

**Synthesis and Characterization of Novel Macromolecules/Networks via
Side Chain Modifications of Amorphous Poly(Arylene Ethers)**

by

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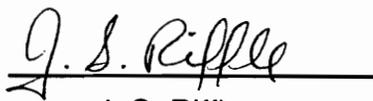
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THE SYNTHESIS AND CHARACTERIZATION OF NOVEL
MACROMOLECULES/ NETWORKS VIA SIDE CHAIN MODIFICATIONS OF
PENDANT AMINES ON AMORPHOUS POLY(ARYLENE ETHERS)

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(ABSTRACT)

The synthesis, characterization and reactivity of linear and network macromolecules by chemical modification of amorphous poly(arylene ethers) with pendant amines were investigated. A new monomer, 3-aminophenyl-bis(4-fluorophenyl)phosphine oxide was prepared by nitration and reduction of bis(4-fluorophenyl)phenylphosphine oxide. Statistical incorporation of pendant aryl amines into linear polymers was achieved by copolymerization of the 3-aminophenyl-bis(4-fluorophenyl)phosphine oxide with another activated dihalide monomer such as 4,4'-dichlorodiphenylsulfone and bisphenol-A. Step polymerizations employing nucleophilic aromatic substitution with a dipolar aprotic solvent, toluene as the azeotroping agent, and a slight excess of potassium carbonate as the weak base was the preferred methodology. The concentration of amines along the polymer backbone was successfully controlled by varying the ratio of 3-aminophenyl-bis(4-fluorophenyl)phosphine oxide monomer relative to the other comonomers. Characterization of the pendant amines by proton NMR and potentiometric titration indicated good agreement

between the charged amount and the incorporation of this monomer into the copolymer backbone.

The pendant amines could be quantitatively converted to pendant phthalimides by reaction with phthalic anhydride. The pendant amines were also reacted to form crosslinkable groups such as maleimides and phenylethynyl phenyl imides. These were thermally treated to induce crosslinking and formed ductile networks which had improved solvent resistance and higher glass transition temperatures. The poly(arylene ethers) containing pendant amines were also reacted with an epoxy resin and 4,4'-diaminodiphenylsulfone to afford epoxy networks which had significant improvement in fracture toughness at selected compositions.

Bis(o-aminophenol) monomers were investigated as precursors to poly(arylene ethers) having pendant amines by copolymerization with 4,4'-dichlorodiphenylsulfone and bisphenol-A. These studies resulted in insoluble gels, which suggested that reaction of both the o-aromatic amine and the phenolate with the activated dihalide was occurring. This was further confirmed by the successful oligomerization of o-aminophenol itself with 4,4'-dichloro diphenylsulfone, which afforded NMP soluble novel poly(sec-amino phenoxy diphenylsulfones) with high glass transition temperatures ($T_g \sim 276^\circ\text{C}$).

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1.0 INTRODUCTION

Amorphous or semi-crystalline linear poly(arylene ethers) such as the commercially important poly(arylene ether sulfones), poly(arylene ether ketones), and more recently the poly(arylene ether phosphine oxides) are engineering thermoplastics well known for their good oxidative, thermal, and hydrolytic stability as well as good mechanical properties. Applications of these thermoplastics have encompassed a wide spectrum ranging from common household items to applications in the automobile, electronic, and aerospace industries. The main disadvantage of these materials is solubility and stress cracking by common organic solvents. For example, the amorphous systems are soluble in chlorinated solvents such as chloroform and dichloromethane, dipolar aprotic solvents such as N-methylpyrrolidone, and cyclic ethers such as tetrahydrofuran. To expand applications for these polymers, it is desirable to improve solvent resistance by introduction of functionality capable of undergoing crosslinking reactions. Conversion of amorphous thermoplastics into networks may afford materials with better solvent resistance while retaining most of the desirable characteristics of amorphous poly(arylene ethers). One earlier method has been to synthesize amine terminated oligomers by addition of a monofunctional endcapper such as p-aminophenol or m-aminophenol. The amine functionality at the oligomer chain ends provides a reactive site for further chemical modifications to other functionalities capable of undergoing chain extension or crosslinking reactions to afford networks with increased solvent resistance. One such example is conversion of terminal amines to maleimides by reaction with maleic anhydride. The resultant maleimides can then be

crosslinked by either microwave or thermal treatment to afford networks with increased solvent resistance. Final properties of the networks can be varied by controlling the concentration of the amine prior to chemical modification. Since the amines are only on polymer chain ends, the concentration of the amine is dictated by the molecular weight of the oligomer. As the molecular weight of the oligomer increases, the concentration of the amine decreases. There is an inverse relationship between the molecular weight of the oligomer and the concentration of the amine.

This investigation has focused on amination of the polymer backbone instead of on polymer chain ends. With this approach, the amines are no longer restricted to be only on polymer chain ends and this allows independent variation of molecular weight and concentration of amines. With pendant amines, it is possible to obtain high molecular weight polymers with a high concentration of the amine. The structure property relationships of linear and network macromolecules from modification of pendant amines on high molecular weight poly(arylene ethers) have been addressed. The following chapters will discuss synthetic methods for amorphous and semi-crystalline poly(arylene ethers) as well as provide characterization of the materials. Also, methods for functionalization of polymers, both on polymer chain ends and on the polymer backbone will be discussed. Random incorporation of pendant amines by copolymerization of 3-aminophenyl-bis(4-fluorophenyl)phosphine oxide with other comonomers will be discussed. The concentration of amines along the polymer backbone was controlled in a precise manner and characterized prior to further chemical modification. Reaction of pendant amines with anhydrides resulted in phthalimides, maleimides, and phenylethynylphenyl imides. The pendant amines

were also reacted with epoxides and 4,4'-diaminodiphenylsulfone to afford toughened epoxy networks. The final chapter will discuss and present interesting results based on using bis(o-aminophenol) monomers as alternative for forming pendant amines on poly(arylene ethers). Copolymerization of bis(o-amino phenol) monomers with bisphenol-A and 4,4'-dichlorodiphenylsulfone results in reaction of both the phenolate and the aromatic amine with the activated dihalide monomer. Based on these unusual findings, the results describing synthesis and characterization of novel polysulfones containing secondary amines in the polymer repeat unit is also discussed.

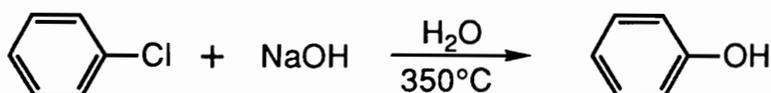
2.0 LITERATURE REVIEW

2.1 Aromatic Nucleophilic Substitution (S_NAR)

There are two main classifications of aromatic substitution reactions, namely, aromatic electrophilic substitution and the aromatic nucleophilic substitution (3). Of these two, only the aromatic nucleophilic substitution (S_NAR) will be discussed, in this review. Furthermore, only the addition-elimination aspect of aromatic nucleophilic substitution reactions will be addressed since it is the widely accepted mechanism for the synthesis of poly(arylene ethers) that will be discussed later.

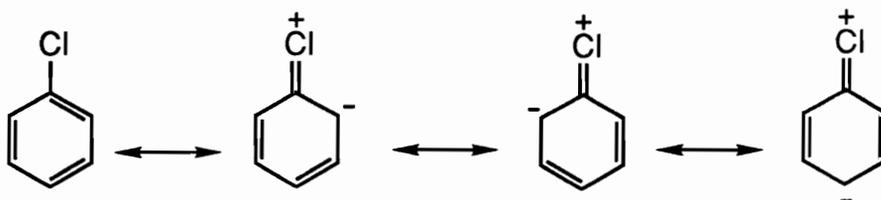
Prior to 1951, only aromatic electrophilic substitution was well understood, and it was not until a comprehensive review of aromatic nucleophilic substitution by Bunnet and Zahler (1) that sparked the interest of scientists to investigate other aspects of aromatic nucleophilic substitution reactions. Since then, there have been numerous reviews and books that have been written about the subject (2-4).

Many primary and secondary alkyl halides readily undergo bimolecular nucleophilic substitution reactions with various nucleophiles. However, nucleophilic substitution of unsubstituted aromatic halides are well known to require very high reaction temperatures. For example, the reaction of chlorobenzene with sodium hydroxide requires the reaction be conducted at 350°C (5).



Conducting the reaction at such a high temperature increases the probability of obtaining other undesirable side products.

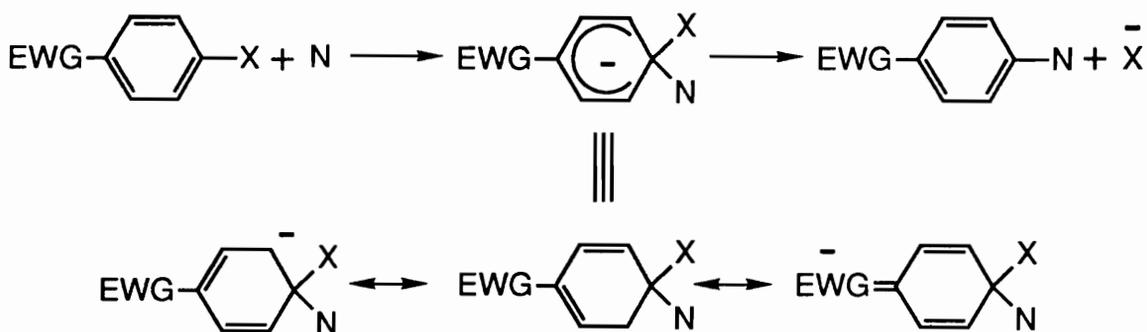
The low reactivity of chlorobenzene can be explained by resonance and the hybridization of aromatic halides. With chlorobenzene, the following resonance structures can be drawn from the electrons donated by the chlorine atom (5).



The resonance hybrid from the above resonance structures imparts a certain double bond character to the carbon bonded to chlorine. The bond length of C-Cl bond in chlorobenzene is 1.69Å, whereas, the C-Cl bonds of alkyl halides are between 1.77-1.80Å (5). In addition to the resonance effect, the hybridization of the aromatic halides also contributes to its low reactivity. In the alkyl halides, the carbon bonded to the halogen is sp^3 hybridized, but the carbon bonded to the chlorine in chlorobenzene is sp^2 hybridized. The sp^2 hybridization has more S character than sp^3 hybridization, therefore, it is more electronegative. Thus, sp^2 hybridized C-Cl bond in chlorobenzene is less likely to donate its electrons to the halogen, and this results in a smaller dipole moment for the C-Cl bond in chlorobenzene than for the alkyl chlorides (5). Therefore, the carbon bonded to the chlorine in chlorobenzene has a less electropositive character than the C-Cl bond of alkyl chlorides.

Even though the unsubstituted chlorobenzene has a low reactivity, the presence of electron withdrawing substituents on the ortho and/or the para position to the halogen remarkably increases the rate of nucleophilic substitution. By incorporating a nitro group on the para position to the chlorine, the reaction of chloronitrobenzene with sodium hydroxide can be conducted at a much lower reaction temperature.

