultaneously when cyclic aryl ether oligomers prepared from 1,2-bis(4-hydroxyphenyl)cyclopropane were cured above 280°C. After they were cured at 280°C, or above, the resulting materials were no longer soluble in organic solvents, and Tg's increased significantly. Compared to the thermally cured products, a large increase in Tg was obtained when the cyclic oligomers were cured in the presence of the potassium salt of 4,4'-biphenol. The results are listed in Table 6.4.

The results from ring opening of cyclic oligomers **6.3e**, **6.3f**, **6.3g** and **6.3h** in DMAc at 160°C in the presence of a catalytic amount of sodium salt of 4,4'-biphenol show that these cyclics can readily undergo ring opening polymerizion. Attempts to cure cyclic oligomers **6.3e**, **6.3f**, **6.3g**, **6.3h**, which are extremely high melting solids, at 280 and 300°C were unsuccessful since no significant reaction occurred when they were cured at those temperatures. In order to induce polymerization and cross-linking, the materials have to be cured above their melting points.

No Tg is detected by DSC after 30 minutes curing of all homo cyclics above 350°C in nitrogen. The cured materials also show no observable swelling over 24 hours in chloroform. Curing of all cyclic oligomers at 350°C in nitrogen gave highly cross-linked materials with high solvent resistance.

Curing of cyclic oligomers **6.3a** at 280°C both in the presence of and without catalyst (potassium salt of 4,4'-biphenol) on a glass plate gave films. The film obtained from the curing of cyclic oligomers **6.3a** at 280°C in the presence of the catalyst is good enough to be tested by thermomechanical analysis (TMA) while the film from curing of cyclic oligomers **6.3a** without the catalyst is too brittle to be tested. The Young's modulus of the film at 25°C is 1.0 GPa. The film maintains mechanical properties to temperatures close to the Tg. These results indicate that in the presence of catalyst ring opening polymerization and cross-linking occur simultaneously.

6.3 Conclusions

Cyclic aryl ether oligomers containing the trans-1,2-diphenylcyclopropane moiety were synthesized in high yield from 1,2-bis(4-hydroxyphenyl)cyclopropane and 1-(3-hydroxyphenyl)-2-(4'-hydroxyphenyl)cyclopropane by reaction with 1,2-bis(4-fluorobenzoyl)benzene or 1,2-bis(4-fluorobenzoyl)-3,6-diphenylbenzene. These oligomers undergo melt polymerization readily to give a cross-linked polymer in the presence of a phenolate salt as catalyst. The cyclic oligomers were characterized utilizing GPC, NMR and matrix assisted laser desorption ionization mass spectrometry (MALDI-MS). Thermal analysis was conducted by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Table 6.1 Molecular weight determined by MALDI-MS

n (degree of polymerization)	Cyclics **6.3a** determined / calculated	Cyclics **6.3b** determined / calculated
2	1016 / 1017	1321 / 1321
3	1023 / 1026	1980 / 1982
4	2031 / 2034	2640 / 2643
5	2539 / 2543	3300 / 3304
6	3047 / 3051	3961 / 3965
7	3553 / 3560	4621 / 4625
8	4060 / 4068	5281 / 5286

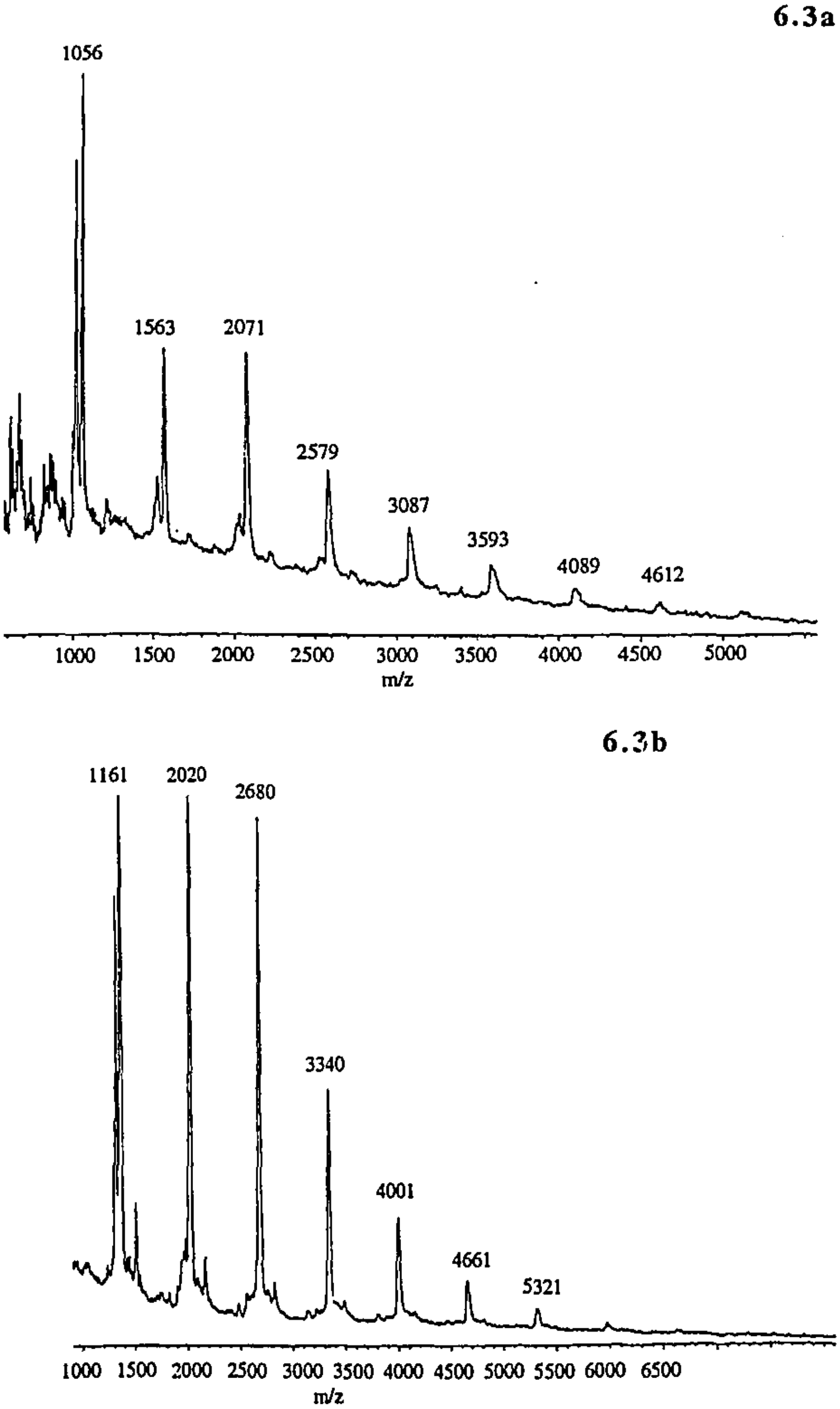


Figure 6.1 MALDI-MS spectrum of cyclic oligomers **6.3a** and **6.3b**

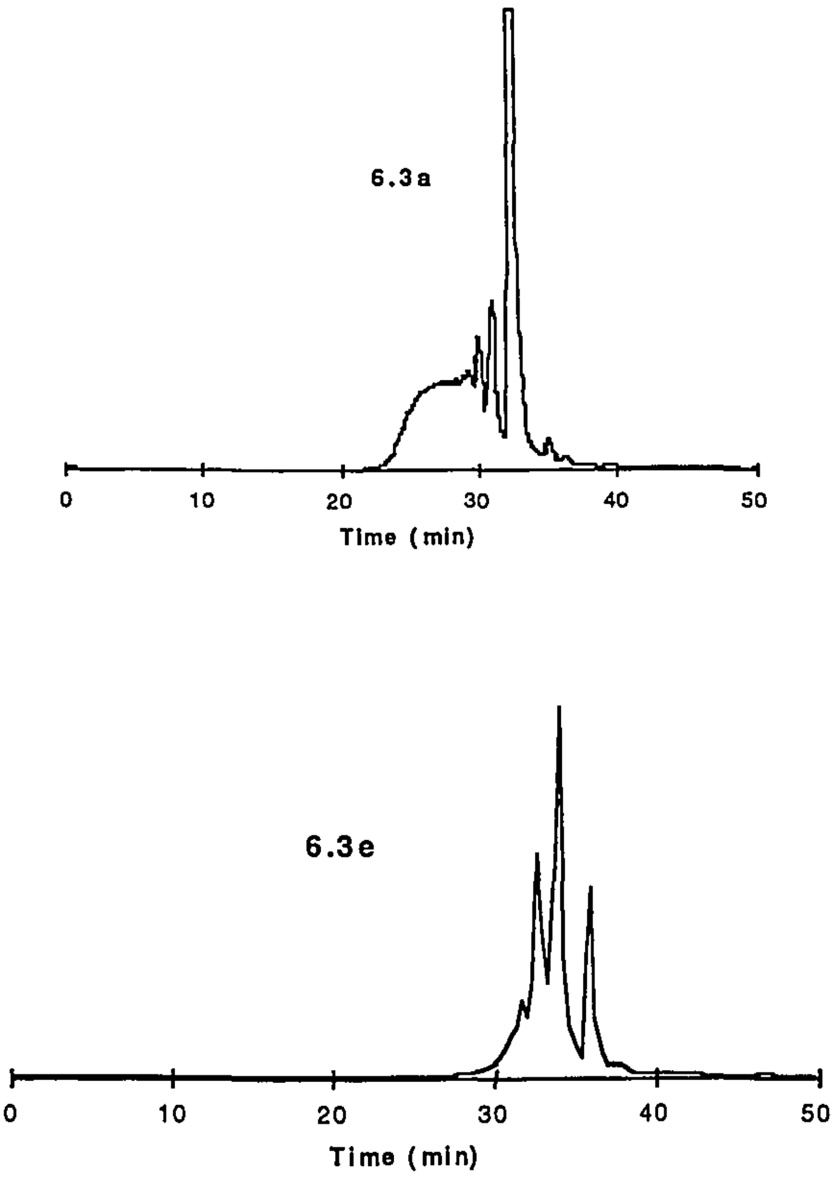


Figure 6.2 GPC trace of cyclic oligomers **6.3a**, **6.3e**

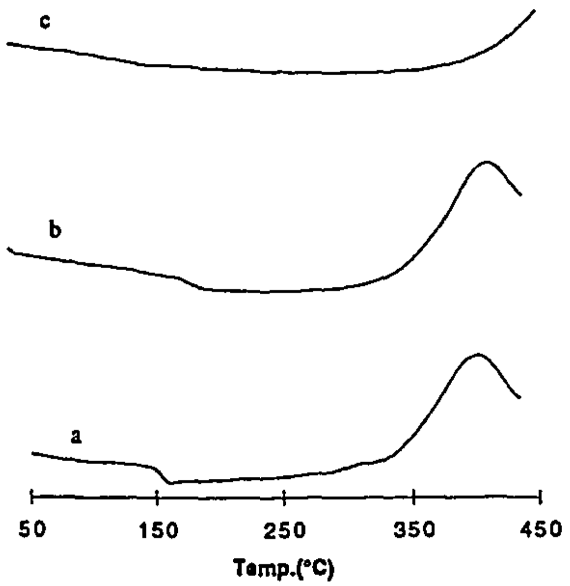


Figure 6.3 DSC scans of cyclic oligomers **6.3a.** a. first scan, b. after heating at 300°C for 30 min, c. after heating at 350°C for 30 min.

Table 6.2 Composition (%) of cyclics by GPC analysis

Cyclic oligomer	mono-cyclic n = 1	dimer n = 2	trimer n = 3	tetramer n = 4	pentamer n = 5	higher homologues
6.3a	0	40.5	11.1	8.6	4.9	34.9
6.3b	0	38.1	12.4	7.2	11.7	30.6
6.3c	0	25.4	11.4	6.4	4.6	52.3
6.3d	0	33.6	14.3	7.7	4.7	39.7
6.3e	21.7	42.3	23.8	12.2	0	0
6.3f	21.9	36.0	22.0	8.7	11.4	0
6.3g	0	55.4	22.1	11.1	11.4	0
6.3h	0	40.9	26.0	13.0	20.1	
6.3i	0	37.7	14.9	7.4	7.1	32.9

Table 6.3 Properties of cyclics containing the 1,2-diphenylcyclopropane moieties

Cyclic oligomer	Tg[a] (°C)	Tm[a] (°C)	exotherm[a] T_{onset}/T_{max}	TGA(-5%)[b] (°C)
6.3a	154	-	300/401	431
6.3b	185	325	302/404	430
6.3c	183	-	300/397	404
6.3d	139	-	300/409	437
6.3e		363	-/405	401
6.3f		370	-/415	426
6.3g		356	-/420	395
6.3h		394	-/420	380
6.3i	163	-	302/404	409

[a] Measured by DSC under nitrogen atmosphere, heating rate 10°C / min. [b] Reported 5% weight loss under nitrogen atmosphere, heating rate was 10°C / min.

Table 6.4 Tg's (°C) of cured cyclic oligomers at 280 and 300°C

Curing Temp.	280°C without salt	300°C without salt	280°C with salt*	300°C with salt
6.3a	176	188	215	242
6.3b	214	223	224	260
6.3c	196	198	228	242
6.3d	157	162	165	173
6.3i	174	180	176	200

*1.0(mol)% of KOPhPhOK was used.

6.4 Experimental

1,2-Bis(4-hydroxyphenyl)cyclopropane 6.1a. It was synthesized according to the method described in reference 13. 1.0 g (3.9 mmol) of trans-3,5-bis(4-hydroxyphenyl)-2-pyrazoline was mixed with 1.0 g of powdered sodium hydroxide. The mixture was heated to 250°C under nitrogen and the decomposition proceeded for 30 min. The cooled reaction product was dissolved in water, neutralized with hydrochloric acid and extracted with ether. The ether layer was washed with water to remove the salt . Removal of the ether left the product which was crystallized from acetic acid; mp 190-191°C; ^{1}H NMR (DMSO-d_6) δ1.1.16-1.22 (t, 2H), 1.80-1.98 (t, 2H), 6.60-6.70 (d, 4H), 6.90-6.96 (d, 4H), 9.15 (s, 2H). MS m/z 226 (M^+, 100), 131 (15), 121 (45), 107 (20). Calcd. for $C_{15}H_{14}O_2$ (226.27): C, 79.62; H, 6.24. Found: C, 79.40; H, 6.24.

Trans-1-(3-hydroxyphenyl)-2-(4-hydroxyphenyl)cyclopropane 6.1e. mp 123-125°C; ^{1}H NMR (DMSO-d_6) δ1.23-1.30 (t, 2H), 1.94-2.07 (m, 2H), 6.50-7.06 (m, 8H), 9.16 (s, 1H), 9.25 (s, 1H). MS m/z 226 (M^+, 100), 131 (31), 120 (16), 107 (27). Calcd. for $C_{15}H_{14}O_2$ (226.27): C, 79.62; H, 6.24. Found: C, 79.08; H, 6.33.

1,2-Bis(4-fluorobenzoyl)benzene 6.2a mp 90-91°C. 1H NMR (500 MHz, CDCl3) δ7.06 (dd, 4H), 7.62 (s,4H), 7.74 (dd, 4H). MS(EI) m/e: 322.

1,2-Bis(4-fluorobenzoyl)-3,6-diphenylbenzene 6.2b mp 157-158°C. 1H NMR (500 MHz, CDCl3) 6.84 (dd, 4H), 7.14-7.29 (m, 10H), 7.57 (dd, 4h), 7.62 (s, 2H). MS(EI) m/e: 474.

Characterization

GPC analyses were performed on a Waters 510 HPLC equipped with 5μ phenogel columns (linear, 3 x 500 A) arranged in series with chloroform as solvent, and a UV detector. DSC scans were obtained using a Seiko 220 DSC instrument at a heating rate of 10°C / min in N_2 (160 mL / min). When recording Tg values samples were never heated above 300°C, to avoid cross-linking, and the values recorded are from the second scan. The Tg was taken from the midpoint of the change in slope of the baseline. The weight loss data were obtained from a Seiko 220 TG / DTA instrument at a heating rate of 10°C / min in nitrogen. Polymer samples were cured under nitrogen in the TGA instrument. A DSC was then employed to determine the Tg increase. Potassium chloride in 2,5-dihydroxybenzoic acid was used as the matrix material to record the Laser TOF mass spectra. ^1H, ^{13}C-NMR spectra were recorded at 500 MHz using a Varian XL-500 spectrometer in $CDCl_3$ with $(CH_3)_4Si$ as the internal standard. Measurement of mechanical properties were made on the films using Seiko TMA/SS 120.

General procedure for cyclization reaction

The cyclization reaction was conducted in a 100 mL three-neck, round bottom flask, equipped with a mechanical stirrer, Dean-Stark trap, condenser, thermometer and nitrogen inlet. The flask was charged with 50 mL of DMF, 10 mL of toluene and 5.0 g of K_2CO_3. The mixture was magnetically stirred and heated to reflux at 140°C and kept there for 1 h. Then, a solution of difluoro substituted monomer (2.2 mmol) and bisphenol (2.2 mmol) was added over 8 h via a syringe pump. At the end of addition, the resulting solution was refluxed for another 10 h at 150°C. The reaction mixture was cooled and filtered to remove the salt. The solution was concentrated by rotary evaporation. The concentrated solution was added dropwise to a large excess of 0.2 N hydrochloric acid solution (200 mL) with vigorous stirring. The precipitate was filtered and washed several times to remove any residue with water. The solid was then dried at 100°C under vacuum overnight.

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Chapter 7

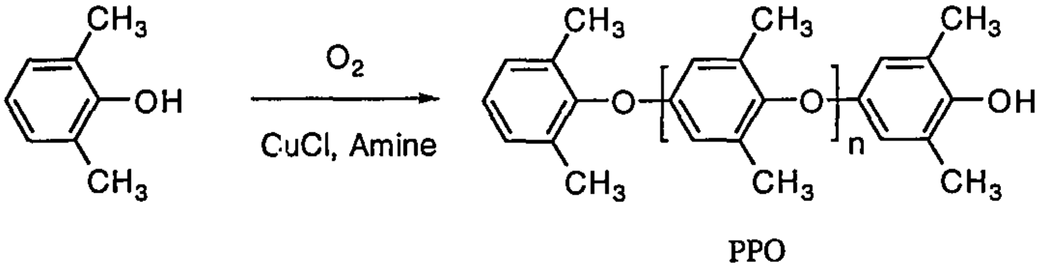
Cross-linkable Polyphenylene Oxide Containing Pendent 1,2-Diphenylcyclopropane Groups

7.1. Introduction

7.1.1 Polyphenylene oxide

In 1959, a novel synthesis of a high molecular weight linear polyphenylene oxide (PPO® resin) by the oxidative polymerization of 2,6-dimethylphenol was reported.[1,2] The polymerization takes place in solution at room temperature by the oxidation of the phenol with molecular oxygen in the presence of an amine complex of a copper salt. Among the various substituted phenols, 2,6-dimethylphenol gave the polymer with the most attractive properties (**Scheme 7.1**).