In the addition-elimination aromatic nucleophilic substitution reactions (S_NAr), the first step involves the attack of the nucleophile on the carbon bonded to the leaving group (1-5). In most instances, the leaving group is a halogen, but other leaving groups such as nitro, alkoxy, and even hydrogen has been reported (6-8). The negative charge that develops in the intermediate is stabilized via resonance by the aromatic ring and the electron withdrawing group. The intermediate has often been referred to as the Meisenheimer complex and in certain cases the intermediate is stable enough to be isolated and analyzed (9-11). The second step of S_NAr is the displacement of the leaving group and generation of a new bond with the nucleophile as shown on Scheme 1.



Scheme 1 Generalized mechanism of addition-elimination aromatic nucleophilic substitution reactions (5)

Here, EWG is the electron withdrawing group, X is the leaving group and N is the nucleophile. The relative stabilities of the nucleophilic anion and the anion of the leaving group determines the relative rates of the two step process. If the anion of the leaving group is more stable than the anion of the nucleophile, then the displacement of the leaving group is rapid and the formation of the intermediate is the rate determining step.



However, if the anion of the nucleophile is more stable than the anion of the leaving group, then the formation of the intermediate is the rapid process and the displacement of the leaving group is the rate determining step.



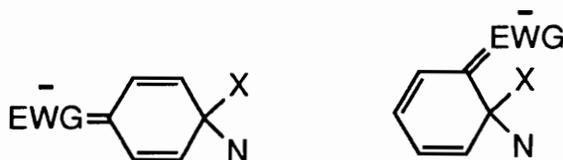
If the anionic stabilities of the of the nucleophile and the leaving group are about equal, then the formation of the intermediate as well as the displacement of the leaving group is a slow process.



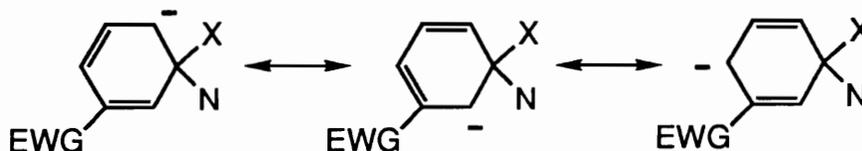
In the synthesis of poly(arylene ethers) (19), the leaving group is usually a halogen, either fluorine or chlorine and the nucleophile is a phenoxide anion. Since the anions of halogens are more stable than the phenoxide anions, the first

step is the rate determining step, and once the intermediate is formed, the displacement of the leaving group is a rapid process (12-13).

There are various factors that influence the rate of the overall S_NAr reactions. These are: the nature of the electron withdrawing group, the nucleophilic reagent, the leaving group and the solvent. The electron withdrawing groups stabilize the negative charge in the intermediate as well as activate the carbon bonded to the leaving group. Some of the more important electron withdrawing groups, in decreasing order are: $NO > NO_2 > SO_2Me > CF_3 > CN > CHO > COR > COOH > F > Cl > Br > I > H > > Me > CMe_3 > OMe > NMe_2 > OH > NH_2$ (14-15). With the same nucleophile, better electron withdrawing groups increase the rate of nucleophilic substitution reaction. Electron donating groups such as methoxy and amine deactivate, as a result of their ability to donate unpaired electrons and destabilize the intermediate. In addition, where the electron withdrawing groups are substituted on the aromatic ring relative to the leaving group also affect the overall rate. Nucleophilic substitution reactions are greatly enhanced if the electron withdrawing group(s) are on ortho and/or para position to the leaving group. (3). Clearly, if the electron withdrawing group is either on ortho or para position to the leaving group, resonance structures can be drawn that delocalize the negative charge by the electron withdrawing group.



Having the electron withdrawing group on the meta position to the leaving group prevents such resonance stabilization.



Therefore, the only way the electron withdrawing group on the meta position can stabilize the intermediate is through a very slight inductive effect. Also, the presence of more than one electron group on the ortho and the para position produce an additive effect and enhance the rate of nucleophilic substitution reactions.

The nucleophilicity of the nucleophile also affects the overall rate of S_NAr reactions; ie, the better the nucleophile, the faster the overall reaction rate. Some of the more important nucleophiles in decreasing order of nucleophilicities are: $ArS^- > RO^- > R_2NH^- > ArO^- > OH^- > ArNH_2 > NH_3 > I^- > Br^- > Cl^- > H_2O > ROH$ (1). Generally, nucleophilicities can be correlated with basicity; ie, as basicity increases, nucleophilicity also increases (5). However, this is only a general trend, and caution must be exercised when applying this principle. An exception is the comparison between a hydroxide anion and a phenoxide anion. Even though the hydroxide anion is more basic than the phenoxide anion, the phenoxide anion is more nucleophilic (1). Nucleophilicity is also influenced by the polarizability of the attacking atom on the nucleophile. The electron density of a polarizable atom can be distorted more easily than the electron density of a less polarizable atom. Therefore, polarizability increases the nucleophilicity of a

nucleophile. The relative polarizability accounts for the greater nucleophilicity of the thiophenoxide anion relative to the phenoxide anion (1).

The leaving group must of course also be considered in S_NAr reactions. In S_NAr reactions, the leaving group must stabilize the negative charge that results from the displacement and those functional groups that can best stabilize the negative charge will be a better leaving group. General trend of some of the leaving groups in decreasing order are: $F^- > NO_2^- > Cl^- > Br^- > I^- > ^-SO_3R > ^-NR_3 > ^-OAr > ^-OAlkyl > ^-SAlkyl > ^-SArO > ^-SO_2Alkyl > amino$ (1). Commonly investigated leaving groups are the halogens and in the alkyl halides, the order of the leaving groups in unactivated systems for the halogens are $I > Br > Cl > F$. In activated S_NAr displacement reactions, the trend for the halogens are just opposite from that of the alkyl halides and the observed trend is $F \gg Cl > Br > I$ (1,12,16,17). In a nucleophilic substitution of a alkyl halide, the transition state consists of partial bond formation between the nucleophile and the carbon bonded to the halogen and a partial bond breaking between the carbon and the halide. Because the weaker C-X bond is easier to break, the observed halogen order can be explained on the basis of relative bond strengths of the carbon bonded to the halogens. The same rationale does not account for the observed behavior for the halogens in S_NAr reactions. The C-F bond is strongest of the carbon halogen bonds, and yet, fluorine is displaced much more rapidly than the other halogens. The explanation for the observed behavior is largely due to the electronegative nature of fluorine. Because fluorine is the most electronegative halogen, it influences the carbon it is directly bonded to by making the carbon more electropositive than the other halogens. Also, fluorine can better stabilize the negative charge that develops in the intermediate than the other halogens. In

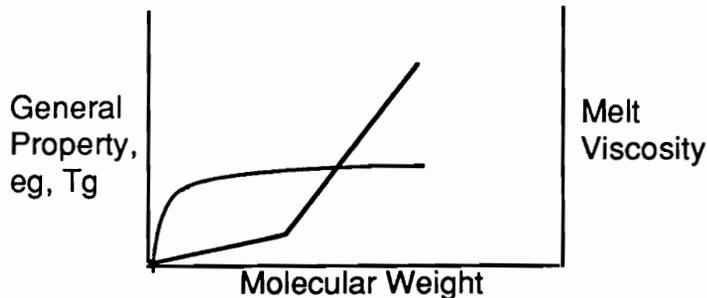
addition, fluorine is a smaller atom than the other halogens and the carbon bonded to fluorine is less sterically hindered. In S_NAr reactions, unlike the nucleophilic substitution reactions of alkyl halides, the bond breaking between the carbon and the halogen is relatively fast compared to the formation of the bond. Therefore, the relative bond strengths of C-X are not as crucial in S_NAr reactions as in the alkyl halide displacement reactions.

Another major variable that must also be considered in S_NAr reactions is the choice of solvent for the reaction. Commonly utilized solvents for S_NAr reactions are dipolar aprotic solvents such as dimethyl sulfoxide (DMSO), N,N-dimethyl acetamide (DMAc), N,N-dimethylformamide (DMF), and N-methyl pyrrolidone (NMP). These dipolar aprotic solvents are good solvents for cations and not particularly a good solvent for anions. Therefore, nucleophiles are more nucleophilic in these solvents than in protic solvents. Also, due to the dipolar nature of these solvents they can better stabilize the intermediate formed in S_NAr reactions. Nucleophiles in protic solvents such as alcohols can be hydrogen bonded with the solvent and become less nucleophilic in the protic solvents. Mayanna et al.(18) have conducted kinetic measurements of p-nitro chloro benzene with sodium methoxide in mixtures of DMSO and methanol. Their results indicated that as concentration of DMSO increased in the mixture, the rate of the nucleophilic substitution also increased.

2.2 Variables to Consider for Linear High Molecular Weight Polymers

One of the variables which affect polymeric properties such as the glass transition temperature (T_g) and mechanical properties is the molecular weight of

the polymer. The behavior of a general polymer property as a function of molecular weight is shown below



Initially, there is a rapid increase in the measured property as the molecular weight increases, then it plateaus or increases only slightly with further increase in molecular weight. The threshold molecular weight at which useful properties are obtained is the molecular weight at which entanglement of polymer chains occur. Below this molecular weight, poor mechanical and thermal properties can be expected due to the inability the polymer chains to form entanglements. Molecular weights higher than the entanglement molecular weight result in only a slight improvement in the mechanical property, but the melt viscosity increases dramatically, which make processing very difficult. It is thus desirable to synthesize, controlled relative high molecular weight polymers to obtain useful mechanical and thermal properties.

For the synthesis of linear high molecular weight poly(arylene ethers) by a step growth or polycondensation process, many important variables must be considered and these include:

- 1). **Very High Purity of Monomers (>99.9).** In the step growth polycondensation, the number average degree of polymerization (\bar{X}_n) is defined by the following equation

$$\bar{X}_n = \frac{1}{1-P}$$

where P is the extent of conversion. Since there is an inverse relationship between \bar{X}_n and P, as P approaches 1, \bar{X}_n will become larger. The extent of conversion is highly dependent on the purity of the monomer(s). If the monomer(s) is only 99% pure, then the maximum value of P can only be 0.99 which corresponds to \bar{X}_n of 100, but if the purity of the monomer is 99.5% then \bar{X}_n could be 200. Since a small deviation in P causes a large change in \bar{X}_n , it is crucial that the monomer(s) be as pure as possible to synthesize high molecular weight linear polymers.

2). **Very High Conversions (P > 0.99).** In contrast to the chain addition or addition polymerizations, in the step growth polycondensations the molecular weight increases gradually as the extent of conversion increases. This is due to the nature of the reaction. Initially, two monomers will react with each other to produce a dimer, the dimer can then react with another monomer to produce a trimer or it can react with another dimer to produce a tetramer. This process is repeated over and over again until essentially all of the monomers, dimers, trimers, etc. react to yield only high molecular weight polymer. Any two reactive species in the reaction mixture can react with each other and a rapid increase in molecular weight does not occur until the extent of conversion approaches 0.99. The molecular weight as a function of % conversion is shown in Figure 1(19).

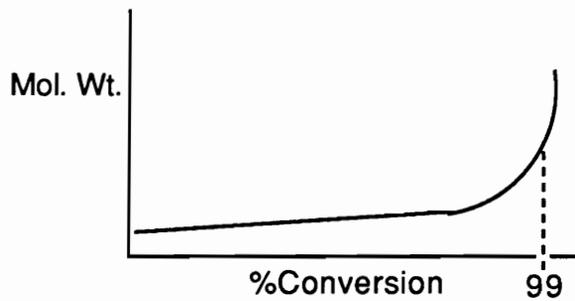


Figure 1 Molecular weight as a function of conversion for step polymerization

3). **Difunctionality ($f=2.0$)** In order to synthesize linear high molecular weight polymers, functionality of the monomers have to be very close to 2.0.

Functionality of less than 2.0 which can be due to the presence of a monofunctional monomer or impurities will decrease the molecular weight of the polymer, and the larger the deviation from 2.0 the lower will be the molecular weight. Functionality of greater than 2.0 will result in the formation of branched polymers or even three dimensional insoluble networks.

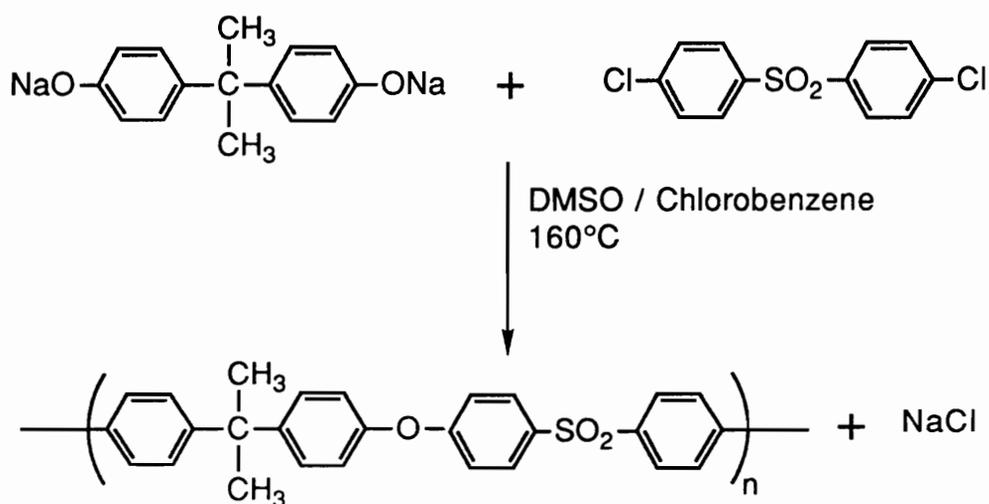
4). **One to One Stoichiometry of the monomers.** For the polymerization of AA and BB type monomers, there must be present in the reaction mixture an equal amount (mole %) of each monomers to be polymerized. Any deviation from the one to one stoichiometry of the monomers will decrease the molecular weight of the resulting polymer. This is one of the methods for controlling the molecular weight as well as the functionality of the polymers synthesized by the step growth polycondensations, of course, the polymerization of an AB type monomer, one to one stoichiometry is automatically ensured if the monomer is pure .

5). **No Side Reactions.** There must not be other competing side reactions which will upset the one to one stoichiometry required for the synthesis of linear high molecular weight polymers. It is crucial that the solvents, and the monomers be very pure to prevent the possibility of side reactions.

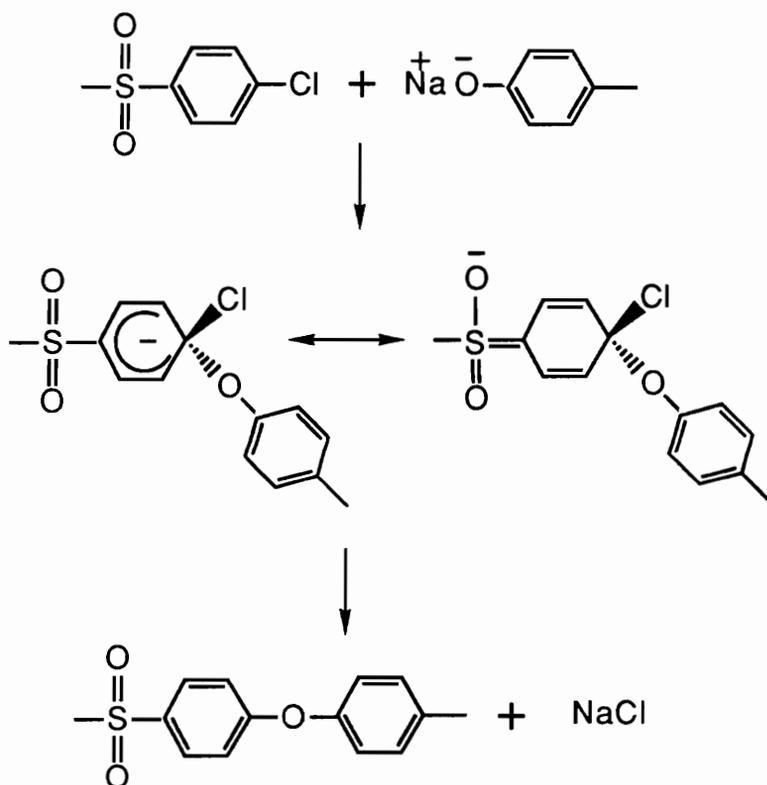
6). **Accessibility of Mutually Reacting Groups.** In order to synthesize linear high molecular weight polymers, all of the reactive species that are present in the reaction mixture must have the opportunity to react with each other. This pertains to the choice of solvent and its ability to solubilize the growing polymer chains with reactive end groups as well as other reactive species in the reaction mixture. The inability of the solvent to keep both the growing polymer chains and the other reactive species in solution will prevent the attainment of high molecular weight polymers due to premature precipitation of oligomeric polymer chains. This is particularly important for semi-crystalline materials.

2.3 Synthesis of Amorphous Poly(Arylene Ethers)

In 1967, Johnson et al.(19) published the results on the synthesis and the characterization of poly(arylene ether sulfones) and poly(arylene ether ketones) synthesized by the aromatic nucleophilic substitution. Using dimethyl sulfoxide (DMSO) as the solvent, they were able to synthesize various high molecular weight amorphous poly(arylene ethers). The synthesis of poly(arylene ether sulfones) from 4,4'-dichlorodiphenyl sulfone (DCDPS) and bisphenol-A is shown in Scheme 2. For the synthesis of amorphous poly(arylene ether ketones), poly(arylene ether phosphine oxides) (74), or other amorphous poly(arylene



Scheme 2 Synthesis of poly(arylene ether sulfones) from DCDPS and the bisphenolate of bisphenol-A (19)

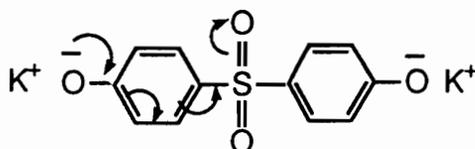


Scheme 3 Mechanism for the synthesis of poly(arylene ether sulfones) by aromatic nucleophilic substitution (40)

ethers), similar reaction conditions can be used by replacing the sulfone with a ketone, a phosphine oxide, or other electron withdrawing groups which can activate appropriate halides for nucleophilic substitution. The reaction most likely proceeds via an intermediate complex in which the electron withdrawing group (sulfone) stabilizes the complex by accepting the negative charge that develops from the attack of the phenolate on the carbon bonded to the activated halide. This is shown in Scheme 3. The effect of the stabilization by the sulfone is highly effective when the halogen is positioned ortho or para to the sulfone and not when the halogen is meta to the sulfone (20,21). The halogen ortho to the sulfone is sterically hindered and the synthesis of high molecular weight polymers is sterically unfavored; also undesirable side reaction such as hydrolysis has been reported (20). Polymerization involves the formation of bisphenolates by first dissolving bisphenol-A in DMSO and chlorobenzene mixture and when a homogeneous solution is obtained at ~ 60-80°C stoichiometric amounts of sodium hydroxide or potassium hydroxide may then be added as an aqueous solution. Bisphenolate derived from potassium hydroxide reacts faster than bisphenolates from sodium hydroxide. Lithium, calcium, and magnesium salts of the bisphenol A are insoluble in DMSO and cannot be used. The reaction flask was heated until chlorobenzene began to reflux and this solvent functioned as an azeotrope to remove the water from the system. When essentially all of the water was removed, 4,4'-dichlorodiphenyl sulfone (DCDPS) was then added as a chlorobenzene solution and the homogeneous polymerization was conducted at ~160°C until a viscous solution was obtained (~1hr). Johnson (19) recognized that careful dehydration was critical to avoid the hydrolytic side reaction of the chlorosulfone. The phenolate end groups may be neutralized and terminated

with methoxy groups by passing methyl chloride into the reaction mixture. Functionality can also be controlled by using a slight excess of either monomer. A slight excess of bisphenolate will result in phenolate end groups which can be converted by acidification to afford phenol terminated polymers. Likewise, addition of a slight excess of DCPDS will result in chlorine terminated polymers. Using this method a wide variety of high molecular weight amorphous poly(arylene ethers) can be synthesized in a short time.

The reactivity of the bisphenolates were dependent on the relative acidities of the corresponding bisphenols. More acidic bisphenols were shown to be less reactive. Bisphenols with electron withdrawing groups are more acidic because the negative charge on the phenolates can be stabilized by the electron withdrawing groups. This is shown below with a bisphenolate (bisphenol-S) which contains a sulfone as the electron withdrawing group.



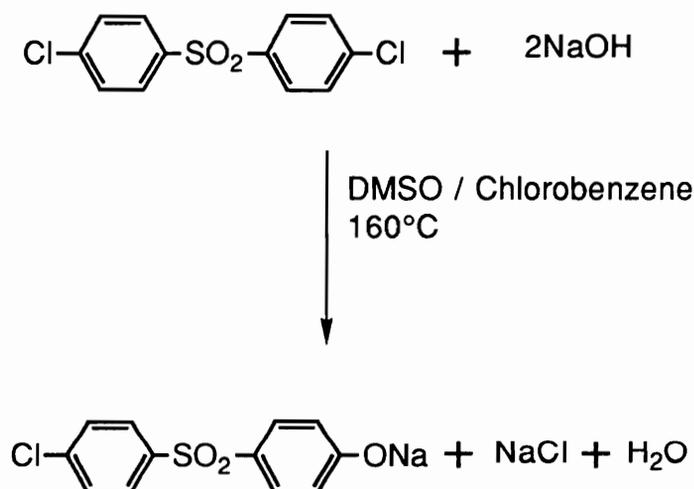
Lower viscosity was obtained for polymers from less reactive bisphenolates for a given reaction time and temperature. In those cases, the polymerization temperature was increased by using a higher boiling solvent which effectively increased the rate. Sulfolane may be used for polymerizations that require higher temperatures than 160°C, however, contact times must be kept to a short time (<5hrs) due to a slow base consuming side reaction (19).