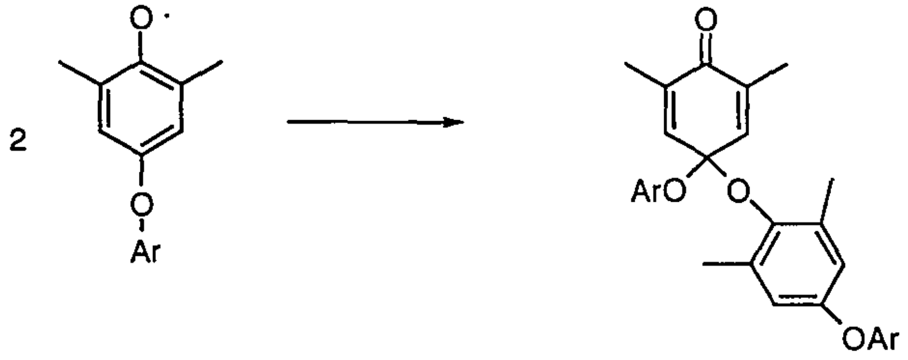
Subsequently, because of the property profile of this polymer, an effort to explore a commercial process for making the monomer, 2,6-dimethylphenol, was undertaken and resulted in a simple reaction discovered by Stephen Hamilton at GE.[2a] However, PPO was found to be difficult to process due to the high Tg which required high process temperatures and resulted in a pronounced tendency to oxidize at the process temperatures. Fortunately, a rather rare compatibility was found between PPO and polystyrene throughout the composition range. The reduced melt viscosity and lower processing temperature required for this blend resulted in a processable material. The blends appeared to combine the favorable features of both polymers and it was named Noryl® resin. Noryl resin is one of the five major engineering thermoplastics manufactured today.[3,3a]



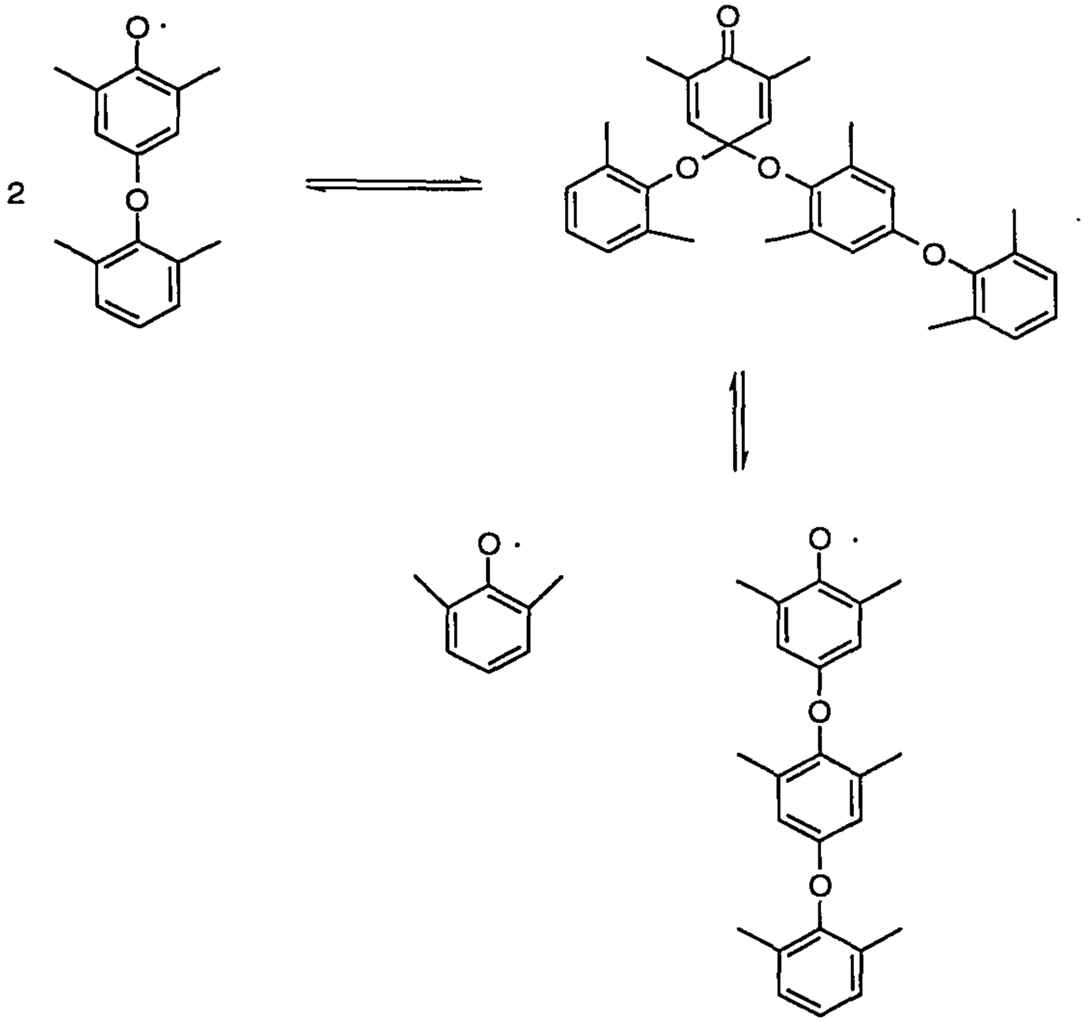
Scheme 7.1

7.1.2. Mechanism of the oxidative polymerization reaction

Because of the industrial significance of PPO and the novelty of the polymerization reaction, much effort has been made to understand the mechanism of this polymerization.[4-6] Initially it seemed that this reaction mechanism could be categorized as a chain growth propagation mechanism by simple radical addition of one unit to the growing polymer chain which is similar to vinyl type polymerizations. But the molecular weight - conversion profile does not correspond to the chain growth pattern. In fact, high molecular weight polymer is only formed at latter stage of the reaction. It is apparent, therefore, that mechanistically the polymerization behaves as a typical step reaction rather than a chain reaction. Two prevailing mechanisms, redistribution mechanism and rearrangement mechanism have been proposed based on the experimental evidence. Both mechanism are similar in that both require the initial formation of phenoxyl radicals that couple to produce a quinone ketal intermediate **(Scheme 7.2).**



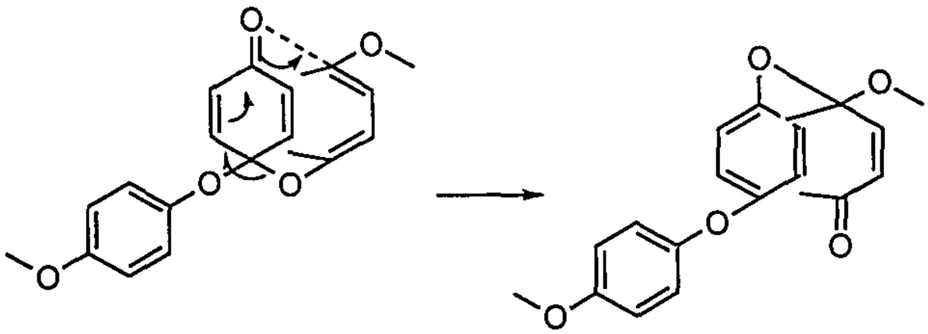
Scheme 7.2



Scheme 7.3

In the redistribution mechanism it is suggested that the ketal intermediates are not stable and dissociate to either their precursor or form two dimer radicals. This process is demonstrated in the scheme 7.3 in which the ketal formed from two dimer radicals dissociates to a trimer radical and a tetramer will be produced whenever trimer radical couples with the monomeric radical co-product of the dissociation.

The second mechanism, quinone ketal rearrangement, also requires that the first step proceed by coupling of two phenoxy radicals to generate a quinone ketal intermediate **(Scheme 7.4)**.



Scheme 7.4

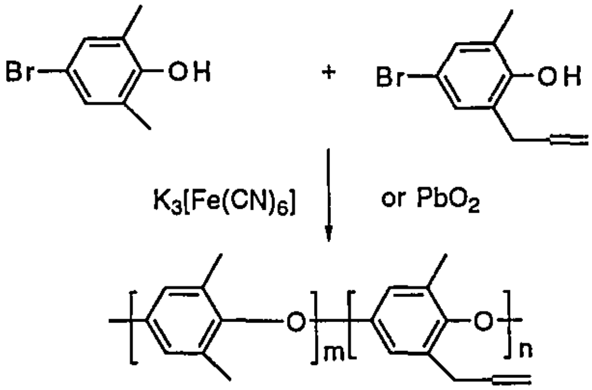
Molecular modeling of this intermediate suggested that the carbonyl oxygen atom of the quinone ketal lies within the bonding distance of the para carbon of one of the ketal aromatic rings providing the possibility of rearrangement by simultaneously breaking and forming an ether linkage. It was suggested that this process occurs concurrently with the redistribution reaction and becomes dominant at lower temperatures. The reason is that at a higher temperature, the ketal intermediate may dissociate before reaching the end of the chain.

7.1.3. Properties of polyphenylene oxide

PPO has excellent mechanical along with exceptional electrical properties, such as low dielectric constant and a low dielectric dissipation factor, as well as relatively good heat resistance.[3] PPO has excellent resistance to acids, alkalis and hot water and would be an excellent candidate as a material for printed circuit boards except that it has poor resistance to solvents, particularly aromatic hydrocarbons and chlorinated hydrocarbons in which it is soluble.

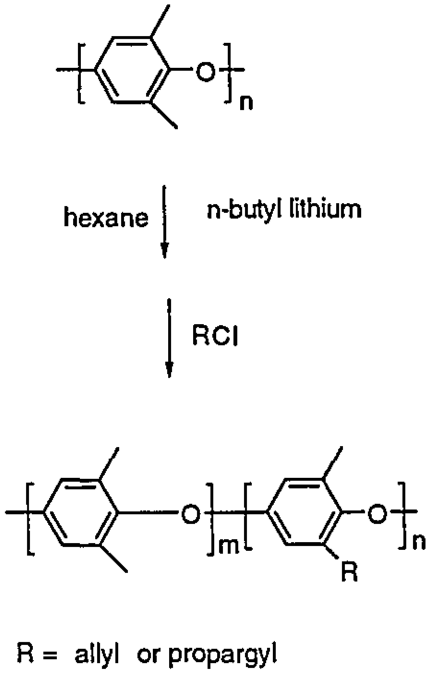
7.1.4 Cross-linkable polyphenylene oxide

Cross-linkable polyphenylene oxide copolymers containing allyl groups have been synthesized by copolymerization of 4-bromo-2,6-dimethylphenol with 2-allyl-4-bromo-6-methylphenol.[4] The polymers containing the allyl groups can be thermally cured to give insoluble materials. In addition the alkylene groups of the resulting polymers can be epoxidized, which also results in polymers that can be cured in the presence of amines or anhydrides as catalysts (**Scheme 7.5**).



Scheme 7.5

More recently allyl- and propargyl-substituted polyphenylene oxides have been synthesized by metallation of PPO with butyl lithium followed by reaction with allyl chloride or propargyl chloride. The resulting resins were combined with triallyl isocyanurate and cured by the reaction with peroxides.[5] (Scheme 7.6)



Scheme 7.6

Curable resins have also been synthesized by the introduction of amino substituents on polyphenylene oxide, synthesized by nitration of PPO followed by reduction. These materials can be combined with epoxy resins.[6] PPO has been combined with various epoxy resins and the mixtures have been cured,[7] and blends with diallylphthalates have been cured in the presence of a free radical catalyst.[8]

7.1.5. Strategies and goals

Our efforts have been directed toward the synthesis of cross-linkable polyphenylene oxides by synthesizing new monomers containing reactive groups which are stable to the oxidative coupling conditions and can subsequently give cross-linked polymers when heated above their glass transition temperature without producing volatile compounds. In this manner the composition of the polymers can be easily controlled to achieve any desired amount of cross-linking.

Recently we have developed a new type of cross-linkable polymer containing the trans-1,2-diphenylcyclopropane moiety.[9] The polymers, which have been synthesized from the monomer trans-1,2-bis(4-hydroxyphenyl)cyclopropane by solution polycondensation with activated bishalides, can be thermally cross-linked when heated above their glass transition temperatures without producing volatile byproducts. The resulting cross-linked networks are insoluble in all solvents tested. We also developed a facile method for the synthesis of mono and dihydroxysubstituted-1,2-diphenylcyclopropanes by the base catalyzed decomposition of the corresponding hydroxyl substituted 3,5-diphenyl-2-pyrazolines which were synthesized by the reaction between hydroxychalcones and hydrazine monohydrate.[10-12]

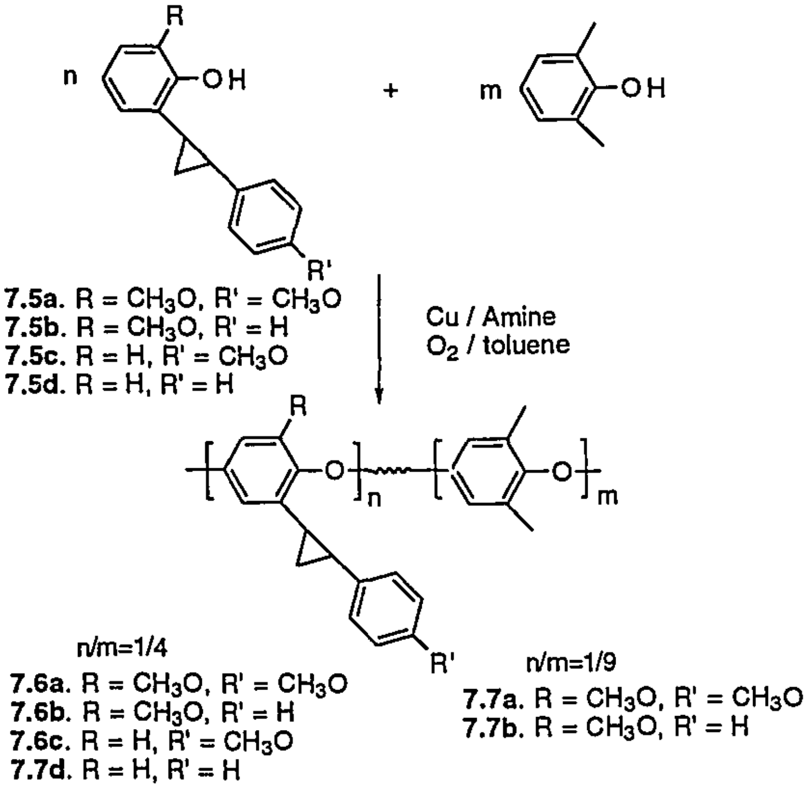
In this chapter the synthesis and thermal cross-linking of novel polyphenylene oxides containing a 1,2-diphenylcyclopropane moiety will be discussed.

7.2. Results and discussion

7.2.1 Preparation of polyphenylene oxides

Four new phenols **7.5a-d** containing the 1,2-diphenylcyclopropane group were synthesized according to the method we recently developed[10] (Chapter 2).

The oxidative polymerization of a large number of 2,6-disubsttituted phenols has been studied in detail.[3] It was found that polymer formation readily occurs only if the substituent groups are relatively small and not too electronegative. Phenols with substituents of intermediate size, such as 2-methyl-6-methoxyphenol, are readily oxidized to high molecular weight polymers.



7.5a. R = CH_3O, R' = CH_3O
7.5b. R = CH_3O, R' = H
7.5c. R = H, R' = CH_3O
7.5d. R = H, R' = H

n/m=1/4
7.6a. R = CH_3O, R' = CH_3O
7.6b. R = CH_3O, R' = H
7.6c. R = H, R' = CH_3O
7.7d. R = H, R' = H

n/m=1/9
7.7a. R = CH_3O, R' = CH_3O
7.7b. R = CH_3O, R' = H

Scheme 7.7

The cyclopropane-functionalized monomers were incorporated into PPO by copolymerization with 2,6-dimethylphenol, according to a recently described procedure [13] as shown in **Scheme 7.7**. N,N'-di-t-butylethylenediamine, N, N'-dimethyl-n-butylamine and di-n-butylamine were employed as ligands for the copper catalyst. A vibromixer was used to maintain efficient mixing of the oxygen in the liquid phase to avoid mass transfer effects. The stirrer rod attached to the vibromixer motor was placed just below the surface of the solution which caused the liquid to spray above the solution in a fountain which gave efficient liquid-oxygen mixing. Either 10 or 20 mol% of the functionalized monomers were used in the preparation of the copolymers. The phenylcyclopropanyl-substituted monomers **7.5a** and **7.5b** can be directly incorporated into polyphenylene oxide to give copolymers **7.6a-b** (20% mol of **7.5a** or **b**), **7.7a-b** (10% mol of **7.5a** or **7.5b**) by simultaneous oxidation of a mixture of 2,6-dimethylphenol and phenylcyclopropanyl-substituted monomers, **7.5a**, **7.5b**. The incorporation of these substituted monomer units into PPO was confirmed by proton NMR (Figure. 7.1). The extra peaks at 6.0-7.4 ppm, 3.6-4.0 ppm and 1.0-2.0 ppm correspond to the signals of aromatic, methoxy and cyclopropane protons on the dimethoxyphenylcyclopropane moiety in the copolymer **7.6a**. The resulting copolymers **7.6a-b** and **7.7a-b** were then subjected to thermal curing. We were not successful in copolymerization of **7.5c** or **7.5d**, which have open ortho positions, with 2,6-dimethylphenol.

7.2.2 Characterization of polyphenylene oxides

Table 7.1 lists the molecular weights, inherent viscosities, composition by NMR, weight losses by thermogravimetric analysis (TGA), glass transition temperatures and the onset temperature for cross-linking (T_{onset}) from the DSC scans of the copolymers **7.6a-b** and **7.7a-b**. The onset temperature for the cross-linking reaction was found to be in the range of 335-340°C. A typical DSC scan of copolymer **7.6a** is shown in Figure 7.2. In the DSC scan a Tg at 176°C and an sharp exotherm starting at 335°C were observed.

7.2.3 Cross-linking of polyphenylene oxides containing the diphenylcyclopropane moiety

Thermal analysis is frequently used to characterize cross-linked polymers. It is well known that the Tg rises while the difference in specific heat capacity (ΔCp) at Tg decreases with increasing numbers of cross-links. The effect of curing time on the difference in specific heat capacity (ΔCp) at Tg (Figure 7.3) and on the Tg (Figure 7.4) of copolymers **7.6a, 7.6b, 7.7a, 7.7d** containing 20 and 10 mole per cent of cyclopropane moieties has been studied. After copolymers **7.6a, 7.6b, 7.7a, 7.7d** were cured at 350°C under nitrogen in TGA for different time periods the cured polymers were examined in the DSC to determine the Tg increase and ΔCp decrease. It was found that ΔCp decreased rapidly and Tg increased as curing time increased as a result of the cross-linking of the polymers. After 30 minute curing the changes in ΔCp and Tg slowed down significantly. As expected, for the same curing time the higher the content of cyclopropane group in the polymers, the larger the change in Tg and ΔCp. No Tg is detected by DSC after 2 hours curing at 350°C in nitrogen when the content of cyclopropane group in PPO copolymers is higher than 20 percent.

As expected for cross-linked polymers, the cured cyclopropane containing PPO polymers were significantly more solvent resistant than the uncured polymers. The polymers which were cured at 350°C were placed in chloroform at room temperature to test solubility and swelling. The cyclopropane containing polymers, which before curing are readily soluble in chloroform, no longer were soluble and did not swell.

From the CP-MAS ^{13}C-NMR studies[9] of poly(ether sulfone)s, polyformals and polyesters containing the 1,2-diphenylcyclopropane moiety, the opening of the cyclopropane rings in the polymers at 350 °C and formation of aliphatic linkage are believed to occur in the cross-linking reaction. This is most probably also involved in the cross-linking chemistry of the polyphenylene oxides containing the 1,2-diphenylcyclopropane pendent groups, which occurs at lower temperature. A variety of substituted cyclopropanes have been shown to undergo thermal structural and geometrical isomerization.[14] Kinetic determinations of the thermal, reversible cis-trans isomerization of 1,2-diphenylcyclopropane in the liquid state over the temperature range 161°C - 220°C have been studied. It is believed that a diradical is the intermediate for the cis-trans isomerization. Three-membered rings can also be cleaved, thermally, to unsaturated products. In the simplest case cyclopropane gives propene when heated to 400 to 500°C.[15] This mechanism is also generally regarded as involving a diradical intermediate. We found that cis-trans isomerization of 1,2-bis(anisyl)cyclopropane proceeds at 350°C in nitrogen. 10% of trans-1,2-bis(anisyl)cyclopropane was converted into the cis isomer after heating at 350°C in nitrogen for 20 minutes. Only 17% of the starting material trans-1,2-bis(anisyl)cyclopropane remained, and many new peaks appeared in the HPLC trace. GPC indicates that most of the products of thermolysis of trans-1,2-bis(anisyl)-cyclopropane are higher molecular weight oligomers. NMR spectra and mass spectra of the mixtures obtained indicate that the products resulted from the ring opening of the cyclopropane moiety, probably proceeding through the singlet diradical as intermediate.

7.3 Conclusions

Cross-linkable polyphenylene oxides containing pendent 1,2-diphenylcyclopropane groups have been synthesized by oxidative polymerization from new phenols **7.5a-d** containing the 1,2-diphenylcyclopropane group. The monomers were prepared by base catalyzed decomposition of the corresponding hydroxyl substituted 3,5-diphenyl-2-pyrazolines which were the products of the reaction between hydroxychalcones and hydrazine monohydrate. Characterization of and cross-linking studies on these polymers were carried out utilizing DSC, TGA, GPC, and NMR. The polymers can be thermally cross-linked when heated to 350°C and the glass transition temperatures (Tg) of the polymers increase after cross-linking. The resulting cross-linked networks are insoluble in all solvents tried. Thermogravimetric analysis shows that no significant weight loss accompanies the cross-linking reaction

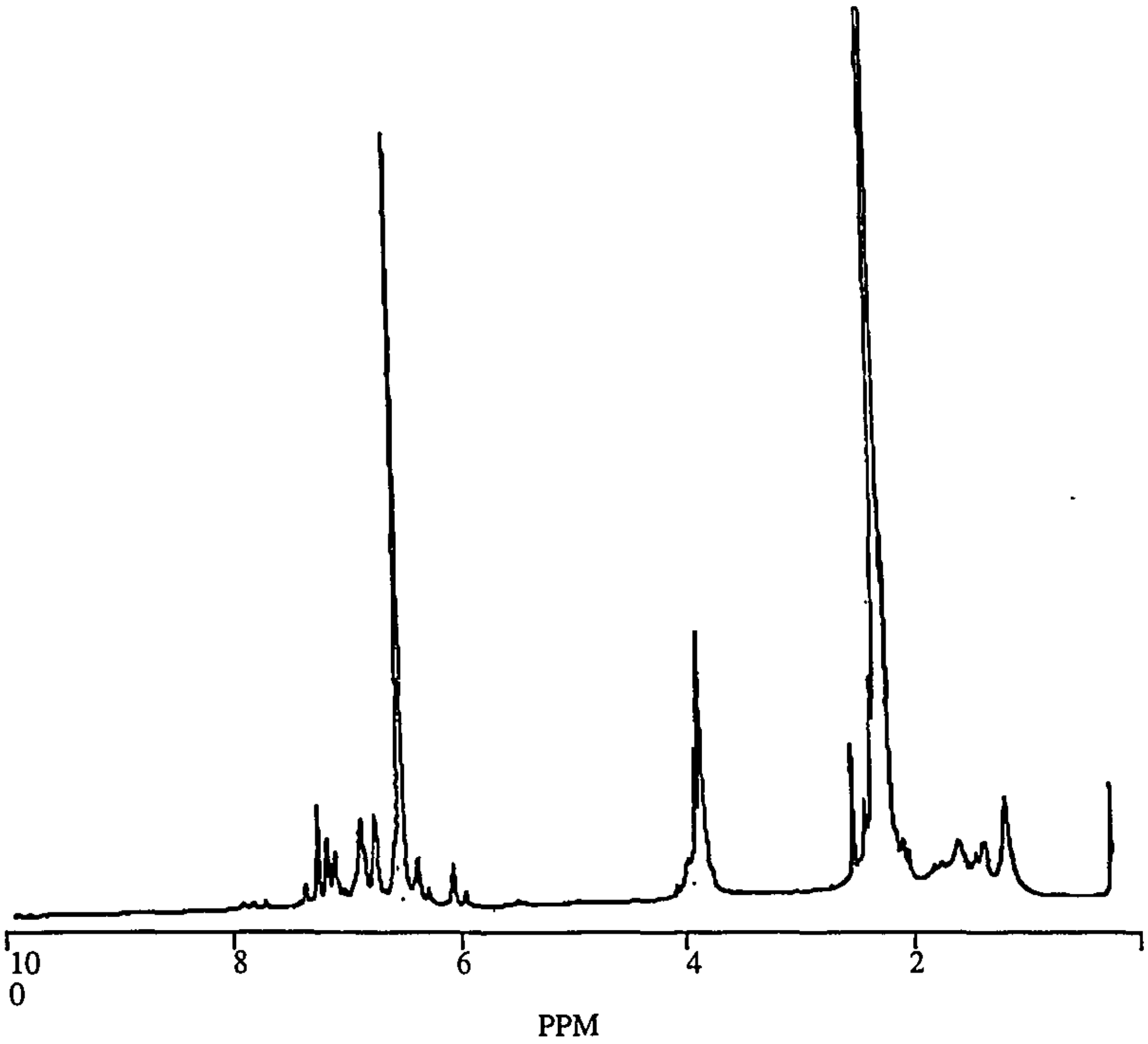


Figure 7.1 ^{1}H NMR spectrum of copolymer **7.6a**

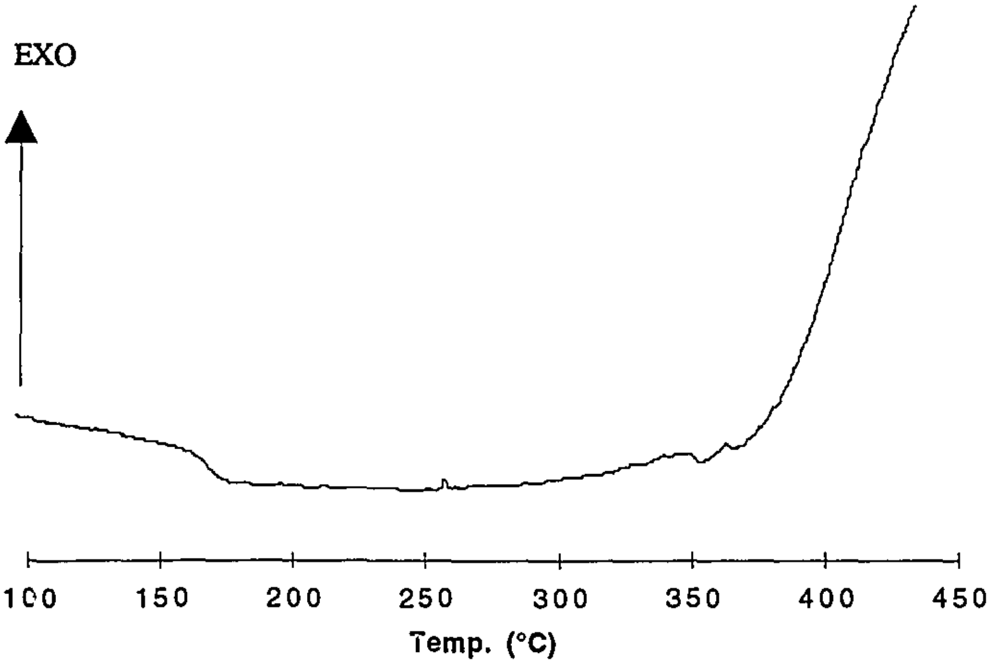


Figure 7.2 DSC scan of copolymer 7.6b

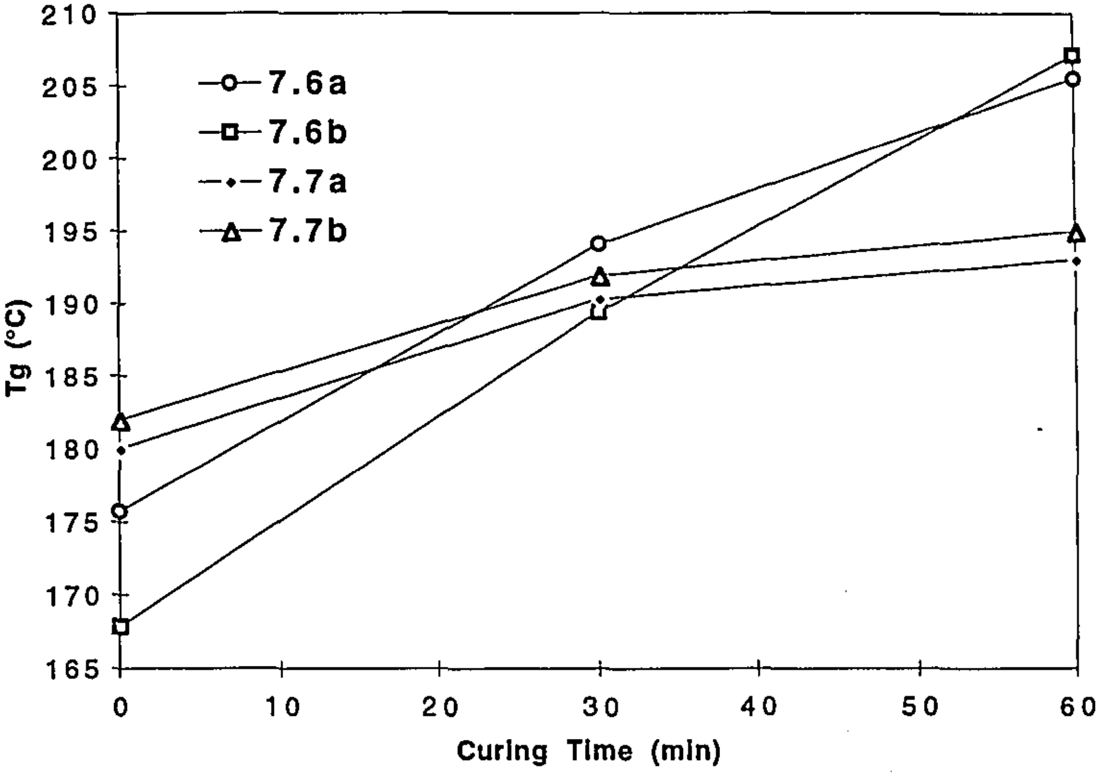


Figure 7.3 Effect of curing time on the Tgs of copolymers. Curing is at 350°C in nitrogen.

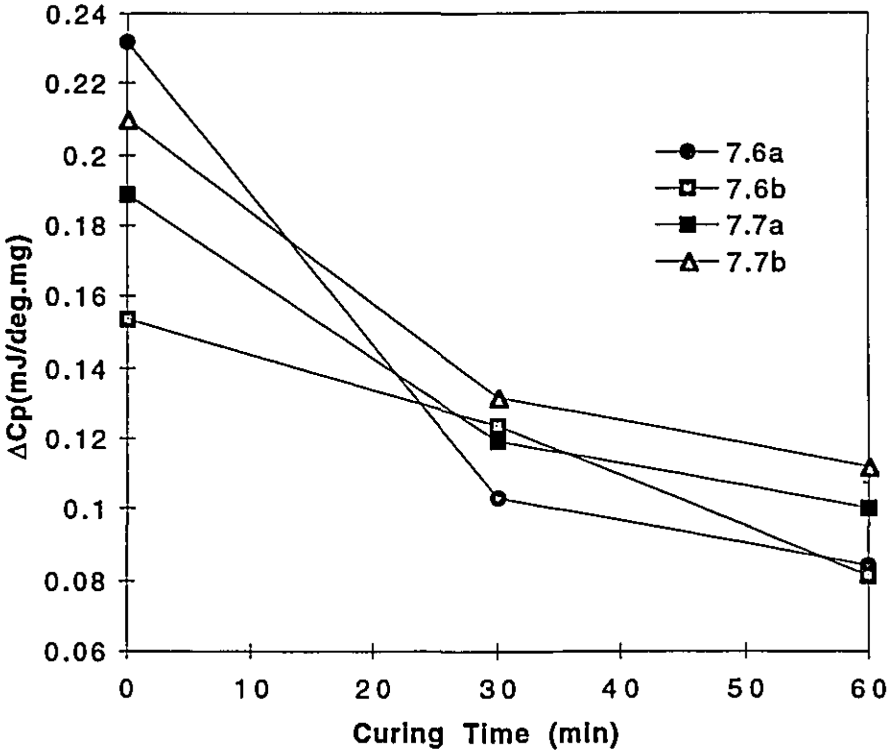


Figure 7.4 Effect of curing time on the ΔCp of copolymers. Curing is at 350°C in nitrogen.

Table 7.1 Properties of polyphenylene oxide copolymers

Polymer	n/m theoretical	n/m (obtained)	Yield (%)	Mw/Mn[a]	η_{inh}[b] (dL/g)	Tg[c] (°C)	TGA(-5%)[d] (°C)	T_{onse} (°C)
7.6a	1/4	0.23	70	27600 /17947	0.30	176	409	335
7.6b	1/4	0.22	65	28676 /14751	0.31	167	412	320
7.7a	1/9	0.09	75	29781 /10648	0.32	180	419	340
7.7b	1/9	0.10	80	26032 /10152	0.28	182	418	340

a GPC. based on polystyrene standard. b 0.5 g / dL in CHCl3 at 25°C. c DSC. heating at 20°C / min. d TGA heating at 20°C / min. e DSC. heating at 20°C / min.

7.4 EXPERIMENTAL

Characterization of Polymers.

Glass transition temperatures of the polymers were obtained using a Seiko 220 DSC instrument at a heating rate of 20°C/min in N_2 (50 mL/min). When recording Tg values samples were never heated above 300°C, to avoid cross-linking, and the values recorded are from the second scan. The Tg was taken from the midpoint of the change in slope of the baseline. The weight loss data were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 20°C/min in nitrogen and air. Polymer samples were cured at 350°C under nitrogen in the TGA instrument. A DSC was then employed to determine the Tg increase. Inherent viscosity data were obtained with a calibrated Ubbelohde viscometer. The measurements were performed in $CHCl_3$ at 25°C with a 1B(205) instrument. Molecular weights were obtained by gel permeation chromatography (GPC) relative to polystyrene standards in chloroform solution using a Waters 510 HPLC instrument equipped with μ–Styragel columns arranged in series and a UV detector. ^{1}H-NMR spectra were recorded at 500 MHz using a Varian XL-500 spectrometer in $CDCl_3$ with $(CH_3)_4Si$ as the internal standard.

General procedure for polymerization reactions

The following toluene stock solutions were prepared for the polymerization reactions.

Stock solution I: Cu: 0.054 mmol/mL; Br: 0.29 mmol/mL. Bromine (5.9 mL, 114.5 mmol) was added to a chilled solution of cuprous oxide (1552 g, 10.85 mmol) and 2,6-dimethylphenol (26.4 g, 216.09 mmol) in methanol (200 mL) over 0.5 h. The solution obtained was diluted with toluene to 400 mL.

Stock solution II: DBEDA (N,N'-di-t-butylethylenediamine): 0.164 mmol/mL.

Stock Solution III: DMBA: 1.64 mmol/mol + 0.77 mmol/mL.

A 50 mL three-neck flask equipped with a condenser, a thermometer, an oxygen inlet and a vibromixer stirrer, was placed in a water bath at room temperature and charged with toluene (12.5 mL), stock solution I (0.76 mL, containing Cu^+ 0.041 mmol, Br^- 0.22 mmol), Stock solution II (0.5 mL, containing DBEDA 0.082mmol) and stock solution III (0.5 mL, containing DMBA 0.82 mmol, and DBA 0.39 mmol). Oxygen was bubbled through the solution for 10 min. and the color of the solution turns to red instantly. Then a solution of 2,6-dimethylphenol (4.636 g) and 2-methoxy-6(2-phenylcyclopropanyl) phenol (0.540 g) in toluene (12.5 mL) was added in one portion and a deep red color developed immediately. Upon the addition of the phenol, a 4°C exotherm of the reaction mixture was observed. The viscosity of the reaction mixture was checked every 10 min. from the time of addition of the phenol by passing the sample (1 mL) from the mixture through a pipette and fed back to the reaction mixture immediately. At 50 min. the viscosity increases significantly. After 60 min. the viscosity of the reaction mixture become so high that stirring ceased. The reaction mixture was added into methanol to precipitate the copolymer which was dried at 80°C under vacuum.

7.5 References

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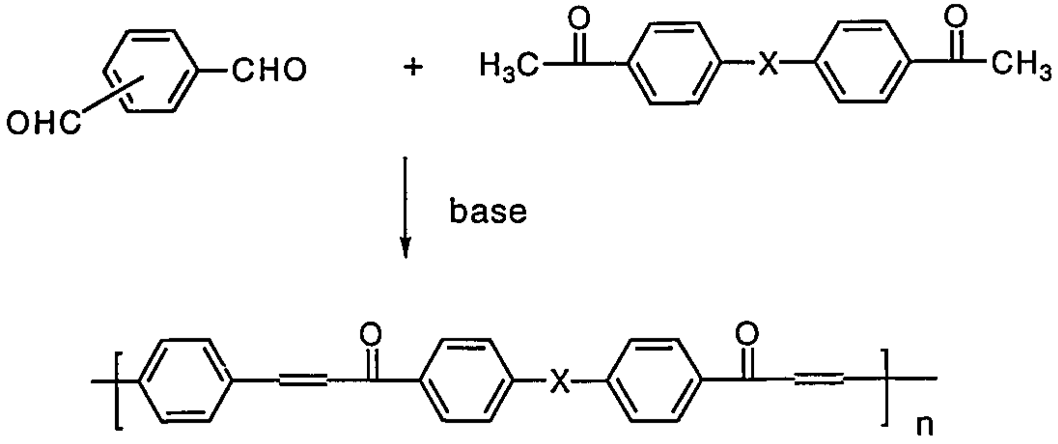
Chapter 8

Thermally Cross-linkable Poly(aryl ether)s Containing a Chalcone Moiety

8.1 Introduction

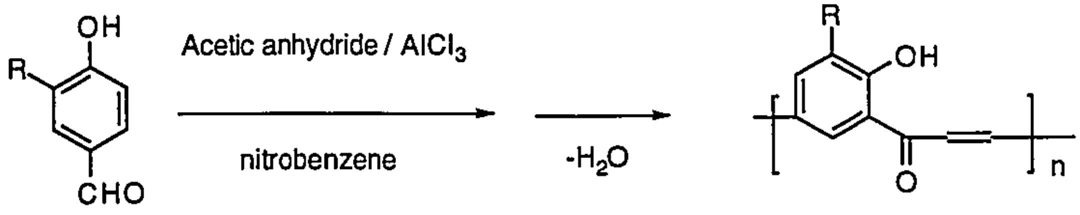
Aromatic and heterocyclic polymers have been investigated for their thermal and chemical stability.[1] Polychalcones which contain the vinyl carbonyl function between two aromatic rings are an interesting group of these polymers. Polymeric materials that contain chalcone-type groups were first reported in 1959.[2] Macromolecules have been synthesized with chalcone-type groups in the side chain, in the main chain, and in epoxy resins.[3] Oleinek et al.[4] and others[5] prepared polychalcones by polycondensation of aromatic diacetyl compounds with aromatic dialdehydes (**Scheme 8.1**). The polymers were semi-conductors and thermally stable. The thermal properties were further improved by transforming the polychalcones to polypyrazolines. Teplyakov et al. [6] investigated the possibility of using the aromatic methyl ketone condensation yielding 1,3,5-substituted benzene rings to synthesize polychalcones. Substituted polychalcones were prepared by a Friedel-Crafts acetylation of vanillin and p-hydroxybenzaldehyde and by a Fries rearrangement of the acetates in nitrobenzene using $AlCl_3$ as catalyst (**Scheme 8.2**).

Due to solubility difficulties arising from the rigid-rod nature of main-chain-containing chalcone polymers, only low molecular weight polychalcones were obtained in some cases discussed above.[7] The condensation polymerization of aromatic dialdehydes with aromatic diacetyl compounds (CH_3CO-Ar-X-Ar-$COCH_3$) gave high molecular weight polymers which are sometimes soluble in N,N'-dimethylformamide when the aromatic diacetyl compounds have flexible linkage like ether linkage.

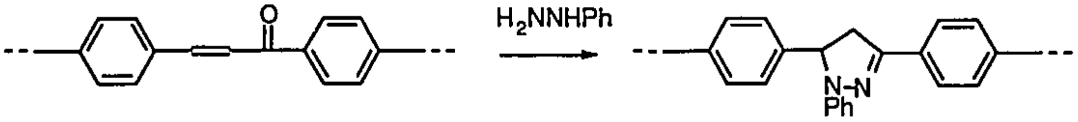


X = CH_2, O or -

Scheme 8.1



Scheme 8.2



Scheme 8.3

Besides the relatively good thermal stability of the polymers, chalcone compounds are light-sensitive. The chalcone group has been incorporated into photodegradable styrene copolymers.[8] Epoxides of hydroxychalcones produce light-sensitive materials for offset printing.[9] Glycidylethers of chalcones have also been investigated in "command-destruct" epoxy resins for easy removal of old epoxy coatings.[10]

It is well known that pyrazolines are generally obtained by the reaction of α,β-unsaturated ketones with hydrazines (**Scheme 8.3**).[11] Therefore, polychalcone can be converted to polypyrazolines by reacting with hydrazines. The corresponding polypyrazolines can also be prepared by cyclocondensation of dichalcones and dihydrazines.[12]

It was demonstrated that base-catalyzed thermal decomposition of substituted 3,5-diphenyl-2-pyrazolines **8.2b** (**Scheme 8.4**), which are the products of the reaction between hydroxychalcones **8.1b** and hydrazine monohydrate, results in the elimination of molecular nitrogen and spontaneously affords substituted 1,2-diphenylcyclopropanes **8.3b**.[13-14] We have found that this method can be used directly on the hydroxychalcones, thus 3,5-bis(4-hydroxyphenyl)-2-pyrazolines **8.2a** can be synthesized by reaction of 4,4'-dihydroxychalcone **8.1a** and hydrazine monohydrate.[15]

We were interested in synthesizing high molecular weight amorphous chalcone or pyrazoline containing polymers. The vinyl group in chalcone containing polymers is a reactive group which may undergo thermal reaction to produce a cross-linked polymer matrix. The 2-pyrazoline group in pyrazoline containing polymers should undergo thermal base-catalyzed decomposition to eliminate nitrogen, which might be useful for forming foam products.