Since fluorine is much more easily displaced than chlorine, the nature of the electron withdrawing group determines which halogen is suitable for

synthesis of high molecular weight polymers. If a strong electron withdrawing group such as sulfone is used, either fluorine or chlorine can be used as the halogen for the synthesis of high molecular weight polymers, but reactivity will be higher if fluorine is the halogen. If a weaker electron withdrawing group such as a ketone is used, then fluorine is preferred, since chlorine may allow only low molecular weight polymers will be obtained. An exception is if the monomer contains two ketone groups, then either chlorine or fluorine can be used to synthesize high molecular weight polymers. Recently, with a bis(4-chlorobenzoyl)benzene monomer which contains two ketone groups, if the halogen was fluorine, then high molecular weight polymers were synthesized from the two bisphenols they investigated which were bisphenol-A and hydroquinone. However, with chlorine as the halogen, high molecular weight polymer was obtained with only bisphenol-A and not from hydroquinone. The inability to obtain high molecular weight polymers from hydroquinone and bis(4-chlorobenzoyl)benzene was attributed to dehalogenation which occurred during polymerization and the mechanism they proposed involved a free radical process(22). Others have also reported similar results for a similar monomer 4,4'-(dichlorobenzophenone).(23).

The bisphenolate route for synthesis of amorphous poly (arylene ether sulfones) from bisphenol-A and DCDPS is believed to be currently utilized for the synthesis of a commercial bisphenol-A poly (arylene ether sulfones) by Amoco Chemical which has a trade name Udel. With this method, high molecular weight polymers can be synthesized in a relatively short time depending on the reactivities of the bisphenol and the activated dihalide monomer. With

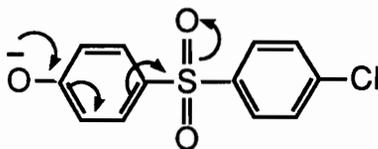
bisphenol-A and DCDPS, high molecular weight polymer can be obtained in about 4 hours or less. From a reaction time point of view, it is a convenient way to obtain high molecular weight polymers in a relative short time. However, there are disadvantages with this method, namely, the need for an exact stoichiometric amount of sodium hydroxide, based on the amount of the bisphenol. Addition of excess or deficient amount of the base has a dramatic effect on the molecular weight of the resulting polymer (19). The presence of excess base can upset the one to one stoichiometry needed for synthesis of high molecular weight polymers by reacting with the activated dihalide monomer. This is shown in Scheme 4.



Scheme 4 The reaction of excess base with the activated halide monomer (19)

In addition to offsetting the one to one stoichiometry, the chlorine on the mono chloro phenolate of diphenyl sulfone is much less reactive due to the bridge effect from the phenolate. The lone pair of electrons from the phenolate is

delocalized by the sulfone and this reduces the electron withdrawing ability of the sulfone.



Also, the excess base can react and cleave the activated aromatic ether linkages on polymer chains which reduces the molecular weight of the polymer.

The presence of a deficient amount of the base also has a detrimental effect on molecular weight. In addition to offsetting the one to one stoichiometry, the free bisphenols can hydrogen bond with other phenolates in the reaction mixture. This is shown in Figure 2.

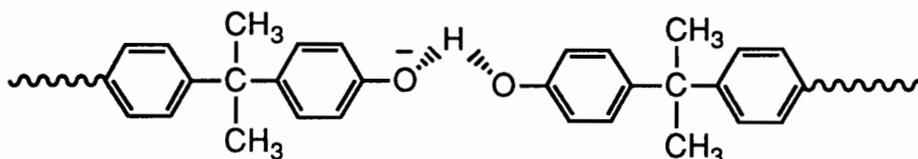
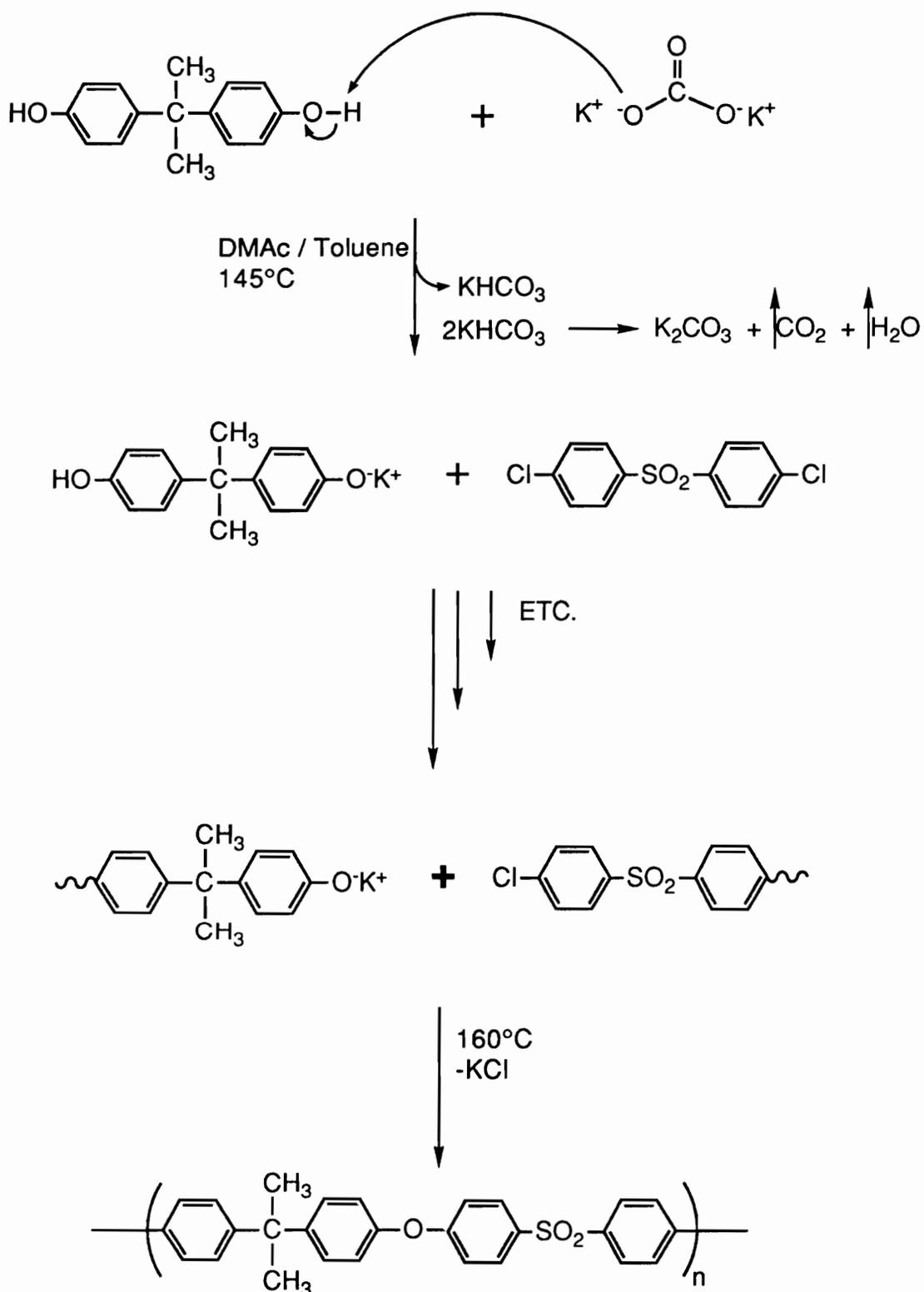


Figure 2 Hydrogen bonding of a phenol and a phenolate (24)

This reduces the nucleophilicity of the phenolate by an order of magnitude (24). In addition to the base consideration, moisture and other protic contaminants must be carefully excluded throughout polymerization. The presence of moisture has a devastating effect on limiting molecular weight by hydrolyzing the activated dihalide monomer. The high concentration of phenolates throughout most of the reaction at elevated temperatures increases the possibility of oxidation by atmospheric oxygen. Also, the DMSO can degrade easily at ~165°C during prolonged use at this temperature. Johnson et al. (19) also investigated other high

boiling solvents such as benzophenone, diphenylsulfone, and bis(*n*-propyl) sulfoxide. With bis(*n*-propyl) sulfoxide, they observed even a faster base consuming side reaction than sulfolane. Benzophenone and diphenylsulfone both were ineffective for the synthesis of high molecular weight polymers from bisphenol-A and DCDPS at the relative moderate temperature investigated. With the bisphenolate route, the advantage of synthesizing high molecular weight polymers in a short time is counterbalanced by many disadvantages which were just discussed.

The dimethylacetamide (DMAc)/potassium carbonate (K_2CO_3) route (25,26) which is shown in Scheme 5. Instead of DMAc, a slightly higher boiling solvent *N*-methylpyrrolidone (NMP) can also be used (25). With this approach, strict adherence to the exact stoichiometric amount of the base is not necessary for the synthesis of high molecular weight polymers. A modest excess of K_2CO_3 has been demonstrated not to hydrolyze the halide, react with polymer chains or prevent the synthesis of high molecular weight polymers. Potassium carbonate is only partially soluble in DMAc and there is an equilibrium of K_2CO_3 in solution and K_2CO_3 as a solid. As K_2CO_3 is consumed throughout the reaction, additional K_2CO_3 dissolves to produce the phenolates which react with activated halides present in the reaction mixture. The water formed from the interaction of K_2CO_3 and the bisphenol is removed by an azeotroping agent such as toluene. The excess K_2CO_3 as well as the by product potassium chloride is removed by filtration prior to coagulation of the polymeric solution. Utilizing this approach, various high molecular weight amorphous poly(arylene ethers) have been synthesized and reported (27, 28). The other difference with this approach and the bisphenolate route is the kinetics which govern the two types of

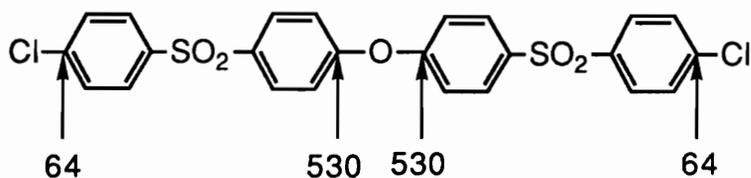


Scheme 5 Mechanism for the synthesis of poly(arylene ether sulfones) from DCDPS and bisphenol-A by the potassium carbonate/ DMAC route (26)

polymerizations. For the bisphenolate route, the overall reaction rate for the polymerization has been reported by Schulze et al.(29) to be a second order polymerization with respect to the bisphenolate and DCDPS, however, others have reported contrasting results (20,30). A plot of the parameters of a second order reaction to the DMAc/K₂CO₃ route does not result in a linear plot, this difference has been attributed to the heterogeneous nature of the polymerization. In addition, the rates for the two polymerizations reveal a significant difference. The bisphenolate route is approximately 10 times faster than DMAc/K₂CO₃ route (26). The reactivity of various bisphenols have been reported (20). From the results based on kinetic measurements, the bisphenolate is much more reactive than the monophenolate. In the DMAc/K₂CO₃ route, it is believed that monophenolates are formed first which then react with the activated halide monomer. In the polymerization mixture, only a fraction of the stoichiometric amount of base needed to convert all of the phenolic groups to phenolates is in solution, monophenolates which are formed in situ may hydrogen bond with free phenols and the effect of this type of association will decrease the nucleophilicity of the phenolates. The reduced rate can also be attributed to the presence of toluene which will lower the overall dielectric constant of the reaction media or it may be that heterogeneous polymerizations by a virtue of its nature is simply slower than homogenous polymerizations.