In this chapter the synthesis of poly(aryl ether)s containing the chalcone moiety and their conversion to 2-pyrazoline containing polymers by reaction with hydrazine will be discussed.

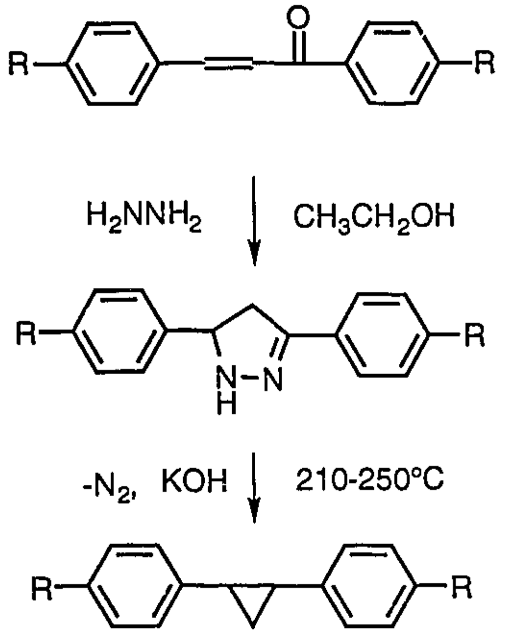
8.2 Discussion and results

8.2.1 Monomer synthesis

4,4'-Dihydroxychalcone **3.1a** was prepared by reaction of 4-hydroxybenzaldehyde with 4'-hydroxyacetophenone by the hot condensation method[16,17] **(Scheme 8.4)**. 3,5-Bis(4-hydroxyphenyl)-2-pyrazoline **8.2a** was synthesized by refluxing the ethanol solution of 4,4'-dihydroxychalcone **8.1a** in the presence of a two fold excess of hydrazine monohydrate. 1,3-Bis(4-hydroxycinnamoyl)benzene **8.6** was prepared by the condensation of isophthalaldehyde **8.5** and 4-hydroxyacetophenone **8.4** under basic conditions **(Scheme 8.5)**. 1,3-Bis(4-hydroxycinnamoyl)benzene **8.6** reacted with hydrazine in ethanol at refluxing to afford the pyrazoline **8.7**.

8.2.2 Preparation of chalcone containing polymers

Two major methods have been developed for the synthesis of poly(ether sulfone)s. One method involves the base mediated nucleophilic displacement of aromatic bisphenols with activated aromatic bishalides. The second major method involves a Friedel-Crafts type polysulfonylation of aromatic substrates with aromatic bis(sulfonyl chlorides). For the first method, dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidinone (NMP) and tetramethylene sulfone have been used as solvents. NMP or tetramethylene sulfone are used if the polymerization needs to be carried out at higher temperature. In the present case polymer hydrolysis and bisphenate insolubility posed a problem in the synthesis when DMSO was used as solvent. Therefore the potassium carbonate/DMAc route was

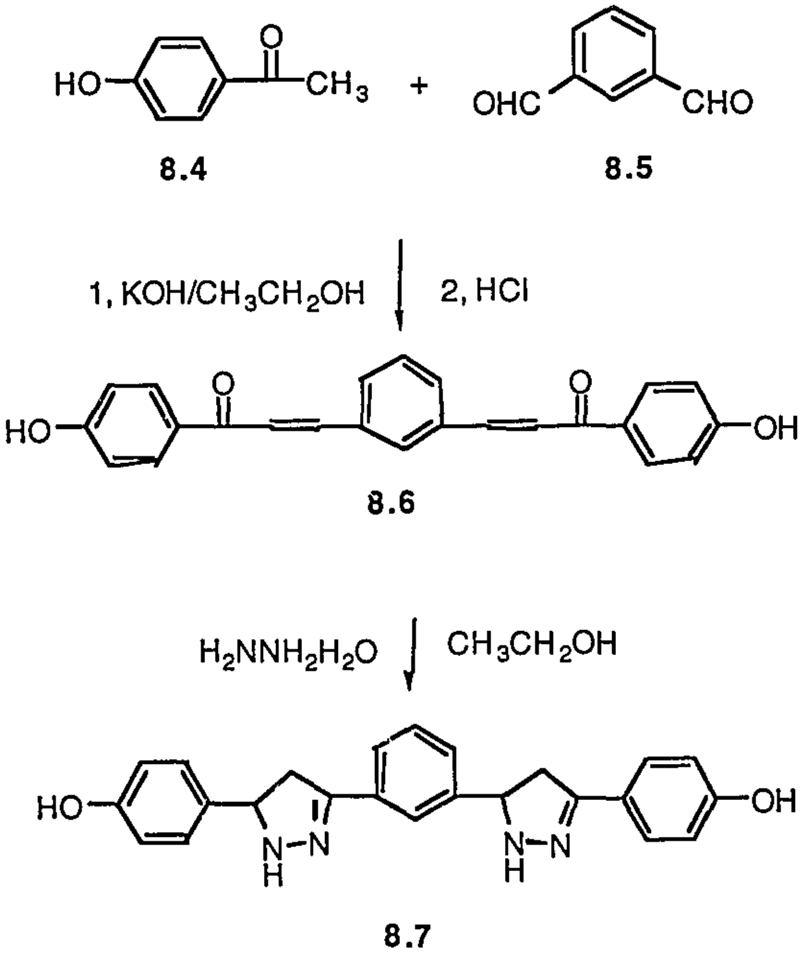


8.1a R = OH
8.1b R = CH_3O

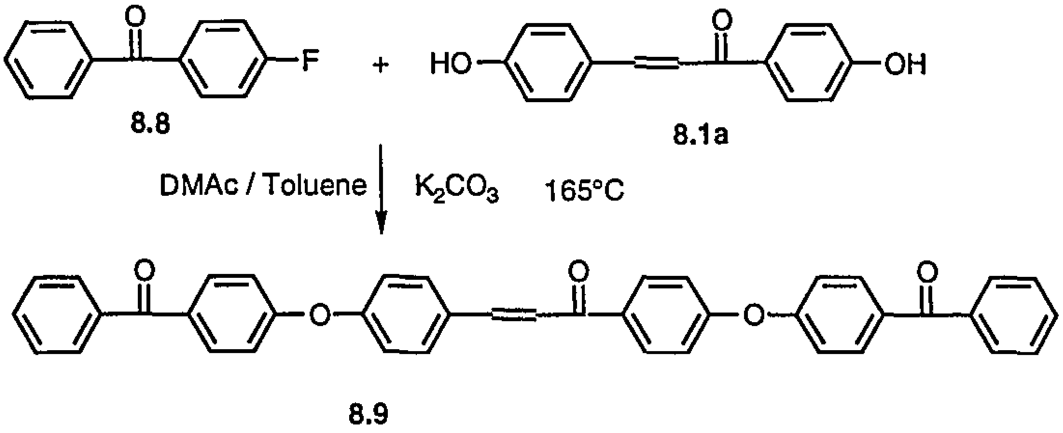
8.2a R = OH
8.2b R = CH_3O

8.3a R = OH
8.3b R = CH_3O

Scheme 8.4


HO
CH3
+
OHC
CHO
8.4
8.5
1, KOH/CH3CH2OH
2, HCl
HO
OH
8.6
H2NNH2H2O
CH3CH2OH
HO
N-N
H
N-N
H
OH
8.7

Scheme 8.5



Scheme 8.6

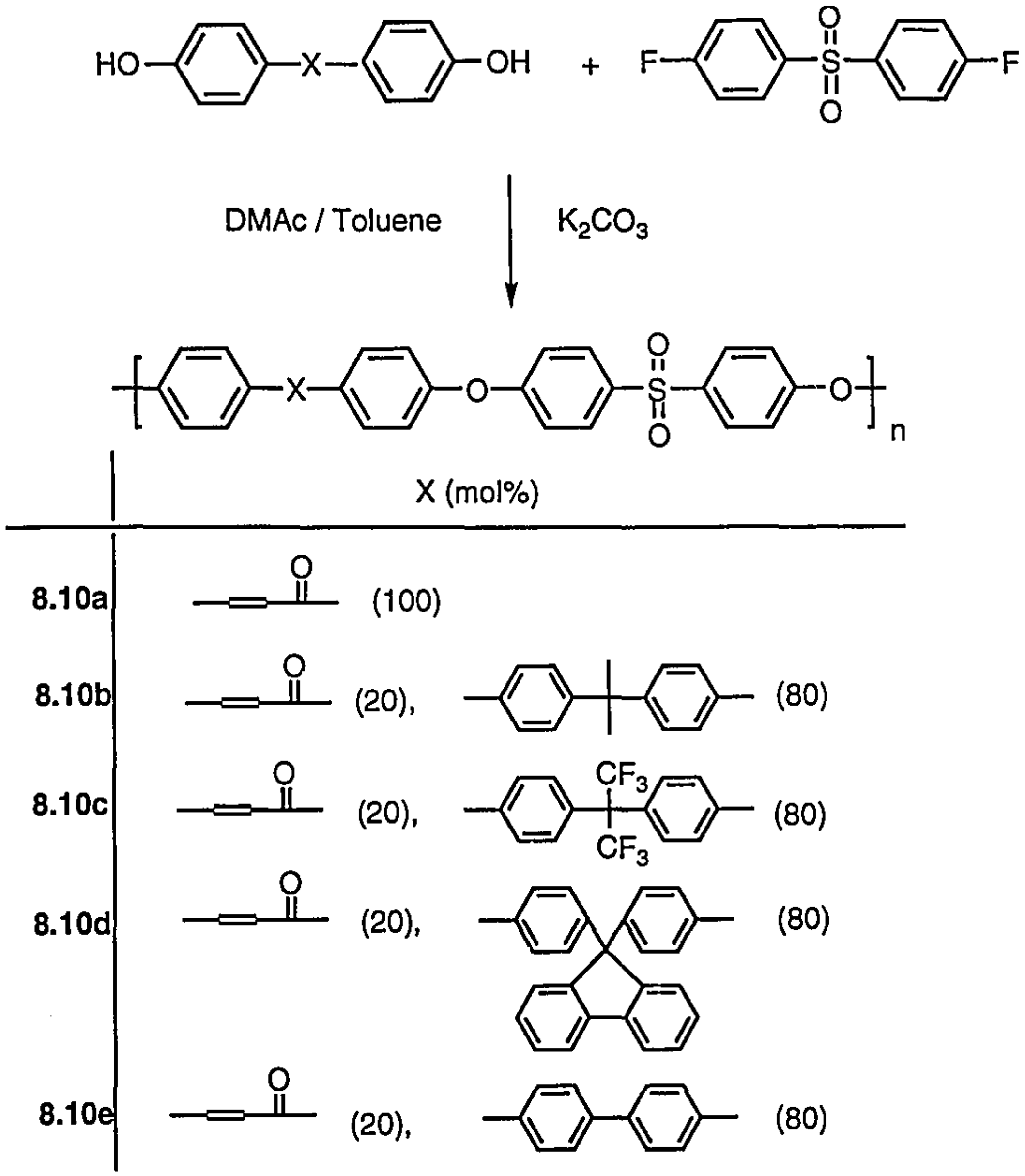
chosen because, in this system, excess potassium carbonate does not prevent the synthesis of high molecular weight macromolecules.[18]

A model reaction (Scheme 8.6) for condensation polymerization was performed under the polymerization conditions used. The reaction of 4,4'-dihydroxychalcone 8.1a and 4-fluorobenzophenone 8.8 in DMAc at 165°C for 2 hours in the presence of potassium carbonate afforded bis[4-(4-benzoylphenoxy)phenyl]-1,3-prop-2-en-1-one 8.9 in quantitative yield (by HPLC). Compound 8.9 was isolated from the reaction mixture, purified and characterized.

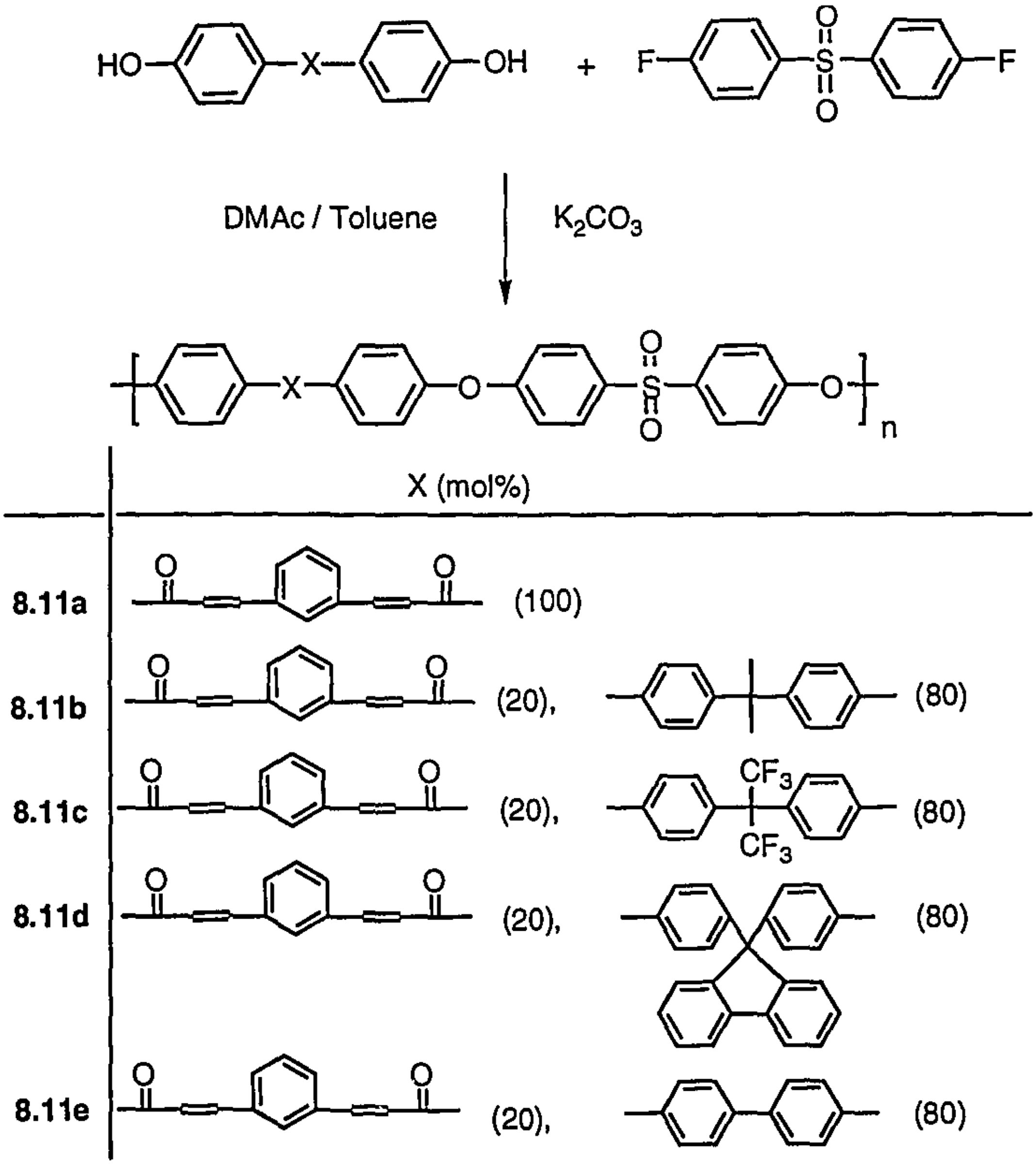
By comparing with the ^{13}C NMR spectrum of 4,4'-dihydroxychalcone **8.1a**, the peaks in the ^{13}C NMR spectrum of compound **8.9** were assigned. A peak at 187.50 ppm for the carbonyl group, a peak at 143.29 ppm for the ethylene carbon bonded to benzene, and a peak at 122.23 ppm for the other ethylene carbon bonded to carbonyl group in the chalcone moiety appeared in the ^{13}C NMR spectrum of 4,4'-dihydroxychalcone **8.1a.** The ^{13}C NMR spectrum of compound **8.9** shows a peak at 188.62 ppm which we have assigned to the carbonyl carbon, a peak at 143.71 ppm assigned to the ethylene carbon bonded to benzene, and a peak at 121.02 ppm assigned to the other ethylene carbon bonded to carbonyl group in the chalcone moiety. The ^{13}C NMR studies indicated no any change in chalcone group when the model reaction was done in DMAc at 165°C in the presence of potassium carbonate, therefore it was concluded that 4,4'-dihydroxychalcone **8.1a** can be polymerized by condensation polymerization under these conditions.

4,4'-Dihydroxychalcone **8.1a** was polymerized with bis(4-fluorophenyl)sulfone to give a poly(ether sulfone) **8.10a** in DMAc in the presence of excess (20%) anhydrous potassium carbonate (**Scheme 8.7**). A series of copolymers **8.10b-e** was also synthesized from 4,4'-dihydroxychalcone **8.1a,** bisphenols and 4,4'-bis(4-fluorophenyl)sulfone under the same conditions. The structure of all polymers were determined by ^{1}H and ^{13}C NMR. The ^{1}H NMR spectrum of homopolymer **8.10a** shows multiple peaks in the range of 7.19-8.22 ppm and no peaks in the aliphatic region. The ^{13}C NMR spectrum of homopolymer **8.10a** exhibits a peak at 187.94 ppm for the carbonyl group, a peak at 143.31 ppm for the ethylene carbon bonded to benzene ring and the other peaks for the remaining carbons in the polymer backbone.

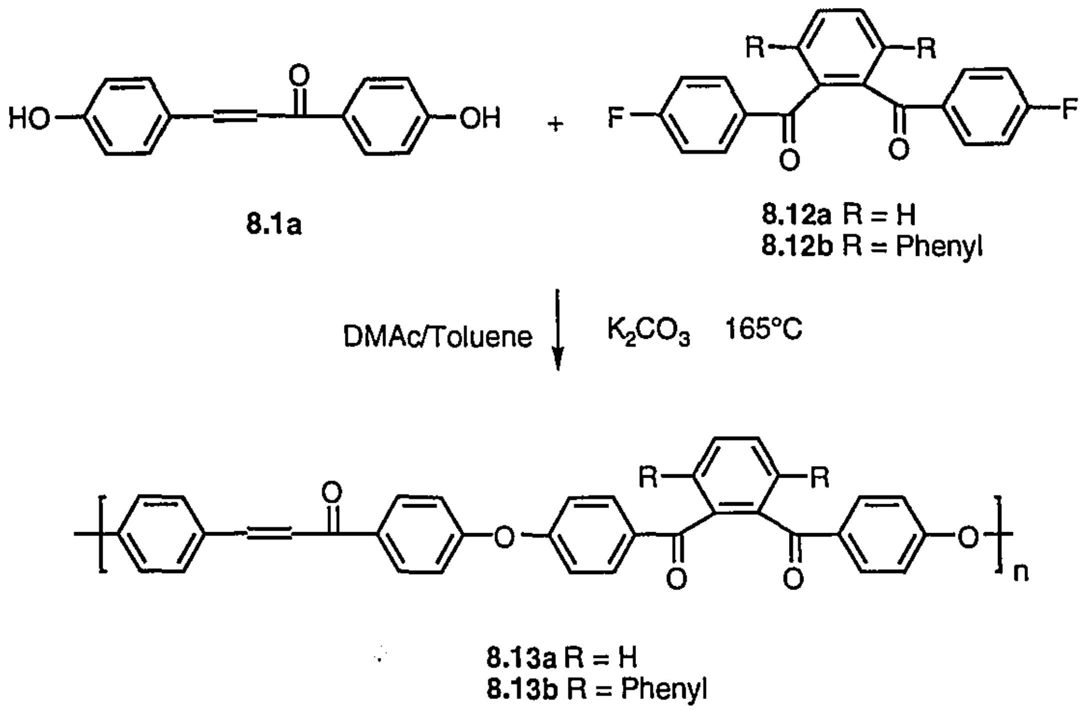
A homopolymer **8.11a** was obtained from the condensation polymerization of 1,3-bis(4-hydroxycinnamoyl)benzene **8.6** and 4,4'-bis(4-fluorophenyl)sulfone using DMAc as solvent in the presence of excess (20%) anhydrous potassium carbonate (**Scheme 8.8**). Several copolymers **8.11b-e** were also prepared from 1,3-bis(4-hydroxycinnamoyl)benzene **8.6,** bisphenols and 4,4'-bis(4-fluorophenyl)sulfone under the same conditions. The structure of all polymers were determined by ^{1}H and ^{13}C NMR. The chalcone group in the polymer backbone was identified by comparison of the ^{13}C NMR spectra of monomer **8.6** and the polymers. A peak at 187.00 ppm for the carbonyl group, a peak at 143.20 ppm for the ethylene carbon, and the other peaks in a range of 160.00-110.00 ppm for the remaining carbons were observed in the ^{13}C NMR



Scheme 8.7


HO
X
OH
+
F
S
O
O
F
DMAc / Toluene
K2CO3
X
O
S
O
O
O
n
X (mol%)
8.11a
(100)
8.11b
(20),
(80)
8.11c
(20),
CF3
CF3
(80)
8.11d
(20),
(80)
8.11e
(20),
(80)

Scheme 8.8



8.1a

8.12a R = H
8.12b R = Phenyl

8.13a R = H
8.13b R = Phenyl

Scheme 8.9

spectrum of monomer **8.6**. Therefore, in the ^{13}C NMR spectrum of hompolymer **8.11a,** a peak at 188.05 ppm was assigned to the carbonyl carbon, a peak at 143.65 ppm was assigned to the ethylene carbon bonded to the benzene ring in the chalcone moiety and the remaining peaks at 160.00 -110.00 ppm for the other carbons in the polymer backbone.

Poly(ketone)s **8.13a-b** were synthesized from 4,4'-dihydroxychalcone **8.1a** and 1,2-bis(4-fluorobenzoyl)benzene **8.12a** or 1,2-di(4-fluorobenzoyl)-3,6-diphenylbenzene **8.12b** utilizing DMAc as solvent, potassium carbonate as catalyst under the same conditions used to synthesize the poly(sulfone)s **(Scheme 8.9).**

The ^{13}C NMR spectrum of homopolymer **8.13a** exhibits a peak at 195.22 ppm for the carbonyl group in the dibenzoylbenzene moiety, a peak at 188.56 ppm for the carbonyl group and a peak at 143.66 ppm for the ethylene carbon bonded to the benzene ring in the chalcone moiety, and the other peaks at 160.86-115.45 ppm for the rest of carbons in the polymer backbone. A similar ^{13}C NMR spectrum was obtained for homopolymer **8.13b**.

8.2.3 Properties of chalcone containing polymers

The properties of the chalcone containing polymers are listed in **Table 1**. The hompolymer **8.10a** from 4,4'-dihydroxychalcone **8.1a** is not soluble in chloroform, but is soluble in hot DMAc, DMSO and NMP. A flexible and transparent film can be obtained by casting a DMAc solution of homopolymer **8.10a** at 100°C. The homopolymer **8.11a** from the monomer **8.6** and 4,4'-bis(4-fluorophenyl)sulfone is soluble in both chloroform and DMAc, DMSO, NMP. A flexible and transparent film was cast from a chloroform solution of homopolymer **8.11a** at room temperature. Polyketones **8.13a-b** synthesized from 4,4'-dihydroxychalcone **8.1a** and 1,2-bis(4-fluorobenzoyl)benzene **8.12a** or 1,2-di(4-fluorobenzoyl)-3,6-diphenylbenzene **8.12b** are more soluble in chloroform, DMAc, DMSO and NMP than polysulfone **8.10a** from 4,4'-dihydroxychalcone **8.1a** and 4,4'-bis(4-chlorophenyl)sulfone. The polymers **8.13a-b** are soluble in chloroform and the flexible and transparent films were cast from chloroform solution at room temperature. All polysulfone copolymers from 4,4'-dihydroxychalcone **8.1a** as well as the monomer **8.6** are soluble in chloroform, DMAc, DMSO and NMP at room temperature, except the copolymers **8.10e** and **8.11e** containing the biphenyl moiety which are only soluble in hot DMAc, DMSO or NMP. All copolymers are amorphous and gave flexible and transparent films.

All polymers are high molecular weight. The inherent viscosities of the polymers are in the 0.30-0.62 dL/g range. The molecular weight distribution of the polymers was determined by gel permeation chromatography (GPC) based on polystyrene standards. GPC results are consistent with their inherent viscosities. Polydispersities of these polymers are less than three suggesting that the polymerization reaction proceeds without any unusual termination reactions that might be ascribed to the chalcone moiety.

All of the polymers are amorphous, since they undergo a glass transition in the range of 150-266°C and show no melting endotherm in their DSC scan. The homopolymers **8.10a** from 4,4'-dihydroxychalcone **8.1a,** as well as the polymer **8.11a** from the monomer **8.6,** have a Tg at 190°C which is close to the Tg of polysulfone from BPA. The thermogravimetric analysis of these chalcone containing polymers in nitrogen and air shows no significant weight loss (-5%) before 420°C. The polymers are thermally more stable if the chalcone moiety is replaced by biphenyl, 1,1,1,3,3,3-hexafluoro-2,2-diphenylpropane or the fluorenone moiety in all cases. The polymers containing the biphenyl moiety are the most stable among these polymers.

8.2.4 Cross-linking studies

The DSC scan of homopolymer **8.10a** is shown in **Figure 8.1.** In addition to a Tg at 190°C, a large exotherm, associated with the cross-linking reaction which begins at 300°C and reaches a maximum at 413°C, was observed in the DSC scan of polymer **8.10a.** The cross-linking reaction proceeds readily at 350°C. Similar results were observed in the DSC scans of homopolymers **8.11a, 8.13a** and **8.13b.** If polymer **8.10a, 8.11a , 8.13a, 8.13b** are cured at 350°C under nitrogen for longer than 30 minutes no Tg is detected in the DSC scans of the cured polymers. The Tg of polymer **8.10a** increased to 243°C after being cured at 300°C for 30 minutes. No Tg was observed in the DSC scan of polymer **8.11a** after it was cured at 300°C for 30 minutes.

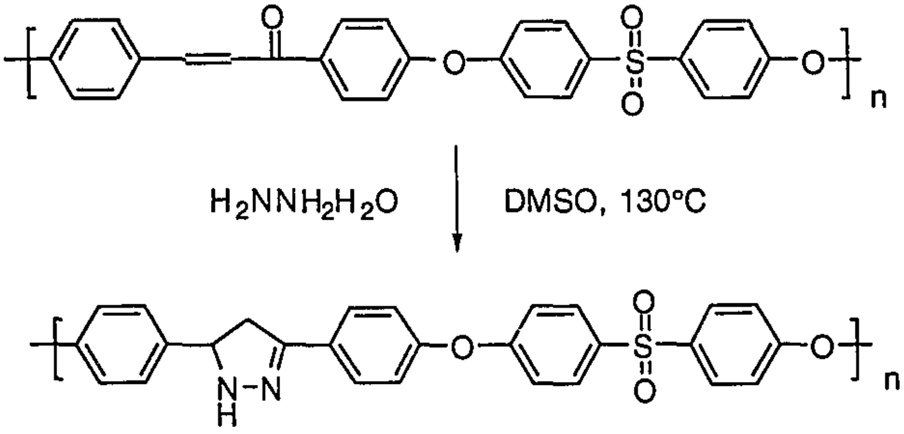
Thermal analysis is frequently used to characterize cross-linked polymers. It is well known that the Tg rises while the difference in specific heat capacity (ΔCp) at Tg decreases with increasing numbers of cross-links. The effect of curing time on the Tg **(Figure 8.2)** of the poly(ether sulfone) copolymers containing 20 mole per cent of chalcone moieties, and the difference in specific heat capacity (ΔCp) **(Figure 8.3)** at Tg has been studied. After copolymers **8.10b-e** were cured at 350°C under nitrogen in the TGA instrument for different time periods the cured polymers were examined in the DSC to determine the Tg increase and ΔCp decrease. It was found that ΔCp decreased rapidly and Tg increased as curing time increased as a result of the cross-linking of the polymers. After one hour the changes in ΔCp and Tg slowed down significantly.

The Tgs of all polymers after curing at 350°C for 2 h under nitrogen are listed in Table 8.1. A higher increase in Tg was found for the polymers from 1,3-bis(4-hydroxycinnamoyl)benzene **8.6** than the other polymers from 4,4'-dihydroxychalcone **8.1a.**

The solvent resistance of all cured polymers was to certain extent improved significantly. All cured polymers are insoluble in all solvent tried. The cured copolymers swelled while the cured homopolymers did not swell in chloroform.

8.2.5 Conversion of polychalcone to polypyrazoline

The reaction of polychalcone **8.10a** and hydrazine monohydrate in DMSO at 100°C for 6 h afforded polypyrazoline **8.14** **(Scheme 8.10)**. Polychalcone **8.10a** is less soluble in chloroform and soluble in hot DMSO. Therefore DMSO was chosen as solvent. The resulting polypyrazoline **8.14** is more soluble in DMSO than precursor polychalcone **8.10a.** The ^1H NMR spectrum of polypyrazoline **8.14** is shown in Figure 4. A triplet at 4.90 ppm for the benzylic protons in the 2-pyrazoline moiety and two sets of multiplets at 3.60-2.80 ppm for the methylene protons were found in the ^1H NMR spectrum of polypyrazoline **8.14.**



8.14

Scheme 8.10

The DSC scan of polypyrazoline **8.14** is shown in **Figure 8.5**. A Tg at 234°C and an exotherm was observed in the DSC scan of polymer **8.14.** Thermogravimetric analysis of polymer **8.14** under nitrogen shows a 5% weight loss at 403°C. Heating polymer **8.14** at 300°C for more than 30 minutes in the presence of a catalytic amount of sodium hydroxide under nitrogen afforded a cross-linked polymer. It was observed that gas was generated during the heating.

8.3 Conclusions

High molecular weight poly(aryl ether)s containing internal chalcone groups have been synthesized from 4,4'-dihydroxychalcone and 1,3-bis(4-

hydroxycinnamoyl)benzene by solution polycondensation. The polymers can be thermally cross-linked when heated to above 350°C and the glass transition temperatures (Tg) of the polymers increase after cross-linking. The resulting cross-linked networks are insoluble in all organic solvents tried. Thermogravimetric analysis shows that no significant weight loss accompanies the cross-linking reaction. Those polymers can be converted into polypyrazolines by reacting with hydrazine monohydrate.

Table 8.1

Properties of chalcone containing polymers from 4,4'-dihydroxychalcone

polymers	η_{inh}[a] (dL/g)	Mw/Mn[b] x10^{-4}	Tg[c](°C) (uncured)	Tg[d](°C) (cured)	TGA[e](°C) N_2/Air
8.10a	0.54		190	ND	435/430
8.10b	0.43	7.01/2.96	188	208	446/435
8.10c	0.62	10.3/5.22	197	222	474/467
8.10d	0.38	6.81/2.74	266	296	450/447
8.10e	0.34	-	219	256	480/473
8.11a	0.32	6.53/2.42	190	ND	422/420
8.11b	0.55	8.35/2.78	188	222	428/424
8.11c	0.30	6.02/2.49	176	223	472/471
8.11d	0.46	8.01/3.15	255	295	448/432
8.11e	0.31	-	206	266	469/465
8.13a	0.36	6.62/2.32	150	ND	434/432
8.13b	0.52	8.21/2.44	207	ND	450/436

[a] 0.5 g/dL in $CHCl_3$ at 25°C or in DMAc at 50°C. [b] based on polystyrene standards. [c] DSC, heating at 10°C / min. [d] after curing for 2 h at 350°C under nitrogen, DSC, heating at 10°C / min. [e] TGA, heating at 10°C / min.

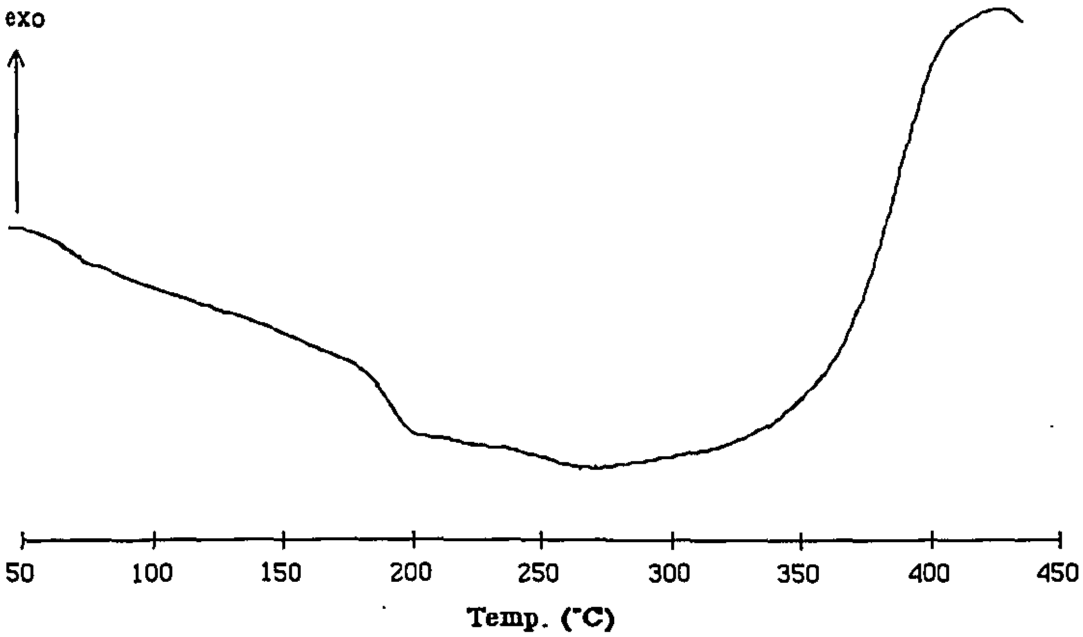


Figure 8.1 DSC scan of homopolymer **8.10a**

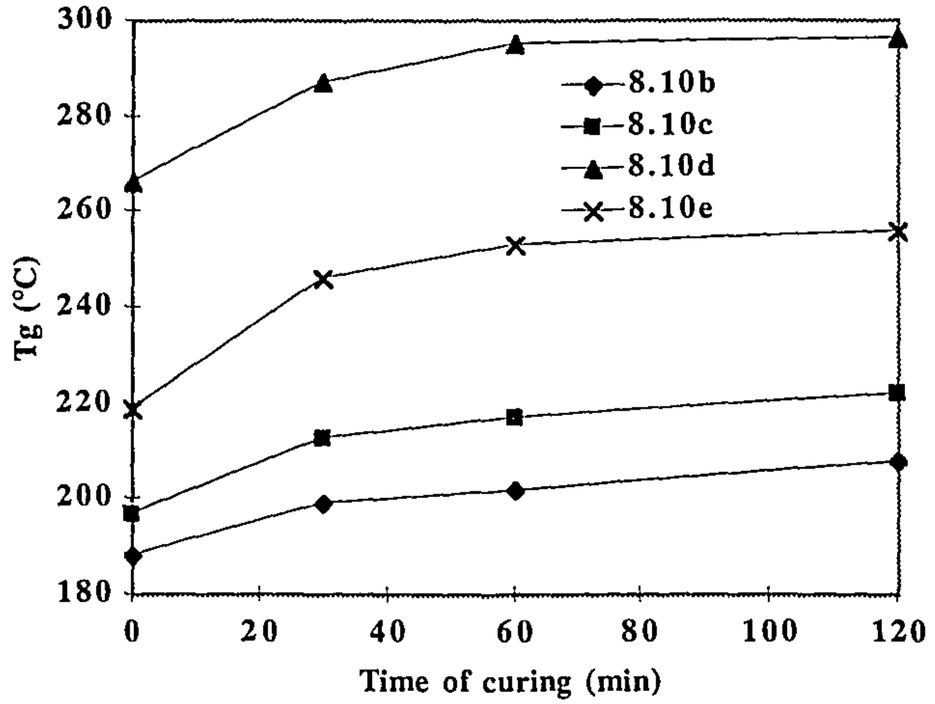


Figure. 8.2 DSC scans showing the effect of curing time on Tg (350°C under nitrogen, heating rate 10°C / min.)

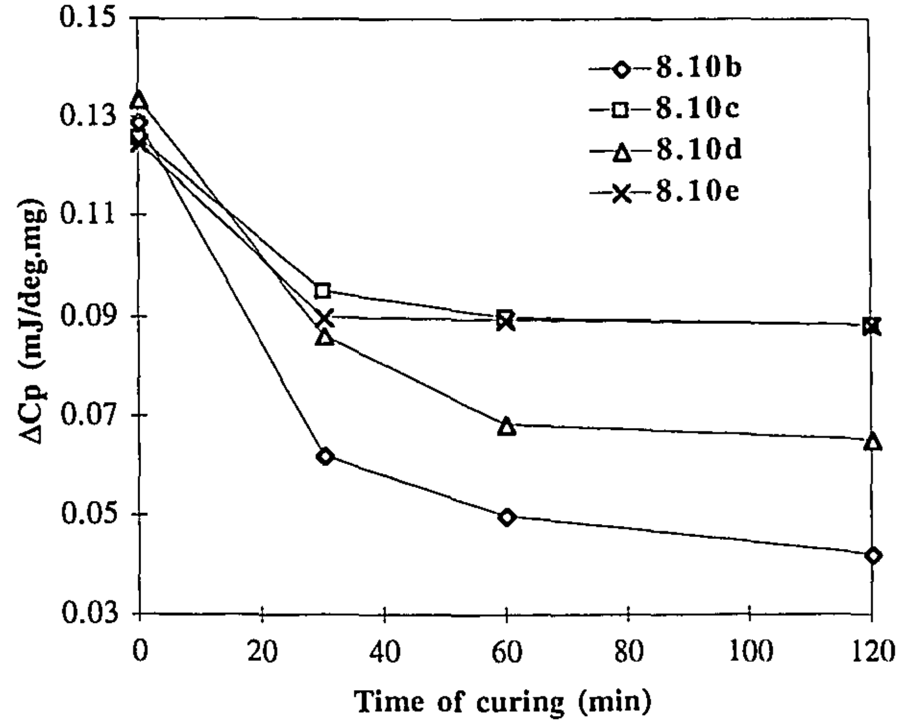


Figure. 8.3 Effect of curing time on ΔCp at Tg (350°C under nitrogen, ΔCp at Tg was obtained in a DSC).