Usually, phenyl ether bonds are stable, however, the oxygen on the ether is positioned para to the sulfone. As a consequence, the ether is activated by the sulfone and the ether is susceptible to attack by nucleophiles such as phenolates. This has been demonstrated from kinetic investigation of a model compound

which shows the relative rates of attack by hydroxide ion on possible reaction sites (20).



$$k_2 \times 10^5 \text{ (1 mol}^{-1} \text{ sec}^{-1} \text{)}$$

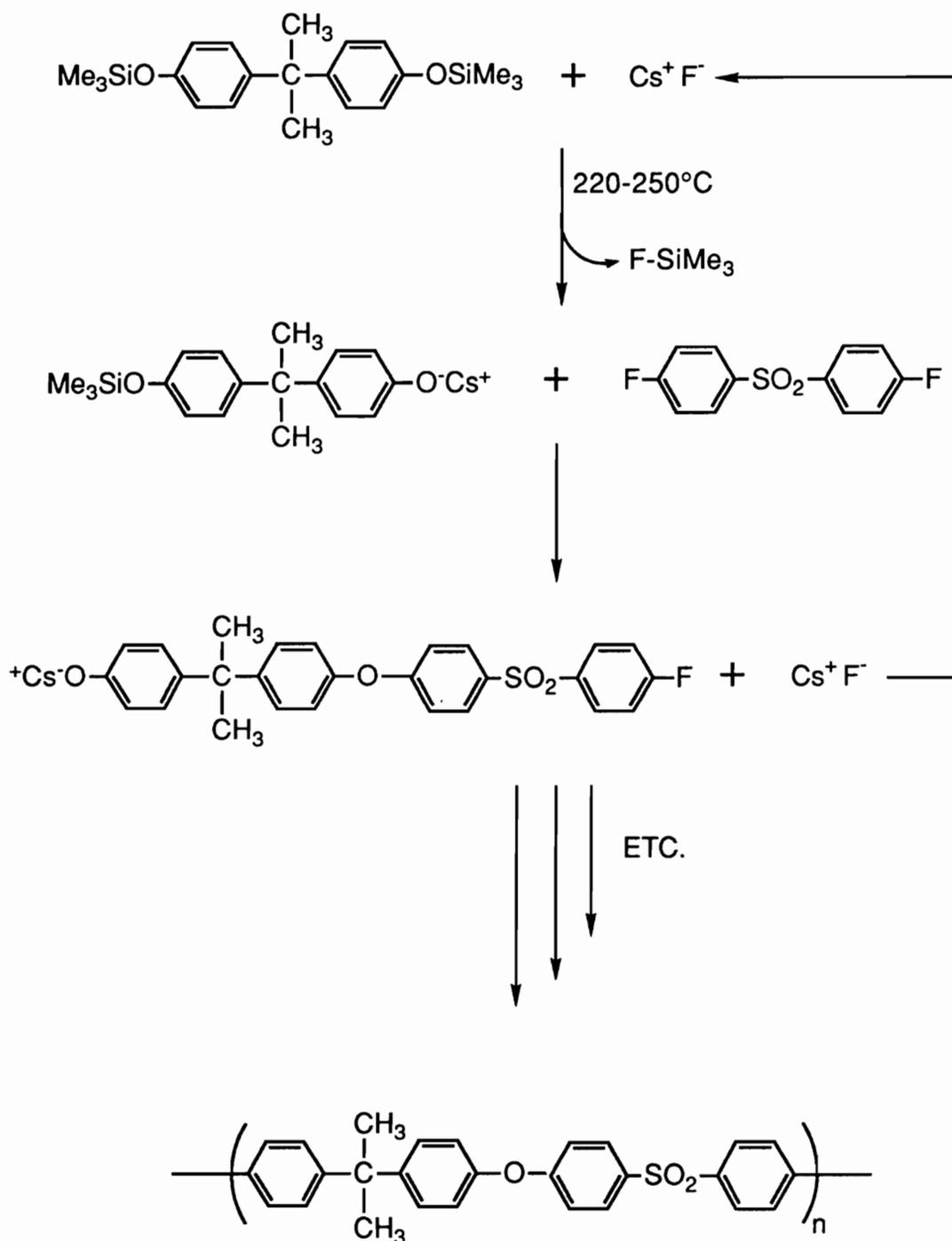
This has been commonly referred to as the ether-ether interchange and this process is present in the synthesis of poly(arylene ethers). The ether-ether interchange which occur during the polymerization prevent the synthesis of block copolymers from the reaction of a phenol terminated oligomer with a halogen terminated oligomer.

As ether bonds are formed during polymerization, the by product of the reaction is an inorganic halide (KCl or KF). If the activated monomer contains fluorine as the halide, the resulting potassium fluoride has been reported to also act as a nucleophile and promote cleavage of polymeric chains in an analogous manner to the ether ether interchange which causes the molecular weight of the polymer to decrease (30, 31).

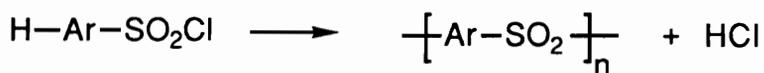
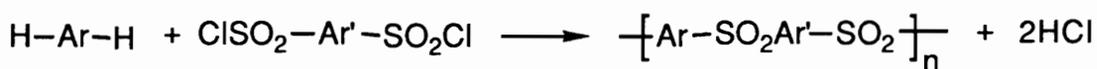
Another interesting approach which can be used for the synthesis of amorphous poly(arylene ethers) has been reported by Kricheldorf (32-36). This approach involves reacting various trimethylsilyl ether derivatives of bisphenols with various activated dihalide monomers. The mechanism for this route is shown in Scheme 6. The two previous methods that have been mentioned so far involve isolation of the polymer from the salt by products, excess K_2CO_3 , and the solvent. The by products from polymerizations with this method is fluorotrimethyl

silane which is a volatile gaseous product and this allows easy isolation of the polymer. Polymerizations are usually conducted in the melt using catalytic amounts (~0.1 wt% relative to sum of both monomers) of cesium fluoride or potassium fluoride. With this approach, the activated halide monomer must contain fluorine as the halide, even when sulfone is the electron withdrawing group. This certainly is due to fluorine being a better leaving group than chlorine, but also the Si-F bond is more stable than any other silicon bond which serves as the driving force for this type of polymerization. Attempted polymerizations using chlorinated monomers such as 4,4'-dichlorodiphenyl sulfone, silylated chlorohydroquinone, and silylated tetrachlorobisphenol-A by the melt polymerization only resulted in a low conversion. It is believed a halogen exchange occurs in the presence of chlorine to convert cesium fluoride to cesium chloride which is insoluble in the polymerization media. Consequently, chlorinated monomers such as dichlorodiphenyl sulfone can be polymerized with trimethylsilyl bisphenol-A using a dipolar aprotic solvent such as N-methyl pyrrolidone (NMP) in the presence of potassium carbonate (37). The interesting characteristic of melt polymerizations using the Kricheldorf method is the apparent absence of ether ether interchange which occurs with the nucleophilic route. Using Kricheldorf's method, synthesis of both random and block copolymers have been reported (32,38).

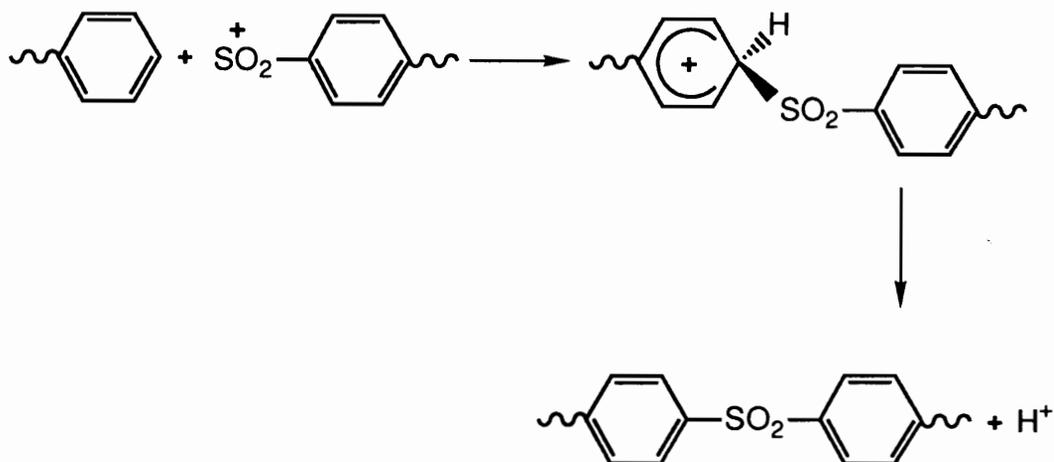
The fourth route for the synthesis of poly(arylene ether sulfones) is the Friedel Craft electrophilic substitution route in which the sulfone linkages are formed by reaction of sulfonyl chlorides with aromatic nuclei (39,40).



Scheme 6 Synthesis of poly(arylene ether sulfones) from trimethylsilyl bisphenol-A and difluorodiphenyl sulfone with cesium fluoride as catalyst (32)



Either AA BB type monomers or AB monomers can be polymerized in the melt as well as in solution using dimethyl sulfone, chlorinated biphenyl and nitrobenzene as the solvent in the presence of catalytic amounts (0.02-5 mole%) of ferric chloride, indium chloride or antimony pentachloride. The mechanism for polysulphonylation is shown in Scheme 7.



Scheme 7 Polysulphonylation for the synthesis of poly(arylene ether sulfones) (39)

Unlike poly(arylene ether sulfones) synthesized by the nucleophilic substitution route which yields all para linkages. This route yields mainly all para structure, however, there is usually a small amount of ortho linkages which may lead to branching depending on the nature of the monomer(s) utilized.

2.4 Methods Available to Vary Polymeric Properties

Various methods are available to obtain the desired polymeric properties, one of the method is to synthesize new polymers, however, this is often easier said than done. Another method is to vary the structural moieties in the repeat unit to modify the T_g, solubility, mechanical properties etc.. This can be accomplished by using different monomers to synthesize various homopolymers or copolymers. Also a monomer containing more than one functional group can be synthesized and polymerized, a monomer which contains both the sulfone and ketone groups have been synthesized and polymerized (41).

Another possibility is to blend polymers together by using a solvent or directly in the melt, if the polymers to be blended are thermally stable. However, many polymers are incompatible with each other and usually a gross macrophase separation occurs which result in poor mechanical properties. The other alternative is to synthesize block, graft, or star shaped polymers. With poly(arylene ether sulfones), block copolymers have been synthesized by modifying phenol terminated polymers (42). Randomly segmented or block copolymers of poly(arylene ether sulfone)-polycarbonate have been synthesized by reacting phenol terminated oligomers of polysulfone with phosgene and bisphenol-A in a mixture of methylene chloride and pyridine. Similarly, copolymers of poly(arylene ether sulfone)-poly(butylene terephthalate) and poly(arylene ether sulfone)-polystyrene have also been synthesized (42). For random block copolymers in which both components are amorphous, the main criteria which determined whether a microphase separation occurred was determined to be the difference in the solubility parameter of the two homopolymers. If the difference in solubility parameter was small (~0.7),

microphase separation was not observed with low molecular weight oligomers (<10K), whereas, if the difference was larger (~1.6), microphase separation did not occur only for very low molecular weight (<2K) oligomers of polystyrene in polystyrene-poly(arylene ether sulfone) block copolymers. Perfectly alternating block copolymers of poly(arylene ether sulfone)-polydimethylsiloxane have also been synthesized (43).