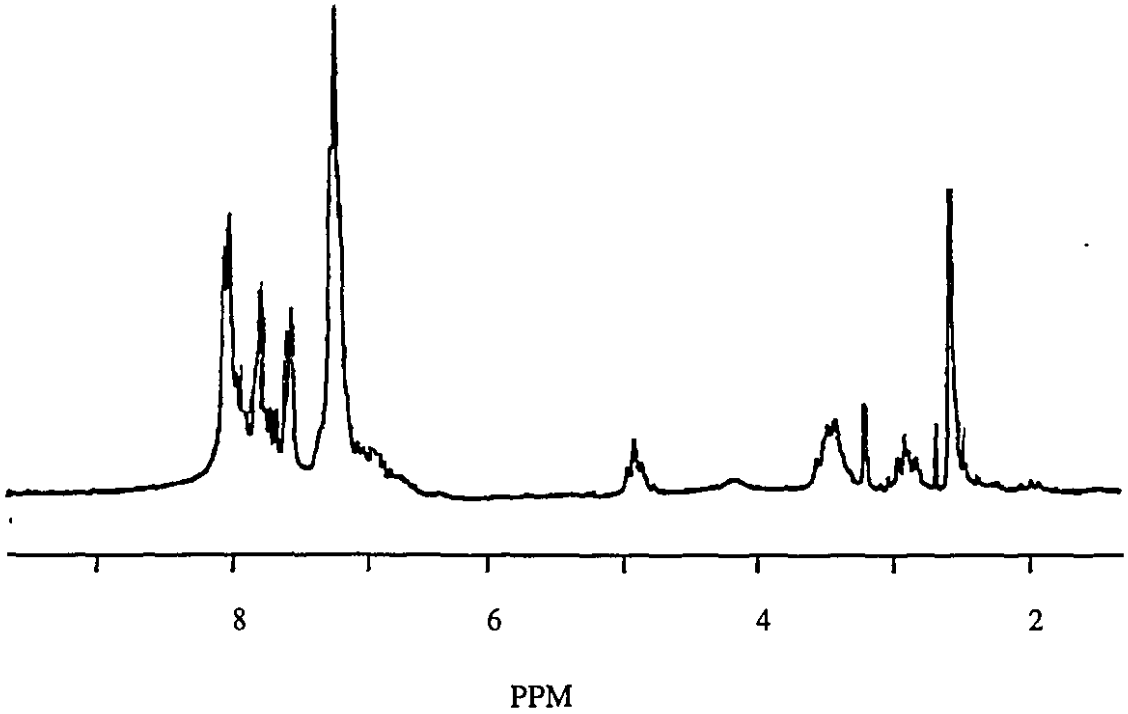


Figure 8.4 ^{1}H NMR spectrum of homopolymer **8.14**

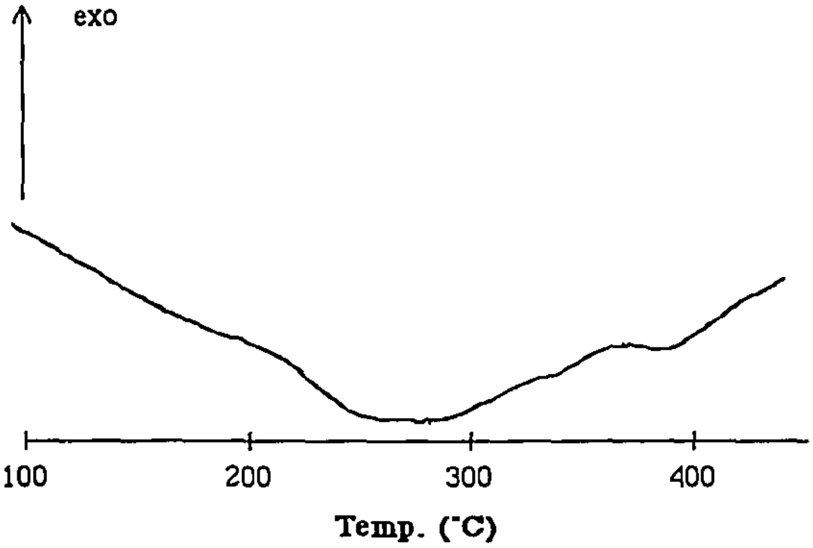


Figure 8.5 DSC scan of homopolymer **8.14**

8.4 Experimental

4,4'-Dihydroxychalcone (8.1a). It was synthesized according to the previously described method[16, 17], mp 203-205°C (203.5 - 204.0°C[3]); ^{1}H NMR (DMSO-d_6) δ6.75-6.95 (two d, 4H), 7.60-7.75 (d, 2H), 7.70 (s, 2H), 7.98-8.06 (d,2H), 10.22 (s, 2H).

Trans-3,5-bis(4-hydroxyphenyl)-2-pyrazoline (8.2a).

To a solution of 30.7 g (128 mmol) of 4,4'-dihydroxychalcone in 300 mL of ethanol, 30 mL (618 mmol) of hydrazine monohydrate was added. The resulting solution was refluxed for 1.5 h. Ice water was then added. The precipitate was collected, dried and crystallized from ethanol; yield > 90%; mp 183-185°C; ^{1}H NMR (CD_3OD) δ 2.90–3.45 (octet, 2H), 4.70-4.80 (t, 1H), 6.74-6.83 (two d, 4H), 7.18-7.22 (d, 2H), 7.51-7.56 (d, 2H). MS m/z 254 (M^+, 100), 161 (30), 134 (15), 120 (20). Calcd. for $C_{15}H_{14}N_2O_2$ (254.29): C, 70.85; H, 5.55. Found: C, 70.10; H, 5.75.

Trans-1,2-bis(p-hydroxyphenyl)cyclopropane (8.3a)

1.0 g (3.9 mmol) of trans-3,5-bis(4-hydroxyphenyl)-2-pyrazoline **(8.2a)** was mixed with 1.0 g of powdered sodium hydroxide. The mixture was heated to 250°C under nitrogen and the decomposition proceeded for 30 min. The cooled reaction product was dissolved in water, neutralized with hydrochloric acid and extracted with ether. The ether layer was washed with water to remove salts . Removal of the ether left the product which was crystallized from acetic acid; mp 190-191°C; ^{1}H NMR (DMSO-d_6) δ1.1.16-1.22 (t, 2H), 1.80-1.98 (t, 2H), 6.60-6.70 (d, 4H), 6.90-6.96 (d, 4H), 9.15 (s, 2H). MS m/z 226 (M^+, 100), 131 (15), 121 (45), 107 (20). Calcd. for $C_{15}H_{14}O_2$ (226.27): C, 79.62; H, 6.24. Found: C, 79.40; H, 6.24.

1,3-Bis(4-hydroxycinnamoyl)benzene 8.6

5.446 g (40 mmol) of 4-hydroxyacetophenone **8.4** and 2.68 g (20 mmol) of isophthalaldehyde **5** were dissolved in 80 mL of boiling alcohol. To this solution at 55°C was added 26 mL of 60% potassium hydroxide solution and the clear solution was allowed to stand at room temperature for one week. The mixture set to a mass of solids; it was worked up by acidification in the cold and recrystallization of the product from alcohol; yield 80-85%. m.p.165-167°C. ^{1}H NMR (200 MHz,DMSO) δ8.10-8.06 (d, 4H), 8.34-6.78 (m, 8H), 6.91-6.86 (d, 4H). MS (m/e, relative intensity %): 370 (M^+, 100).

Pyrazoline 8.7

To a solution of 1.85g (5 mmol) of 1,3-bis(4-hydroxycinnamoyl)benzene **8.6** in 20 mL of ethanol, 2.2 mL of hydrazine monohydrate was added. The resulting solution was refluxed for 1.5 h. Ice water was then added. The precipitate was collected, dried and crystallized from ethanol; yield > 90%; m.p.145-147°C; ^{1}H NMR (200 Mhz, DMSO) δ9.64 (s, 2H), 8.7.45-7.43 (d, 4H), 6.78-6.75 (d, 4H), 7.33-7.22 (m, 4H), 4.75(t, 2H), 3.40-2.72 (octet, 4H). MS (m/e, relative intensity %): 398 (M^+, 100).

Bis[4-(4-benzoylphenoxy)phenyl]-1,3-prop-2-en-1-one 8.9

A mixture of 4,4'-dihydroxychalcone (**8.1a**; 3.0 mmol, 0.7208 g), K_2CO_3 (5.6 mmol, 0.774 g) and 4,4'-difluorobenzophenone **8.8** (6.0 mmol, 1.2013 g) in toluene (4 mL) and N,N'-dimethylacetamide (8 mL, freshly purified) was heated with stirring under nitrogen atmosphere with azeotropic removal of water for 3 h. Some toluene was bled continuously from the Dean-Stark trap until the temperature rose to 155°C. The reaction mixture was lightly colored and was maintained at this temperature for 2 h. At this time the reaction was assumed to be complete. The reaction mixture was cooled to 100°C and diluted with DMAc (5 mL) and filtered. The filtrate was neutralized with acetic acid and coagulated into methanol. The precipitate was filtered and washed with methanolic water and finally with water. It was then boiled in distilled water for 1 h to remove any trapped salts, filtered and dried in a vacuum oven at 80°C; yield > 90%. m.p. 190-191°C. MS (m/e, relative intensity %): 599 (M^+, 1), 301 (100). ^{1}H NMR (500 MHz,DMSO) δ 8.09-7.08(m, 28H). ^{13}C-NMR (500 Mhz, ppm, $CDCl_3$), 1195.39, 188.62, 160.37, 160.08, 159.79, 157.94, 143.71, 132.52, 130.87, 130.34, 129,84, 128.31, 121.02, 119.85, 118.87, 118.78, 118.06,.

Homopolymer 8.10a

A mixture of 4,4'-dihydroxychalcone (**8.1a**; 3.0 mmol, 0.7208 g), K_2CO_3 (5.6 mmol, 0.774 g) and bis(4-fluorophenyl)sulphone (3.0 mmol, 0.7628 g) in toluene (4 mL) and DMAc (8 mL, freshly purified) was heated with stirring under nitrogen atmosphere with azeotropic removal of water for 3 h. Some toluene was bled continuously from the Dean-Stark trap until the temperature rose to 155°C. The reaction mixture was lightly colored and was maintained at this temperature for 2 h. At this time the reaction was assumed to be complete. The reaction mixture was cooled to 100°C and diluted with DMAc (5 mL) and filtered. The filtrate was neutralized with acetic acid and coagulated into methanol. The precipitate was filtered and washed with methanolic water and finally with water. It was then boiled in distilled water for 1 h to remove any trapped salts, filtered and dried in a vacuum oven at 80°C; yield > 90%. ^{1}H NMR (500 MHz,DMSO) δ 8.40-7.60(m, 10H), 7.50-6.8 (m, 8H). ^{13}C-NMR (500 Mhz, ppm, DMSO), 187.94 (carbonyl), 160.35, 159.16, 159.145, 156.76, 143.31, 135.83, 134.27, 131.84, 131.83,131.81, 131.80, 131.56, 131.53, 131.50,, 130.38, 130.33, 121.90, 120.66,119.81, 119.47,119.455, 118.75.

Polymers **8.13a** and **8.13b** were prepared using the same method described above.

Copolymers 8.10b, 8.10c, 8.10d, 8.10e.

A mixture of 4,4'-dihydroxychalcone (**8.1a**; 3.0 mmol, 0.7208 g), the other bisphenol (2.4 mmol), K_2CO_3 (0.774 g) and bis(4-fluorophenyl)sulphone (3.0 mmol, 0.7628 g), toluene (4 mL) and DMAc (8 mL, freshly purified) was treated as described for the synthesis of the homopolymer.

Homopolymer 8.11a

A mixture of 1,3-bis(4-hydroxycinnamoyl)benzene (**8.6a**; 3.0 mmol, 1.112 g), K_2CO_3 (5.6 mmol, 0.774 g) and bis(4-fluorophenyl)sulphone (3.0 mmol, 0.7628 g) in toluene (4 mL) and DMAc (8 mL, freshly purified) was heated with stirring under nitrogen atmosphere with azeotropic removal of water for 3 h. Some toluene was bled continuously from the Dean-Stark trap until the temperature rose to 155°C. The reaction mixture was lightly colored and was maintained at this temperature for 2 h. At this time the reaction was assumed to be complete. The reaction mixture was cooled to 100°C and diluted with DMAc (5 mL) and filtered. The filtrate was neutralized with acetic acid and coagulated into methanol. The precipitate was filtered and washed with methanolic water and finally with water. It was then boiled in distilled water for 1 h to remove any trapped salts, filtered and dried in a vacuum oven at 80°C; yield > 90%. ^{1}H NMR (500 MHz,DMSO) δ 8.29-7.26(m, 24H). ^{13}C-NMR (500 Mhz, ppm, DMSO), 188.05 (carbonyl), 160.43, 159.24, 144.50, 143.65, 136.40, 134.22, 131.64, 131.56, 131.46, 131.18, 130.99, 130.84,130.77, 130.48, 130.44, 122.96, 119.86, 119.83, 119.78, 119.78119.50,119.48, 117.23..

Copolymers 8.11b, 8.11c, 8.11d, 8.11e.

A mixture of 1,3-bis(4-hydroxycinnamoyl)benzene (**8.6a**; 3.0 mmol, 1.112 g), the other bisphenol (2.4 mmol), K_2CO_3 (0.774 g) and bis(4-fluorophenyl)sulphone (3.0 mmol, 0.7628 g), toluene (4 mL) and N,N'-dimethylacetamide (8 mL, freshly purified) was treated as described for the synthesis of the homopolymer.

Characterization of Polymers. Glass transition temperatures of the polymers were obtained using a Seiko 220 DSC instrument at a heating rate of 10°C/min in N_2 (50 mL/min) and Seiko 220 TMA instrument at a heating rate of 3°C/min. When recording Tg values samples were never heated above 300°C, to avoid cross-linking, and the values recorded are from the second scan. The Tg was taken from the midpoint of the change in slope of the baseline. The weight loss data were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 10°C/min in nitrogen and air. Polymer samples were cured at 350°C under nitrogen in the TGA instrument. A DSC was then employed to determine the Tg increase. Inherent viscosity data were obtained with a calibrated Ubbelohde viscometer. The measurements were performed in $CHCl_3$ at 25°C or 50°C with a 1B(205) instrument. Molecular weights were obtained by gel permeation chromatography (GPC) relative to polystyrene standards in chloroform solution using a Waters 510 HPLC instrument equipped with μ–Styragel columns arranged in series and a UV detector. ^1H and ^{13}C-NMR spectra were recorded at 500 MHz using a Varian XL-200 spectrometer in $CDCl_3$ with $(CH_3)_4Si$ as the internal standard.

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Chapter 9

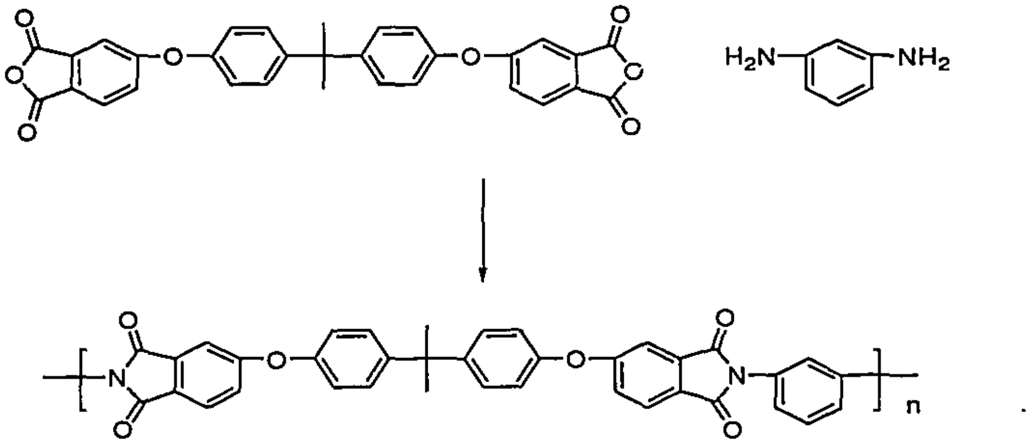
Thermally Cross-linkable Polyimides Containing the 1,2-Diphenylcyclopropane or Diphenylacetylene moiety

9.1 Introduction

Polymers containing heterocyclic rings in the main chain are becoming increasingly important industrially, due to the attractive combination of properties conferred by the presence of these heterocyclic units. In particular, aromatic heterocyclic polyimides exhibit excellent properties with outstanding mechanical properties and oxidative stability, and are of major commercial and industrial importance.[1,2] Polyimides are widely used in place of metals and glass in high performance applications throughout the electronics, automotive, aerospace, and packaging industries.[3-5]

Aromatic polyimides have developed rapidly in recent years due to their outstanding properties.[1,2,6] However, their applications have been limited in many fields because aromatic polyimides are normally insoluble in common organic solvents. The rigid structures have high glass transition temperatures or crystalline melting points and very poor solubility which are important drawbacks to their use. Several soluble polyimides systems have been described. Kurita [7] demonstrated that the introduction of bipyridyl units into the polymer chain enhanced the solubility of the polymers. Takekoshi et al [8,9] have synthesized bisphthalic dianhydrides by the condensation of BPA and 4-nitro-N-methyl phthalimide followed by conversion to the dianhydride, which is polymerized with *meta*-phenylenediamine to give ULTEM®

resin which shows excellent solubility (Scheme 9.1). Harris [10] reported soluble polyimides through the introduction of trifluoromethyl substituents in the 2,2' positions on biphenyl, which forces the aromatic rings into noncoplanar conformation providing good solubility.



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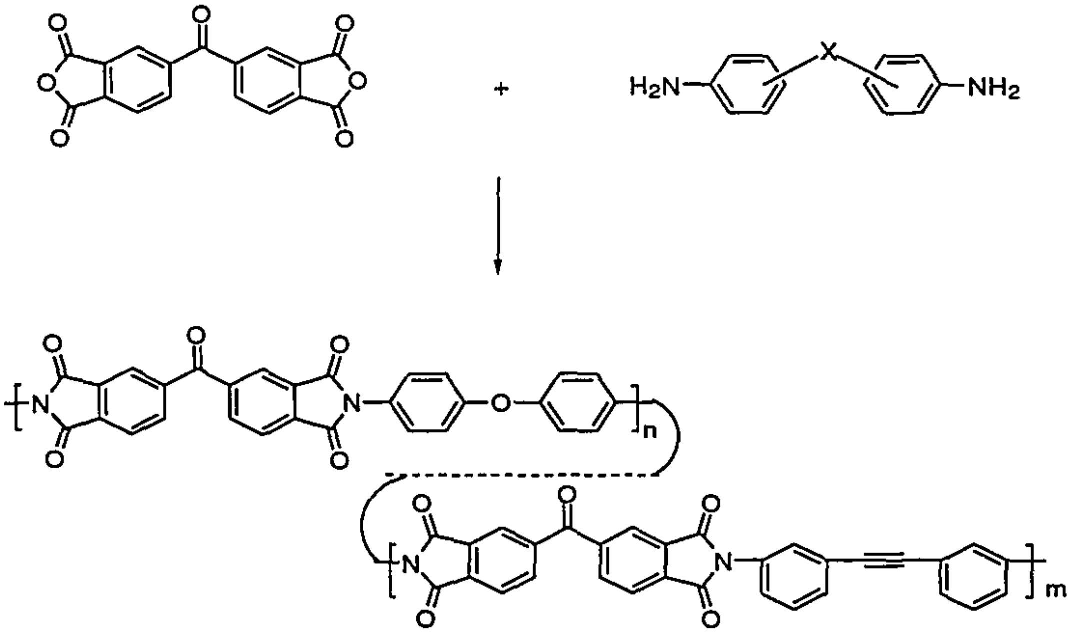
Scheme 9.1



Scheme 9.2

Polyimide copolymers have been synthesized by using bis(3-aminophenyl)acetylene to replace some of the diamines (Scheme 9.2)[11]. The effect of cross-linking of the acetylene moieties on the thermal stability of the polyimides was investigated. When all of these polymers are heated, a strong exothermic reaction takes place with the resulting cross-linking of the polymers. Thermal curing of polyimides containing these internal acetylene groups linked by meta aromatic units afforded polyimides with much improved thermal stability.

The objective of this research is the synthesis of high molecular weight amorphous and soluble polyimides containing internal reactive groups which can undergo thermal reaction resulting in cross-linking of the polymers. We demonstrated that diphenylacetylene containing poly(aryl ether)s[12] and poly(aryl ether sulfone)s, polyesters, polyformals, cyclic aryl ether ketone oligomers and polyphenylene oxides containing 1,2-diphenylcyclopropane groups[13-14] are thermally cross-linkable polymers. After cross-linking, the solvent resistance and glass transition temperatures of the polymers increase. Herein the synthesis of polyimides containing the 1,2-diphenylcyclopropane or diphenylacetylene moiety will be discussed.

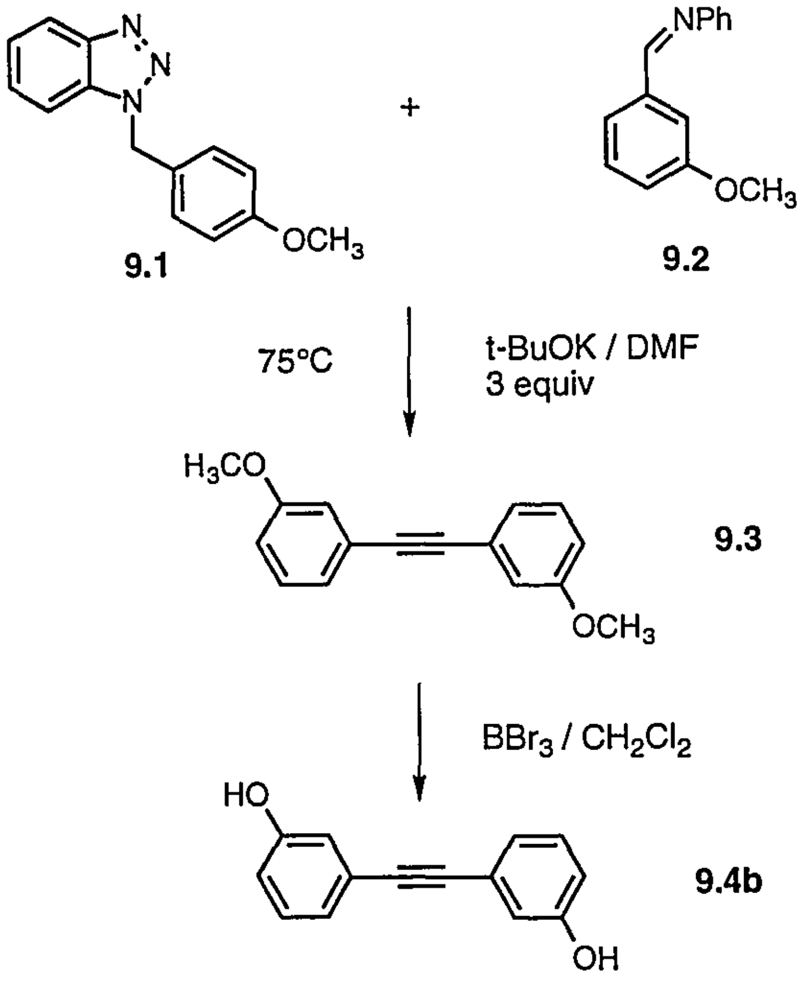
9.2 Results and discussion

9.2.1 Synthesis of monomers

The monomer 1,2-bis(4-hydroxyphenyl)cyclopropane **9.4a** was synthesized by catalytic decomposition of the corresponding hydroxyl substituted 3,5-diphenyl-2-pyrazolines which were the products of the reaction between hydroxychalcones and hydrazine monohydrate according to the simple method we reported recently.[15]

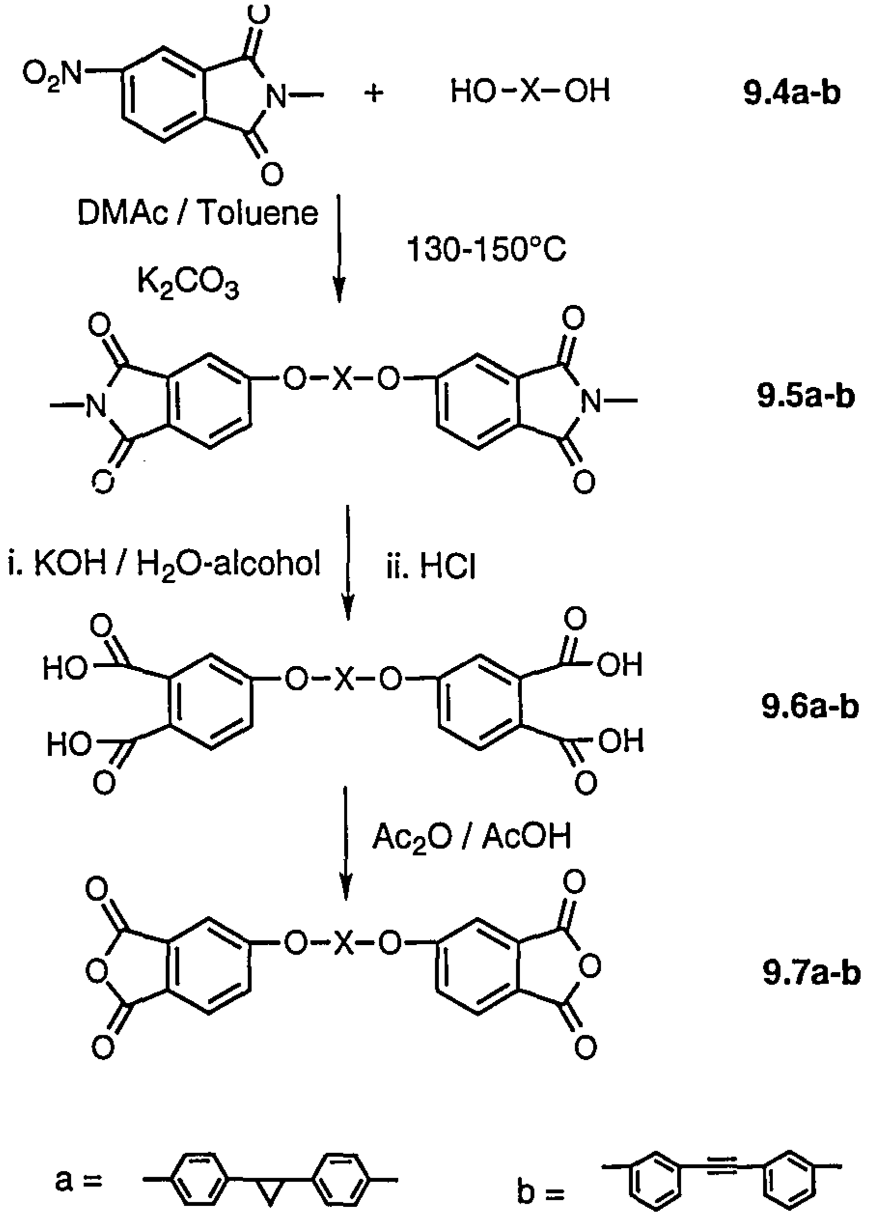
1,1'-(1,2-ethynediyl)bis[3-methoxybenzene] **9.3** was prepared by the reaction of (3-methoxyphenyl)methyl-(1*H*-)benzotriazole **9.1** with N-[(3-

methoxyphenyl)methylene]benzenamine **9.2** (Scheme 9.3)[12]. The demethylation of 1,1'-(1,2-ethynediyl)bis[3-methoxybenzene] **9.3** with BBr_3 in methylene chloride afforded bis(3-hydroxyphenyl)acetylene **9.4b** in high yield.



Scheme 9.3

Recently there has been a considerable effort directed at the nitro displacement reaction by Takekoshi et al.[8-9] They found that nitro displacement of N-phenyl-3 or 4-nitrophthalimide and various bisphenol salts proceeds readily in polar aprotic solvents to form bisetherimides in high yields. The nitro displacement of 4-nitro-N-methylphthalimide with bisphenol A in polar aprotic solvents such as DMF in the presence of solid sodium hydroxide pellets or powdered anhydrous potassium carbonate and 4Å molecular sieves at 145°C was also reported to afford bisetherimides in a very simple way.[16-17]



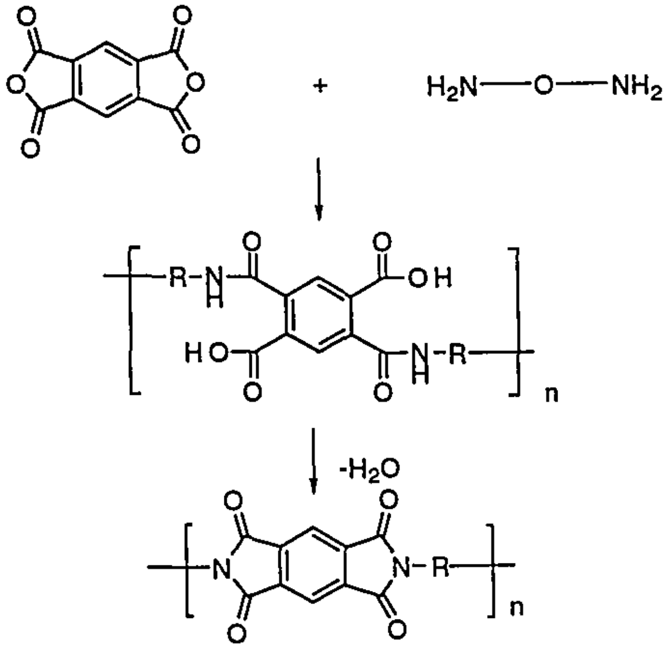
Scheme 9.4

Bis(ether imide)s **9.5a** and **9.5b** (Scheme 9.4) were synthesized by aromatic nitro-displacement of 4-nitro-N-methylphthalimide with the potassium salts of bis(4-hydroxyphenyl)cyclopropane **9.4a** and bis(3-hydroxyphenyl)acetylene **9.4b** in DMAc at 140°C. The potassium salts of bis(4-hydroxyphenyl)cyclopropane and **9.4a** bis(3-hydroxyphenyl)acetylene **9.4b** were prepared by refluxing bis(4-hydroxyphenyl)cyclopropane **9.4a** and bis(3-hydroxyphenyl)acetylene **9.4b** with sodium carbonate in toluene and DMAc for 3 hours at 130°C in a three neck round bottom flask equipped with a Dean-Stark trap which was used to remove water produced in the reaction.

The bis(ether imide)s **9.5a** and **9.5b** were hydrolyzed in the conventional manner in an aqueous sodium hydroxide solution containing alcohol for 3-5 hours at reflux temperature to the corresponding tetracarboxylic acids **9.6a, 9.6b** in quantitative yield. The anhydrides **9.7a, 9.7b** were formed via a ring closing reaction of the dicarboxylic acid in the presence of a dehydrating agent such as acetic anhydride.

9.2.2 Preparation of polymers

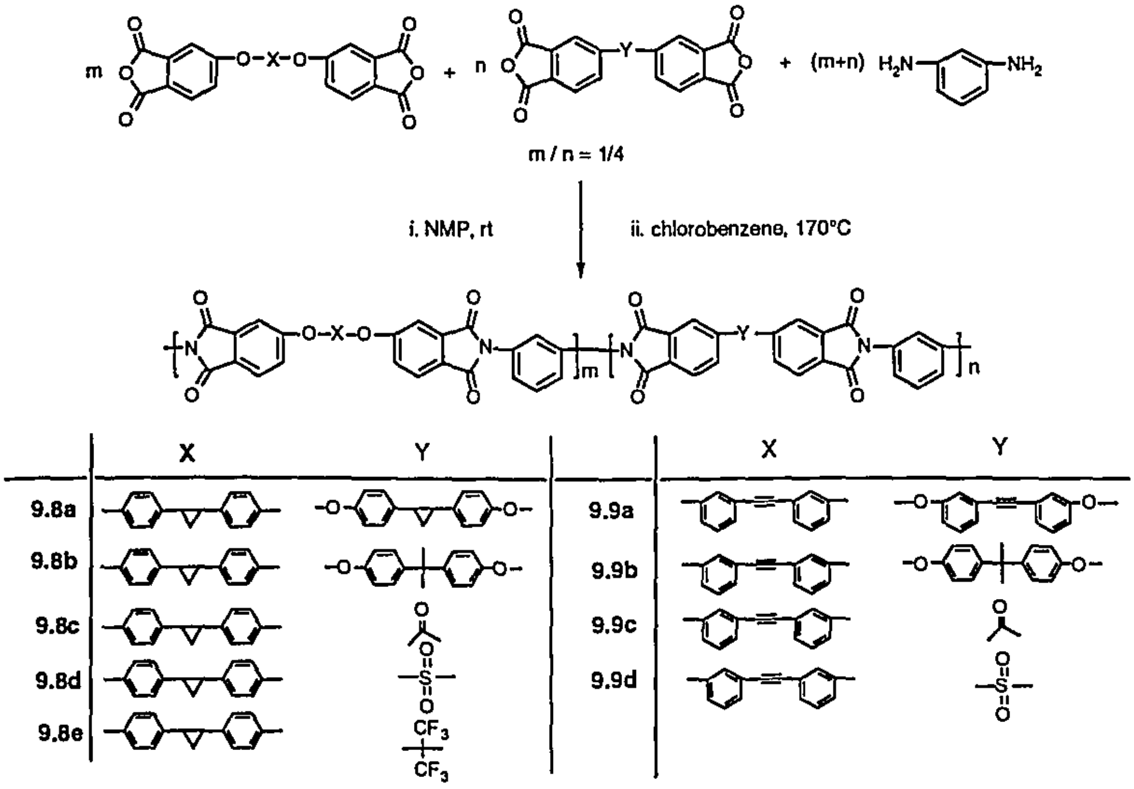
Aromatic polyimides are usually insoluble and infusible so that the polymer either precipitates out of solution, or in a melt process solidifies during the reaction. Therefore, most polyimides are preferably formed in two discrete steps (Scheme 9.5) with isolation of the intermediate polyamic acid, followed by heating to cyclize at high temperature[18-20]. The first stage consists in the acylation of the diamine by a dianhydride in a polar solvent such as NMP, DMSO, DMAc and DMF with the formation of the polyamic acid. The second stage of the reaction, imidization, is carried out thermally or chemically.



Scheme 9.5

We were able to successfully react the bisanhydrides **9.7a** and **9.7b** with *meta* phenylenediamine in NMP to polyamic acids (Scheme 9.6). The polyamic acids were converted to the corresponding poly(ether imide)s by dehydration. The liberated water was removed by azeotropic distillation with toluene. The reaction was maintained at 170°C for 5 hours. In addition to the homopolymers **9.8a** and **9.9a**, some copolymers were also prepared from bisanhydrides **9.7a** or **9.7b**

The ^{1}H NMR spectrum of homopolymer **9.8a** has a triplet at 2.20-2.00 ppm for the benzylic protons, another triplet at 1.90-1.84 ppm for the methylene protons in the cyclopropane moiety and a set of multiple peaks at 7.91-6.47 ppm for the rest of aromatic protons in the polymer backbone. The ^{1}H NMR spectrum of homopolymer **9.9a** shows no peaks in the region for aliphatic protons and multiple peaks at 8.00-6.50 ppm for all aromatic protons. The ^{13}C NMR spectrum of homopolymer **9.9a** exhibits a peak for the acetylene carbons in the backbone of the polymer at 90.00 ppm.



Scheme 9.6

9.2.3 Properties of polyimides containing the diphenylcyclopropane or diphenylacetylene moiety

The properties of polyimides containing the diphenylcyclopropane or diphenylacetylene moiety are summarized in Table 9.1. All polymers are soluble in DMSO, DMAc, DMF and NMP. Poly(ether imide)s with inherent viscosities in the 0.25-0.35 dL/g range and with Tg's in the range from 150 to 261°C were prepared. Thermogravimetric analyses of these polymers show no significant weight loss (-5%)

occurs before 424°C in nitrogen. All of the polymers are amorphous, since they undergo a glass transition in the range of 150-261°C and show no melting endotherm in their DSC scan.

9.2.4 Cross-linking studies

The DSC scan of homopolymer **9.8a** is shown in **Figure 9.1.** In addition to a Tg at 222°C, a large exotherm, which is associated with the cross-linking reaction begins at 340°C and reaches a maximum at 420°C. The cross-linking reaction proceeds readily at 350°C. Similar results are observed in the DSC scan of homopolymer **9.9a** (**Figure 9.2**) which shows a Tg at 150°C and a large exotherm at 435°C. The cross-linking reaction proceeds readily at 350°C.

Thermal analysis is frequently used to characterize cross-linked polymers. It is well known that the Tg rises while the difference in specific heat capacity (ΔCp) at Tg decreases with increasing numbers of cross-links. The effect of curing time on the Tg (**Figure 9.3**) of the poly(ether sulfone) copolymers containing 20 mole per cent of cyclopropane or acetylene moieties, and the difference in specific heat capacity (ΔCp) (**Figure 9.4**) has been studied. After the copolymers were cured at 350°C under nitrogen in the TGA instrument for different time periods the cured polymers were examined in the DSC to determine the Tg increase and ΔCp decrease. It was found that Tg increased and ΔCp decreased rapidly as curing time increased as a result of the cross-linking of the polymers. After one hour the changes in ΔCp and Tg slowed down significantly. The Tgs of all polymers after curing at 350°C for 2 hours under nitrogen are listed in Table 9.1.

The solvent resistance of all cured polymers was improved significantly. All cured polymers are insoluble in all solvents tried. The cured copolymers swelled while the cured homopolymers did not swell in chloroform.

9.3 Conlusions

Poly(ether imide)s containing the 1,2-diphenylcyclopropane or diphenylacetylene moiety have been synthesized from two new dianhydrides by solution condensation with m-phenylene diamine. Characterization of and cross-linking studies on these polymers were carried out utilizing DSC, TGA and NMR. The polymers can be thermally cross-linked when heated above 350°C and the glass transition temperatures (Tg) of the polymers increase after cross-linking. The resulting cross-linked networks are insoluble in all solvents tried. Thermogravimetric analysis shows that no significant weight loss accompanies the cross-linking reaction.

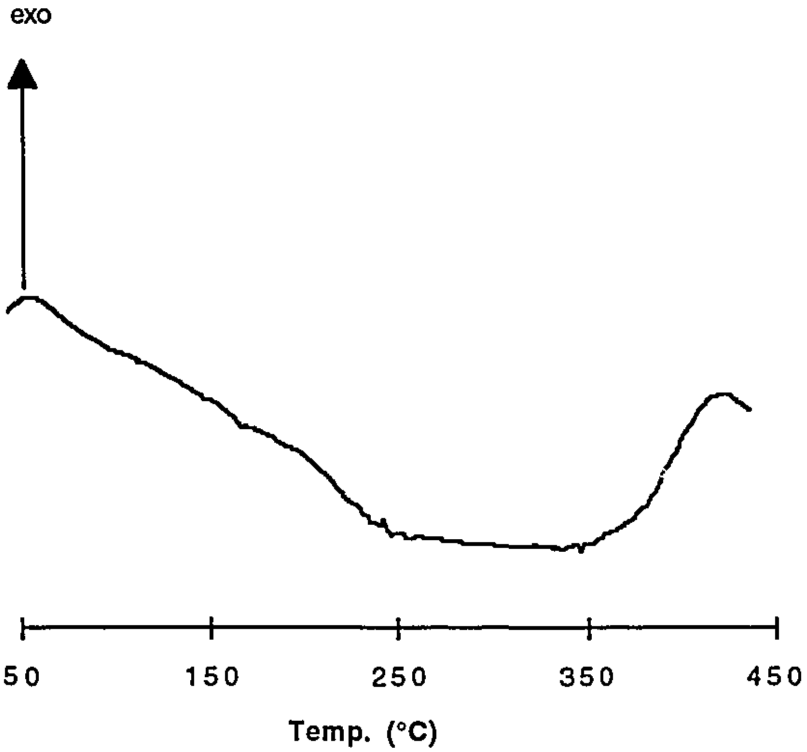


Figure 9.1 DSC scan of homopolymer **9.8a**

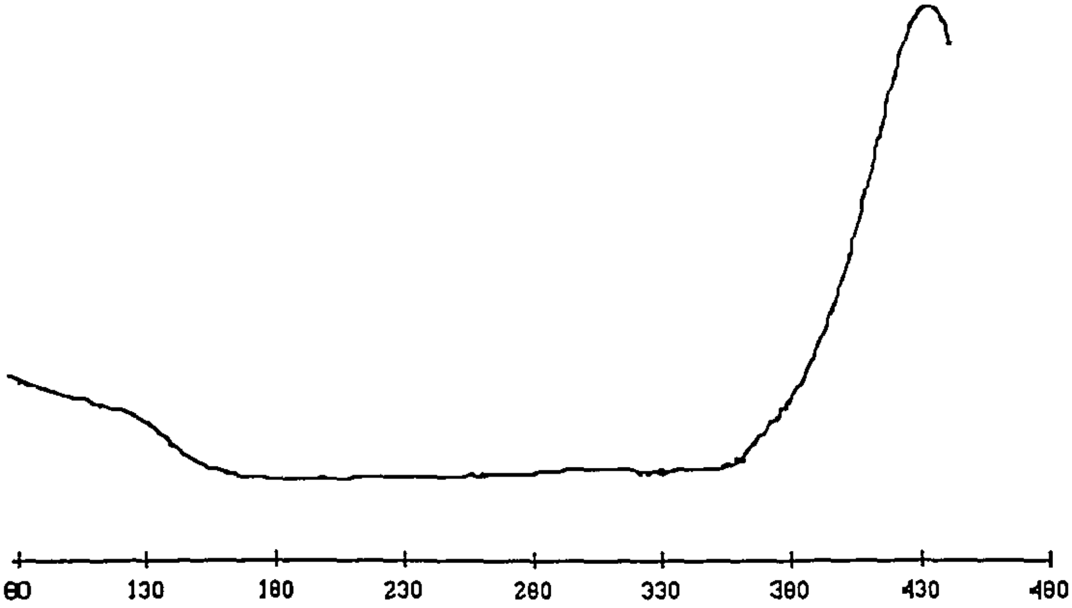


Figure 9.2 DSC scan of polymer 9.9a

Table 9.1

Properties of polyimides containing the diphenylcyclopropane or diphenylacetylene moiety

polymers	η_{inh}[a] (dL/g)	Tg[b](°C) (uncured)	Tg[c](°C) (cured)	TGA[d](°C) N_2
9.8a	0.32	222	ND	452
9.8b	0.35	218	239	490
9.8c	0.30	258	346	430
9.8d	0.29	261	308	424
9.8e	0.28	274	305	450
9.9a	0.25	150	ND	456
9.9b	0.30	209	235	446
9.9c	0.32	254	334	435
9.9d	0.28	252	300	440

[a] 0.5 g/dL in DMAc at 50°C. [b] DSC, heating at 10°C / min. [c] after curing for 2 h at 350°C under nitrogen, DSC, heating at 10°C / min. [d] TGA, heating at 10°C / min.