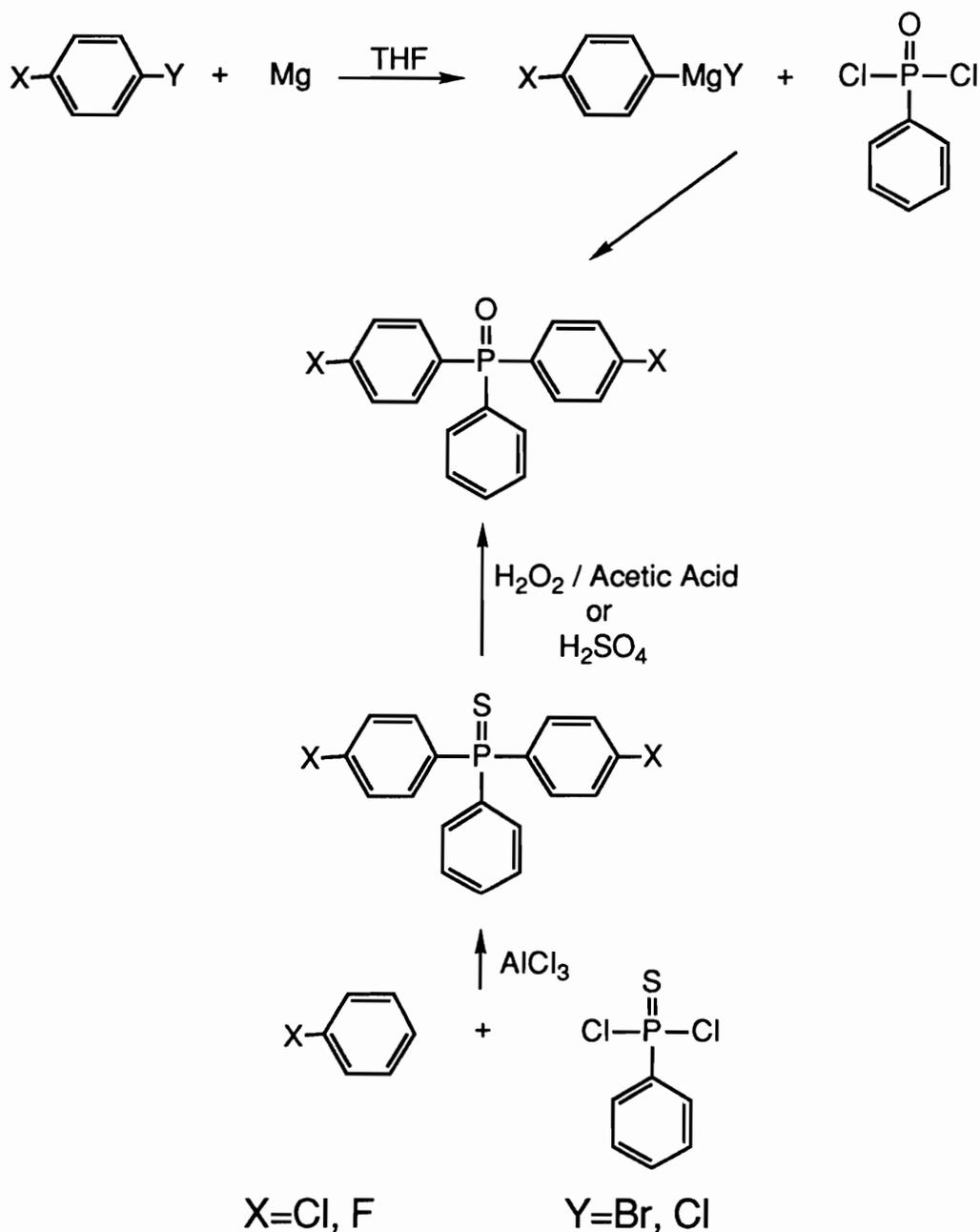
Another interesting modification for application involve the ring opening polymerization of small cyclic species of poly(arylene ether sulfones) (44). Recently, the conditions have been optimized and the yield of the cyclics has been improved. Cyclics have a lower melt viscosity than linear high molecular weight polymers and this method may be applicable to fabrication of composites where it is desirable to have low viscosity materials for good wetting of the resin to the composite fibers. Thermal treatment of the cyclics in the presence of a catalyst can induce the polymerization of the cyclics to obtain high molecular weight polymers.

2.5 Incorporation of Phosphine Oxide Moiety on the Backbone of Poly(Arylene ethers)

Aromatic bishalogenphenyl derivatives in which the halogen is either a chlorine or a fluorine which also contain electron withdrawing groups such as sulfone and ketone groups react with the phenolates of aromatic bisphenols to generate aromatic ether bonds to yield high molecular weight poly(arylene ethers). In the late 1970s, another such monomer was investigated as a possible candidate in which the phosphine oxide was the electron withdrawing group (45). There are two routes available for the synthesis of activated dihalide aromatic

phosphine oxide monomer. The two synthetic routes are shown in Scheme 8. One alternative is by the Grignard route and the other route utilizes Friedel Craft chemistry to synthesize the bis(halogenated phenyl)phenyl phosphine oxide monomer (46-49). Even though the Grignard route is simpler and affords a higher purity and yield of the desired para halogenated product, from safety as well as from a cost point of view, the Friedel Craft route is desirable due to the low cost of the starting materials and less safety precautions that must be considered. Initial attempted polymerizations with bis(4-chlorophenyl)phenyl phosphine oxide with the potassium salt of bisphenol-A in DMSO resulted in only a low molecular weight oligomer with inherent viscosity of only 0.15 dl/g (45). Synthesis of high molecular weight polymers from bis(4-fluorophenyl)phenyl phosphine oxide with aromatic bisphenols resulted in high molecular weight polymers with reduced viscosity in the range of 0.3-0.4 dl/g (50). However, characterization of the resulting polymer was not disclosed and higher molecular weights were synthesized and characterized when reaction conditions were varied and optimized (51,52). Since the initial investigation using bis(4-fluorophenyl) phosphine oxide as the activated dihalide monomer, others have synthesized and characterized high molecular weight polymers by reacting it with various aromatic bisphenols (53-56). Recently, phenolphthalein was reacted with bis(4-fluorophenyl)phenylphosphine oxide to synthesize high molecular weight polymers and the T_g was observed to be approximately 30% higher than poly(arylene ether sulfones) (DCDPS and bisphenol-A) and the modulus was approximately 20% higher (57). This was postulated to be due to the increase in stiffness from the incorporation of the heterocyclics onto the backbone. Aminated derivatives of phenolphthalein monomers were also

synthesized and successfully polymerized with bis(4-fluorophenyl)phenyl phosphine oxide to obtain high molecular weight polymers.



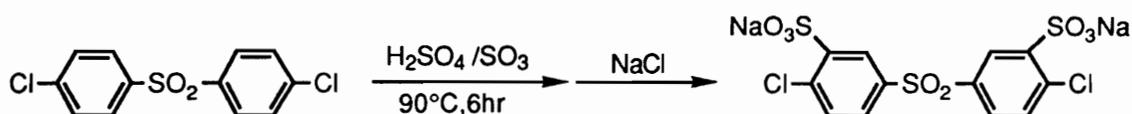
Scheme 8 Synthesis of bis(4-halophenyl)phenylphosphine oxide by Grignard and Friedel Craft Chemistry (46-49)

2.6 Functionalization of Poly(Arylene Ethers)

In the polymerization of two AA and BB type monomers such as DCDPS and bisphenol-A, if one to one stoichiometry of DCDPS and bisphenol-A is used, the resulting high molecular weight polymer will have a statistical distribution of end groups where 25% of the polymer chains will have both chlorine end groups, 25% of the polymer chains will have both phenol end groups and 50% of the polymer chains will have one chlorine end group on one end of the polymer chains and the other end will have a phenol end group. In the polymerization of AA and BB type monomers, functionalization can be controlled by offsetting the one to one stoichiometry and adding a slight excess of the monomer with the desired functionality. If a phenol terminated polymer is desired, a slight excess of the bisphenol-A is added relative to DCDPS. For the polymerization of AB type monomers such as bis(4-hydroxy-4'-chlorophenyl) sulfone, all of the polymer chains will have one hydroxy functionality and the other end will be chlorine terminated. Molecular weight can be controlled by adding a monofunctional encapper to offset the one to one stoichiometry required for the synthesis of high molecular weight polymers.

Another alternative method to achieve the desired functionality is to add a mono functional monomer such as m-aminophenol along with DCDPS and bisphenol-A will result exclusively in polymer chains with terminal amine groups (107). Another approach to achieving functionalized polymers is to derivatize polymers on the backbone instead of on polymer chain ends. Various functional groups have been incorporated on the the backbone of poly(arylene ethers), either by chemically modifying the polymers or by reacting (co-reacting) the monomer with two functionalities.

Poly(arylene ether sulfones) from DCDPS and bisphenol-A have been sulfonated on the phenyl ring of the bisphenol-A portion of the repeat unit by reacting the polymer with chlorosulfonic acid (58) or with a complex from sulfur trioxide and triethyl phosphate (59,60). The latter method was proven to be a better method because the degree of sulfonation can be controlled without branching or network taking place (by the formation of sulfone linkages), also, cleavage of the polymer chains may occur from the acid hydrolysis using the chlorosulfonic acid as the sulfonating reagent. The resulting sulfonic acid on the phenyl ring can be converted to the corresponding sulfonate groups by neutralization with various reagents. Using sodium hydroxide for neutralization will result in sodium as the counterion, other counterions such as zinc and magnesium have also been reported (60). The Tg of the polymer increased as the degree of sulfonation increased and the nature of the counterion influenced the solubility as well as the the modulus of the sulfonated polymer. Recently, another approach to obtain sulfonated poly(arylene ether sulfones) has been reported (61). A monomer which is a derivative of DCDPS was synthesized by the reaction shown below



High molecular weight copolymers were synthesized and characterized by reacting aromatic bisphenols with DCDPS and various amounts of the sulfonated monomer (1-30 mol%) with potassium carbonate as the base, dimethyl acetamide as the solvent and toluene as the azeotrope. The resulting

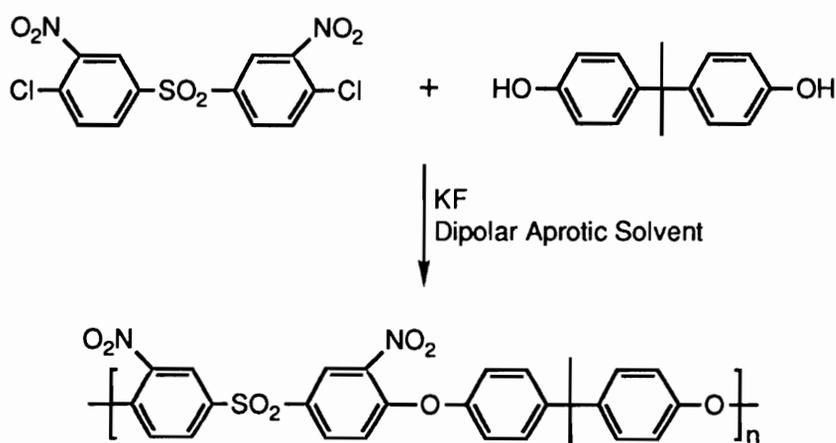
copolymers were soluble in methanol and showed a decrease in degradation temperature as the concentration of the sulfonate groups increased.