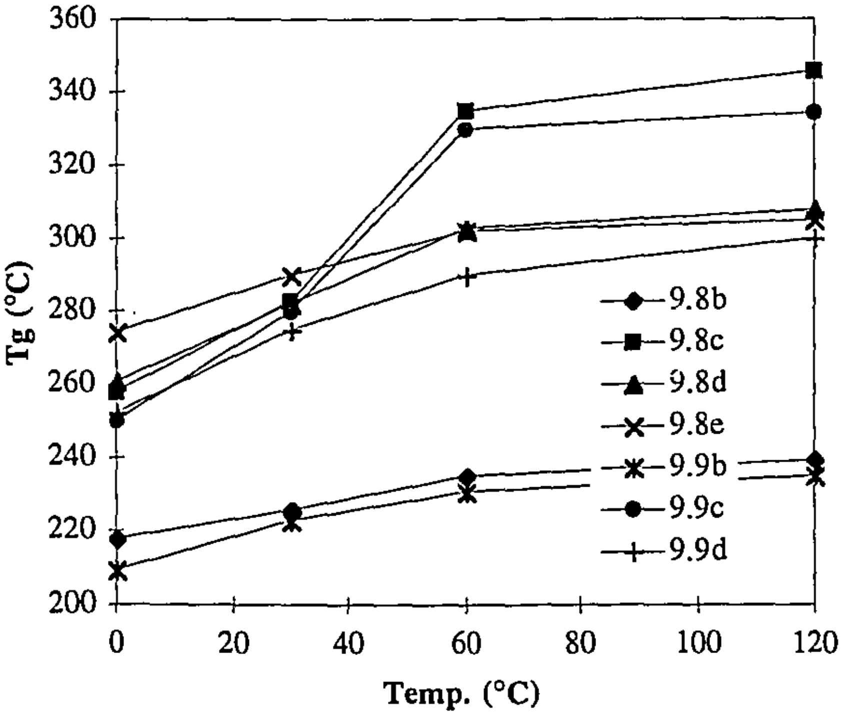


Figure 9.3 Effect of curing time on Tg's of copolymers (350°C under nitrogen, heating rate 10°C / min.)

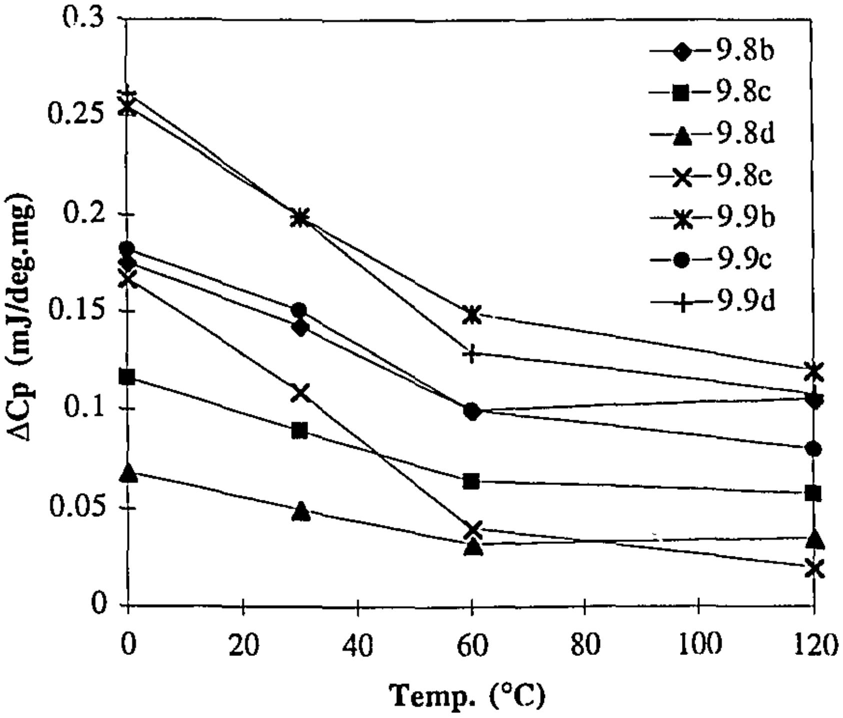


Figure 9.4 Effect of curing time on ΔCp at Tg (350°C under nitrogen, ΔCp at Tg was obtained in a DSC).

9.4 Experimental

(3-Methoxyphenyl)methyl-(1*H*-)benzotriazole 9.1 To 1-(chloromethyl)-3-methoxybenzene (50.0 g,0.319 mol), (1*H*-)benzotriazole (38.0 g, 0.319 mol), and K_2CO_3 (50 g) was added acetonitrile (200 mL) and the mixture was stirred and heated under reflux for 2 h, filtered hot, and washed with hot CH_3CN (100 mL). The filtrate was evaporated and the residual mass, which contained the title compound and (3-methoxyphenyl)methyl-(2*H*-)benzotriazole, was adsorbed on silica gel and chromatographed using petroleum ether (PE)/EtOAc 7:3. The title compound elutes as the second component. The eluant is evaporated and the residual oil is heated with cyclohexane. Upon cooling crystals are obtained. A second recrystallization gave needles 52.7 g (69% yield): mp 53-55°C (cyclohexane); MS (m/e, relative intensity %) 239 (M^+, 100). ^1H NMR (500 MHz, DMSO-d_6) δ 3.73 (s, 3H), 5.98 (s, 2H), 6.87-6.90 (m, 2H), 6.97 (t, 1H), 7.27 (t, 1H), 7.41 (t, 1H), 7.54 (t, 1H), 7.87 (d, 1H), 8.08 (d, 1H); ^{13}C NMR (125.7 MHz, DMSO-d_6) δ 51.04, 55.21, 110.85, 113.43, 113.80, 119.38, 119.91, 124.18, 127.59, 130.12, 132.86, 137.50, 145.52, 159.61.

N-[(3-Methoxyphenyl)methylene]benzenamine 9.2 A mixture of 3-methoxyphenylcarboxaldehyde (99.5 g, 0.731 mol), aniline (68.05 g, 0.731 mol) and benzene (400 mL) were heated to reflux until no more water separated azeotropically, ~2 h. The benzene was evaporated under reduced pressure and the residual oil was distilled using a Kugelrohr apparatus in the range: 145-155°C/1 mbar affording 146.7 g (95% yield) of the title compound which used without further purification below.

1,1'-(1,2-ethynediyl)bis[3-methoxybenzene] 9.3 N-[(3-methoxyphenyl)methylene]benzenamine (21.1 g, 0.10 mol) and 3-methoxyphenylmethyl-(1H)-benzotriazole (23.9 g, 0.10 mol) were added to a solution of potassium tert-butoxide (t-BuOK, 33.6 g, 0.30 mol) and DMF (500 mL) at 75°C and heated at this temperature for 10 min. The reaction mixture was poured into water (2 L) and left to stand overnight to allow for the separation of a precipitate. The oily precipitate was filtered and washed with water. It was dissolved in chloroform and dried ($MgSO_4$). After filtering, the chloroform solution was adsorbed on silica and. chromatographed petroleum ether (PE):ethyl acetate (EtOAc) 97:3. Collection of the fractions and evaporation of the eluant and recrystallization from MeOH gave the title compound 19.1 g (80 % yield) : mp 63-64°C (MeOH);); MS (m/e, relative intensity %) 238 (M^+, 100). ^{1}H NMR (500 MHz, $CDCl_3$) d 3.80 (s, 6H), 6.89 (ddd, 2H), 7.06 (dd, 2H), 7.13 (d, 1H), 7.24 (t, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) d 55.22, 89.09, 114.96, 116.3, 124.13, 124.16, 129.38, 159.32.

Bis(4-hydroxyphenyl)cyclopropane 9.4a It was synthesized by the procedure reported previously[15]; mp 190-191°C; ^{1}H NMR (500 MHz, DMSO-d_6) δ1.1.16-1.22 (t, 2H), 1.80-1.98 (t, 2H), 6.60-6.70 (d, 4H), 6.90-6.96 (d, 4H), 9.15 (s, 2H). MS m/z 226 (M^+, 100), 131 (15), 121 (45), 107 (20).

Bis(3-hydroxyphenyl)acetylene 9.4b 1,1'-(1,2-ethynediyl)bis[3-methoxybenzene] **3** (0.1 mol, 23.8 g) was dissolved in methylene chloride (20 mL). The resulting solution was cooled with an acetone-dry ice bath and 200 mL of a solution of 1M BBr_3 in CH_2Cl_2 was added carefully to the stirred solution. When the addition was complete and the reaction temperature was slowly raised to room temperature with continued stirring. The reaction mixture was then hydrolyzed with saturated $NaHCO_3$ aqueous solution and the aqueous phase was extracted with ether. The organic layer was separated and extracted with 2N sodium hydroxide. The alkaline extract was neutralized with dilute hydrochloric acid, extracted with ether, and the ether extract was dried over anhydrous magnesium sulfate. On removal of the ether, the product was further purified by recrystallization from acetic acid, m.p. 175-176°C. MS (m/e, relative intensity %): 214 (M^+, 100). ^{1}H-NMR (500 MHz, DMSO)· δ 9.67 (s, 2H), 7.20-7.17 (t, 2H), 6.95-6.93 (d, 2H), 6.87 (s, 2H), 6.80-6.78 (d, 2H).

Bis(ether imide)s 9.5a A mixture of bis(4-hydroxyphenyl)cyclopropane **9.4a** (3.44 g, 15.2 mmol), potassium carbonate (6.7 g, 48.48 mmol), DMAc (50 mL) and toluene (25 mL) was stirred under a nitrogen atmosphere at reflux in a three necked flask equipped with a Dean-Stark trap for 3 h. 4-Nitro-N-methylphthalimide (9.4 g, 45.6 mmol) was then added to the flask. The reaction was kept at reflux for 4 h and after cooling to room temperature, the mixture was added to 600 mL of water. The solid was filtered and washed with water. The product was purified by recrystallization from ethyl acetate. yield 70%. m.p. 140-142°C. MS (m/e, relative intensity%) 544 (M^+, 100). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-6.96 (m, 14H), 3.08 (s, 6H), 2.16 (t, 2H), 1.45 (t, 2H).

Tetracarboxylic acids 9.6a A mixture of **9.5a** (2.86 g, 5.26 mmol), methanol (50 mL), water (25 mL) and 50% sodium hydroxide (10 g) was heated at reflux temperature for 7 h. Acidification of the solution with concentrated hydrochloric acid gave 3.10 g of product. MS (m/e, relative intensity%) 554 (M^+, 100). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27-7.02 (m, 14H), 8.03 (broad, H), 2.32 (t, 2H), 1.44 (t, 2H).

Dianhydride 9.7a A mixture of **9.6a** (1.108 g, 2 mmol, acetic acid (15 mL) and acetic anhydride (2 mL) was stirred at reflux for 5 h. The solution was cooled and filtered. Yield 80%. m.p. 155-157°C. MS (m/e, relative intensity%) 537 (M^+, 100). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94-7.01 (m, 14H), 2.22 (t, 2H), 1.54 (t, 2H).

Bis(ether imide)s 9.5b A mixture of bis(4-hydroxyphenyl)acetylene **9.4b** (3.20 g, 15.2 mmol), potassium carbonate (6.7 g, 48.48 mmol), DMAc (50 mL) and toluene (25 mL) was stirred under a nitrogen atmosphere at reflux in a three necked flask equipped with a Dean-Stark trap for 3 h. 4-Nitro-N-methylphthalimide (9.4 g, 45.6 mmol) was added to the flask. The reaction was kept at reflux for 4 h and after cooling to room temperature, the mixture was added to 600 mL of water. The solid was filtered and washed with water. The product was purified by recrystallization from ethyl acetate. Yield 70%. m.p. 110-113°C. MS (m/e, relative intensity%) 528 (M^+, 100). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78-7.03 (m, 14H), 3.08 (s, 6H).

Tetracarboxylic acid 9.6b A mixture of **9.5b** (2.78 g, 5.26 mmol), methanol (50 mL), water (25 mL) and 50% sodium hydroxide (10 g) heated at reflux for 7 h. Acidification of the solution with concentrated hydrochloric acid gave 3 g of product. MS (m/e, relative intensity%) 538 (M^+, 100). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85-7.18 (m, 14H).

Dianhydride 9.7b A mixture of **9.6b** (1.1 g, 2 mmol), acetic acid (15 mL) and acetic anhydride (2 mL) was stirred at reflux for 5 h. The solution was cooled and filtered. Yield 80%. m.p. 126-128°C. MS (m/e, relative intensity%) 521 (M^+, 100). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06-7.20 (m, 14H). ^{13}C NMR (125.7 Mhz, $CDCl_3$) δ

163.33, 154.49, 134.02, 131.15, 128.66, 127.88, 125.02, 124.04, 122.80, 121.21, 113.24, 89.33.

Homopolymer 9.8a

To a 50 mL round bottom flask was added the monomer **7a** (0.6222 g, 1.2 mmol), *meta*-phenylenediamine (0.1298 g, 1.2 mmol) and NMP (7 mL). The flask was purged with nitrogen and the solution was stirred for 3 h under a nitrogen atmosphere at room temperature. The solution became viscous as the polyamic acid formed. Then 4 mL of chlorobenzene was added. The reaction system was heated to reflux with stirring for 3 h while chlorobenzene was distilled off and water removed by azeotropic distillation. The reaction mixture was cooled and precipitated into a large excess of methanol. The polymer was dissolved in chloroform and filtered through celite. The filtrate was reprecipitated in methanol. yield > 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91-6.47 (m, 14H), 2.20-2.00 (t, 2H), 1.90-1.84 (t, 2H).

Homopolymer 9.9a

7b (0.6029 g, 1.2 mmol) was polymerized by the same procedure as described above. yield > 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.0-6.50 (m, 14H).

Copolymers

All copolymers were prepared by same method as described above.

Characterization of Polymers.

Glass transition temperatures of the polymers were obtained using a Seiko 220 DSC instrument at a heating rate of 10°C/min in N_2 (50 mL/min) and Seiko 220 TMA instrument at a heating rate of 3°C/min. When recording Tg values samples were never heated above 300°C, to avoid cross-linking, and the values recorded are from the second scan. The Tg was taken from the midpoint of the change in slope of the baseline. The weight loss data were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 10°C/min in nitrogen and air. Polymer samples were cured at 350°C under nitrogen in the TGA instrument. A DSC was then employed to determine the Tg increase. Inherent viscosity data were obtained with a calibrated Ubbelohde viscometer. ^{1}H-NMR spectra were recorded at 500 MHz using a Varian XL-500 spectrometer in $CDCl_3$ with $(CH_3)_4Si$ as the internal standard.

9.4 References

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Contributions to Original Knowledge

The objectives of this research project were to synthesize new types of thermally cross-linkable high performance polymers. The contributions to knowledge derived from this research, which have been discussed in detail in the chapters (2-9), are briefly summarized in this section.

Chapter 2 described the syntheses of monomers containing reactive groups. A new simple method for the synthesis of hydroxy substituted 1,2-diphenylcyclopropanes was developed. Mono and dihydroxysubstituted-1,2-diphenylcyclopropanes were prepared by base catalyzed decomposition of the corresponding hydroxy substituted 3,5-diphenyl-2-pyrazolines which were the products of the reaction between hydroxychalcones and hydrazine monohydrate.

High molecular weight poly(ether sulfone)s, polyformals and polyesters have been synthesized from the monomer trans-1,2-bis(4-hydroxyphenyl)cyclopropane by solution polycondensation with 4,4'-bis(4-fluorophenyl)sulfone, methylene chloride and phthaloyl chlorides, respectively. Characterization of and cross-linking studies on these polymers were carried out utilizing DSC, TGA, TMA, GPC, and solution and solid state NMR. The polymers can be thermally cross-linked when heated to 350°C and the glass transition temperatures (Tg) of the polymers increase after cross-linking. The resulting cross-linked networks were insoluble in all solvents tried. It was confirmed by MAS-^{13}C NMR that the cyclopropane rings were opened on heating. Thermogravimetric analysis showed that no significant weight loss accompanied the cross-linking reaction.

High molecular weight polymers from 1,1-bis(4-hydroxyphenyl)ethylene and trans-4,4'-dihydroxystilbene with 4,4'-bis(4-fluorophenyl)sulfone were synthesized by a nucleophilic displacement reaction using DMAc as solvent in the presence of potassium carbonate. Characterization and crosslinking studies of these polymers were carried out by DSC, TGA, TMA, X-Ray diffraction, solution and solid state NMR. It was found that all polymers can be crosslinked to some extent on heating to 350°C. We also studied the epoxidation of these polymers with hydrogen peroxide in the presence of methyltrioctylammonium tetrakis (diperoxotungsto) phosphate (3-) as the catalyst in a biphasic system. The epoxidized polymers are thermally cross-linkable. Very efficient cross-linking was obtained by heating the epoxidized polymers at 350°C under nitrogen.

Cyclic aryl ether oligomers containing the trans-1,2-diphenylcyclopropane moiety were synthesized in high yield from 1,2-bis(p-hydroxyphenyl)cyclopropane and 1-(3-hydroxyphenyl)-2-(4'-hydroxyphenyl)cyclopropane by reaction with 1,2-bis(4-fluorobenzoyl)benzene or 1,2-di(4-fluorobenzoyl)-3,6-diphenylbenzene. These oligomers undergo melt polymerization readily to give a cross-linked polymer in the presence of a phenolate salt as catalyst. The cyclic oligomers were characterized utilizing GPC, NMR and matrix assisted laser desorption ionization mass spectrometry (MALDI-MS). Thermal analysis was conducted by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Cross-linkable polyphenylene oxides containing pendent 1,2-diphenylcyclopropane groups have been synthesized by oxidative polymerization from new phenols **7.5a-d** containing the 1,2-diphenylcyclopropane group. The monomers were prepared by base catalyzed decomposition of the corresponding hydroxyl substituted 3,5-diphenyl-2-pyrazolines which were the products of the reaction between hydroxychalcones and hydrazine monohydrate. Characterization of and cross-linking studies on these polymers were carried out utilizing DSC, TGA, GPC, and NMR. The polymers can be thermally cross-linked when heated to 350°C and the glass transition temperatures (Tg) of the polymers increase after cross-linking. The resulting cross-linked networks are insoluble in all solvents tried. Thermogravimetric analysis shows that no significant weight loss accompanies the cross-linking reaction.

High molecular weight poly(aryl ether)s containing internal chalcone groups have been synthesized from 4,4'-dihydroxychalcone and 1,3-bis(4-hydroxycinnamoyl)benzene by solution polycondensation with 4,4'-bis(4-fluorophenyl)sulfone. The polymers can be thermally cross-linked when heated to above 350°C and the glass transition temperatures (Tg) of the polymers increase after cross-linking. The resulting cross-linked networks are insoluble in all organic solvents tried. Thermogravimetric analysis shows that no significant weight loss accompanies the cross-linking reaction. Those polymers can be converted into polypyrazolines by reacting with hydrazine monohydrate.

Poly(ether imide)s containing the 1,2-diphenylcyclopropane or diphenylacetylene moiety have been synthesized from two new dianhydrides by solution condensation with meta-phenylenediamine. Characterization of and cross-linking studies on these polymers were carried out utilizing DSC, TGA and NMR. The polymers can be thermally cross-linked when heated above 350°C and the glass transition temperatures (Tg) of the polymers increase after cross-linking. The resulting cross-linked networks are insoluble in all solvents tried. Thermogravimetric analysis shows that no significant weight loss accompanies the cross-linking reaction.