Bromination of a 60:40 copolymer of poly ether ether sulfone (PEES) and poly ether sulfone (PES) was accomplished by brominating exclusively on the hydroquinone unit of the repeat unit using a mixture of bromine and chloroform (62). As the level of bromination increased, a slight decrease in viscosity was observed which was attributed to the cleavage of the polymer chains by HBr which is a by product from the reaction. Also, when more than 50% of the hydroquinone rings needed to be brominated, a second bromination on the hydroquinone ring was observed.

In an attempt to obtain pendant carboxyl groups, a further modification of the resulting brominated copolymers of PES and PEES was attempted (63) by conducting a coupling reaction of the aromatic bromines with methyl acrylate and allyl alcohol by an organopalladium catalyzed reaction. Although not quantitative, they were able to use polymers with different levels of bromination and couple the aromatic bromine and methyl acrylate onto the polymer chains. Hydrolysis of the methyl acrylate to the carboxylic acid using tetrabutylammonium hydroxide resulted in a decrease in viscosity. Methoxy anions which are formed during hydrolysis probably cleaved the polymer chains by reacting with the ether link para to the sulfone to give methoxy end groups. They were much less successful in grafting allyl alcohol which often resulted in non reproducible results even under the same experimental conditions.

Nitro groups have also been incorporated on the backbone of poly(arylene ether sulfones) by reacting bis(4-chloro-3-nitrophenyl) sulfone with bisphenol-A using potassium fluoride (KF) in dipolar aprotic solvents (64). The reaction

scheme is shown in Scheme 9. The reaction was conducted using at least 500 mol% of KF relative to bisphenol-A and it is believed that potassium fluoride hydrogen bonds with bisphenol-A and enhance the nucleophilicity of the bisphenol sufficiently enough to allow nucleophilic displacement of the activated halide by the bisphenol. The optimum temperature and time was determined to be approximately 100°C for 48 hours. Only low molecular weight oligomers were obtained as judged by the inherent viscosity results and the highest value obtained was only 0.28 dl/g. Also, the attempted polymerization of bis(4-chloro-3-nitrophenyl) sulfone and bisphenol-A by interfacial polymerization using various phase transfer catalysts and solvents were reported (65).



Scheme 9 Reaction of bis(4-chloro-2-nitrophenyl)sulfone with bisphenol-A using KF in dipolar aprotic solvent (64)

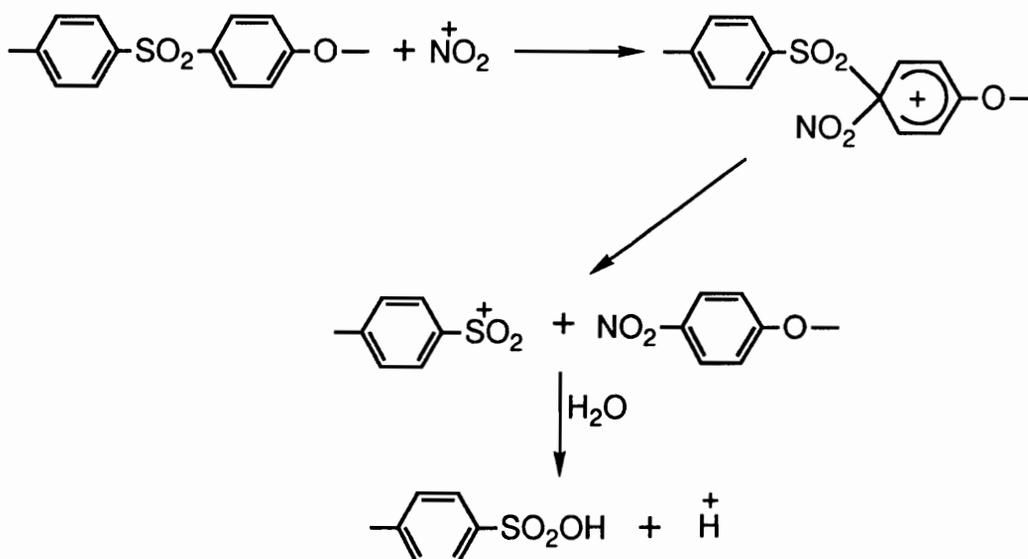
Using this method, higher inherent viscosities were obtained than by using KF, inherent viscosity as high as 0.84 dl/g was obtained using potassium hydroxide as the base, methylene chloride as the solvent and dicyclohexyl-18-crown-6 (DC-18-C) as the catalyst at 20°C for 24 hours. Attempted solution polymerization of

bis(4-chloro-3-nitrophenyl) sulfone with bis(4-hydroxyphenyl)sulfone in either NMP-toluene or DMSO-toluene using KOH as the base at 140°C for 24 hours resulted in inherent viscosities in the range of 0.10-0.15 dl/g (66).

Nitro groups on the backbone of poly(arylene ether sulfones) have also been obtained by nitrating the polymer directly. Poly(arylene ether sulfones) from DCDPS and bisphenol-A have been nitrated using mixtures of metal nitrates in trifluoroacetic anhydride (67). Nitration under the acidic conditions promoted partial cleavage of the polymer chains and a reduction in molecular weight was observed. After some difficulty, the nitro groups were reduced to the corresponding amines with stannous chloride and hydrochloric acid in refluxing tetrahydrofuran.

Successful nitration and reduction was also reported for a copolymer of PES and PEES by nitrating the hydroquinone unit of the repeat unit with a stoichiometric quantity of sulfuric acid and nitric acid mixture, using nitrobenzene as the solvent (68). They were able to nitrate various percentages of the hydroquinone units. Again, after various trials with different reducing reagents, it was possible to reduce the nitro groups using sodium dithionate in dimethyl formamide. For the copolymers with various degrees of substitution, the T_g increased as the extent of substitution increased, however, the increase in T_g was greater for the aminated copolymers than for the nitrated copolymers. This was attributed to the increased chain stiffness or resistance to rotation due to the presence of the amines which have the ability to hydrogen bond with other polar sulfone groups. The resulting aminated copolymers were successfully converted to maleimides by reacting it with maleic anhydride in cyclopentanone with sodium acetate and acetic anhydride.

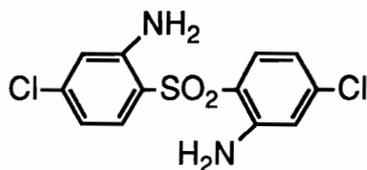
With the PES system, it was demonstrated that it was stable in sulfuric acid and that the composition remain unchanged (69). Attempts to nitrate the PES with different nitrating agents such as potassium nitrate/sulfuric acid and fuming nitric acid/sulfuric acid mixtures resulted in both a decrease in the viscosity and the percent yield of the recovered product. They attributed the decrease in the molecular weight from the ipso attack of the nitronium ion at the carbon bonded to the sulfone. This is shown in Scheme 10.



Scheme 10 Proposed mechanism for the reduction in molecular weight during nitration of PES (69)

Reduction of nitrated PES to the amines did not yield favorable results even when sodium dithionate was used as the reducing agent. Reduction often resulted in incomplete conversion even after extended reaction times and the products obtained after reduction contained less nitrogen than expected which was due to the occurrence of undesirable side reactions. They also conducted

copolymerizations using the monomer bis(2-amino-4-chlorophenyl)sulfone which contains both the activated halides and the amino functionalities.



They conducted copolymerizations of the above monomer (10 and 20 mol%) with DCDPS and bis(4-hydroxyphenyl)sulfone (Bis-S) using potassium carbonate and diphenylsulfone as the high temperature solvent. Inherent viscosity of the copolymerizations were relatively low, 0.25 dl/g for the 10 mol% incorporation and 0.22 dl/g for the 20 mol% incorporation respectively. Even though high reaction temperatures were used, the low inherent viscosities were probably due to the presence of the amine on the ortho position to the sulfone which reduces the electron withdrawing capacity of the sulfone. The next logical step would be to use a better leaving group and to use fluorine instead of chlorine. When copolymerizations (5 and 20 mol%) with the fluorine derivative were conducted under the same conditions as described above (70), the number average molecular weight decreased from 22,000 g/mol for the control to 14,000 and 10,000 for the 5 and 20 mol% incorporation of bis(4-fluoro-2-aminophenyl)sulfone.

Other functional groups such as pendant perfluoroalkyl groups by nucleophilic displacement (71) and low molecular weight oligomers with pendant maleimides by the electrophilic route have also been reported (72).

2.7 Characterization of Amorphous Poly(Arylene Ethers)

Amorphous poly(arylene ethers) are engineering thermoplastics which display good mechanical, chemical, and thermo-oxidative properties. Recently, poly(arylene ether phosphine oxides) have emerged as a possible new important material because in addition to the above desirable characteristics, they also function as a flame retardant (73) and show high char yields upon thermal degradation. Incorporation of phosphine oxides also increases the T_g. High molecular weight polymers from the reaction of bisphenol-A and bis(4-fluorophenyl)phenyl phosphine oxide has a T_g of 205°C as compared to 190°C for high molecular weight poly(arylene ether sulfones) from 4,4'-dichlorodiphenyl sulfone and bisphenol-A (74). The presence of triaryl phosphine oxides on the polymer repeat unit also enhances solubility and more importantly show very good resistance to degradation by atomic oxygen (74). In addition to these properties, phosphine oxides can also complex with various metals and the resulting complex of phosphine oxides with metals along the backbone has demonstrated enhanced thermal and mechanical properties. (75).

The desirable properties of poly(arylene ethers) such as chemical and thermooxidative stability is due to the presence of aromatic moieties which impart a certain degree of rigidity and stability to polymer chains. The bond strength of carbon-oxygen bond of aromatic ethers is comparable to the carbon-carbon bond. The bond strength of the former is 84.0 kcal/mol and the latter is 83.1 kcal/mol. Many poly (arylene ethers) are tough and the toughness has been attributed to the presence of the aromatic ether bonds (80). The toughness of poly(arylene ethers) has been investigated by many researchers using various experimental techniques such as dynamic mechanical analysis, dielectric

measurements and even nuclear magnetic resonance (76-80). Even though there still exist controversies and disagreements pertaining to how various factors such as the presence of water affect the toughness, it is generally agreed that toughness is the result of the the rotation of aromatic rings about ether bonds at temperatures well below the primary glass transition (T_g) temperature (77,79 80). These molecular movements has been commonly referred to as the beta (β) relaxation. For many poly(arylene ether sulfones), the β relaxation occurs at approximately -80°C . Structural variation in in the repeat unit of polymers has been determined to influence the notched impact strength (81). For poly(arylene ether sulfones), no direct correlation on the impact strength was observed as a function of T_g . The important variable turned out to be symmetry of the polymer chains. Structural changes that diminished symmetry such as deviation from all para orientation by inclusion of even a small amount of ortho or meta isomers reduced the impact strength. Also, para orientation with large asymmetric substituents resulted in a dramatic decrease on the impact strength. Poly(arylene ether ketones) showed a higher impact strength than poly(arylene ether sulfones), this behavior was rationalized on the basis of symmetry. The bond angles of C-CO-C and C-O-C in poly(arylene ether ketones) are both nearly identical (124°), whereas, the bond angle of C-SO₂-C in poly(arylene ether sulfones) is 105° . Therefore, poly(arylene ether ketones) are more symmetrical than poly(arylene ether sulfones).

Amorphous poly(arylene ethers) are soluble in chlorinated solvents such as chloroform, cyclic ethers such as tetrahydrofuran (THF), and dipolar aprotic solvents such as N-dimethylacetamide (DMAc) They are insoluble in alcohols and display good stability under mildly acidic and basic conditions (82).

The Tg values for poly(arylene ethers) are approximately between 150-280°C, depending on the nature of the monomers which are used for polymerizations. The Tgs of poly(arylene ethers) from the reaction of bisphenol-A with various activated dihalides are shown in Table 1. In addition to sulfone and ketone as the electron withdrawing groups, other functional groups which can also activate halides for step growth polymerizations are also shown in Table 1. The nature of the electron withdrawing group determines which halogen will be suitable for the synthesis of high molecular weight polymers. If a strong electron withdrawing group such as sulfone is used, then either chlorine or fluorine can be used to synthesize high molecular weight polymers, but fluorine containing monomer will react much faster because fluorine is a better leaving group. If a weaker electron withdrawing group such as ketone is used, then the halogen generally must be fluorine, an exception is if the monomer contains two ketone groups such as bis(halobenzoyl)benzene, then either chlorine or fluorine can be used. Shown are other functional groups which can sufficiently activate halogens for the synthesis of amorphous poly(arylene ethers) and which halogen must be used in order to obtain high molecular weight polymers. Shown in Table 2 are Tgs of amorphous poly(arylene ethers) from the reaction of DCDPS and various aromatic bisphenols. Flexible linking groups on the bisphenol such as methylene and sulfur results in a lower Tg, whereas, more rigid linking groups such as a cycloaliphatic group results in a higher Tg. Generally, substituents which will result in a stiffer polymer chain will increase the Tg. Also, the polarity of polymer chains will influence the Tg because of polar interactions between polymer chains. Incorporation of polar groups such as a sulfone will increase the Tg.

Table 1 Tgs of amorphous poly(arylene ethers) from bisphenol-A and various activated dihalide monomers (1,74)

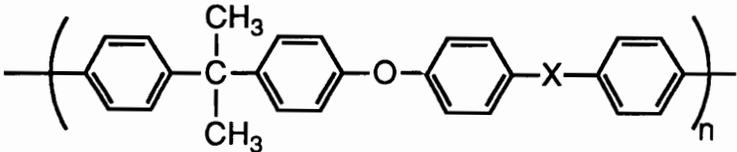
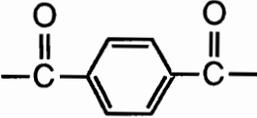
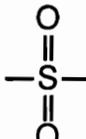
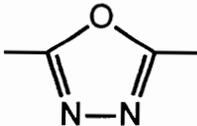
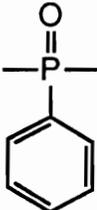
	X	Tg(°C)	Halogen
		155°C	F
		165°C	F, Cl
		165°C	F
		195°C	F, Cl
		180°C	F
		175°C	F
		205°C	F

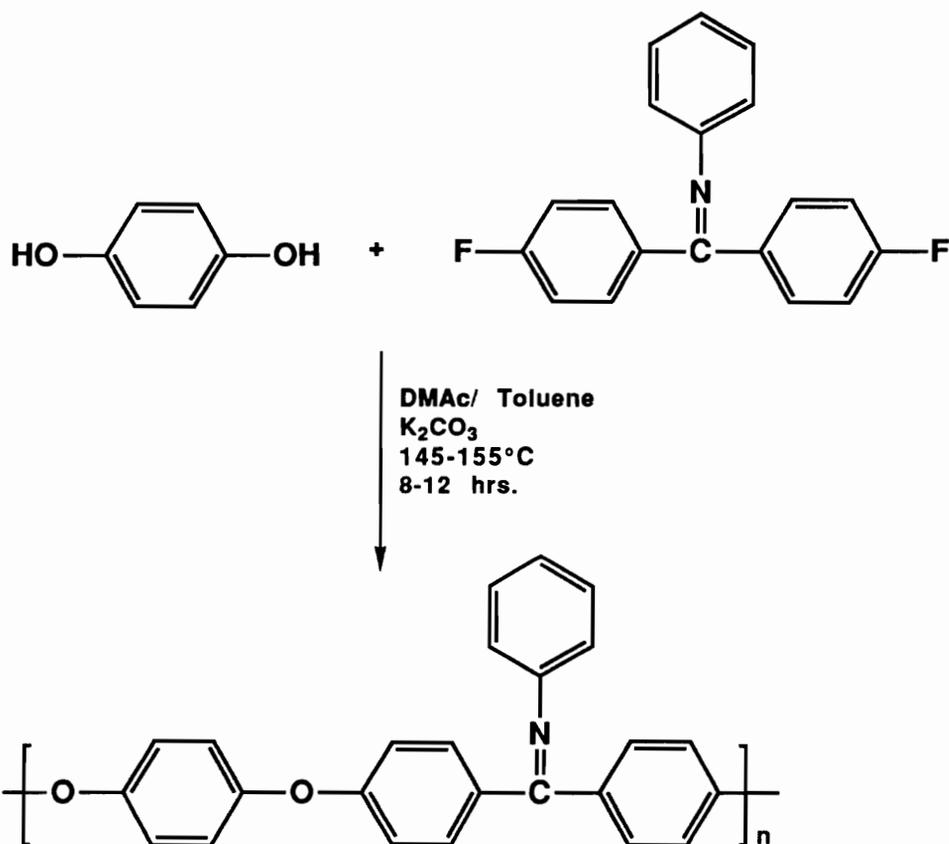
Table 2 The Tgs of amorphous poly(arylene ethers) with DCDPS and various aromatic bisphenols

X	Tg (°C)
—CH ₂ —	180°C
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}- \\ \\ \text{CH}_3 \end{array}$	195°C
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ -\text{C}- \\ \\ \text{C}_6\text{H}_5 \end{array}$	230°C
$\begin{array}{c} \text{CF}_3 \\ \\ -\text{C}- \\ \\ \text{CF}_3 \end{array}$	205°C
	250°C
—S—	175°C
—O—	180°C
$\begin{array}{c} \text{O} \\ \\ -\text{C}- \end{array}$	205°C
$\begin{array}{c} \text{O} \\ \\ -\text{S}- \\ \\ \text{O} \end{array}$	245°C

Since sulfone is a more polar group than ketone, polymers with a sulfone group on the repeat unit will have a stronger dipolar interactions between polymer chains and this results in a higher T_g for the poly(arylene ether sulfones) than poly(arylene ether ketones). These trends are clearly observed in Table 2.

2.8 Synthesis of Semicrystalline Poly(Arylene ethers)

For the synthesis of semicrystalline poly(arylene ethers), due to its semicrystalline nature, the oligomers precipitate from solution if the reaction temperature is well below the T_m of the resulting polymer. Alternative methods for the synthesis of semicrystalline poly(arylene ethers) at lower temperatures involve polymerization of protected monomers which will result in the obtainment of amorphous polymer precursors. The amorphous polymer is then deprotected to yield a semi crystalline polymer. Although many various methods have been reported (83-85), one method for the synthesis of semicrystalline PEEK from amorphous polymer precursor will be discussed to demonstrate the general synthetic rationale (86). The scheme for the synthesis of a amorphous polymer precursor poly(arylene ether ether ketimines) is shown Scheme 11. The protected activated dihalide monomer is synthesized from the reaction of aniline and difluorobenzophenone. The ketimine group, in a analogous manner to other electron withdrawing groups stabilize the intermediate by delocalizing the negative charge on the nitrogen atom. With this approach, the same reaction conditions for the synthesis of amorphous poly(arylene ether sulfones) by the DMAc/K₂CO₃ route can be used. The modified monomer prevents the polymer from crystallizing during polymerization.



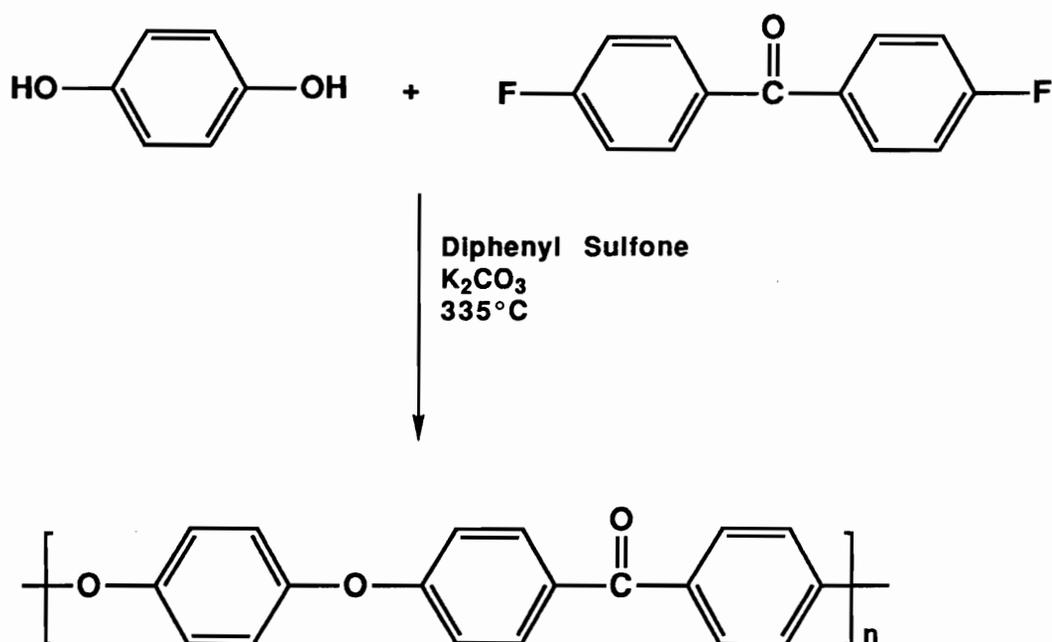
Scheme 11 Synthesis of amorphous poly(arylene ether ether ketimines) (83)

The resulting amorphous poly(arylene ether ether ketimines) can be synthesized and characterized by conventional means such as solution NMR and intrinsic viscosity in common organic solvents such as chloroform. Semicrystalline polymer can be obtained by converting the ketimines to ketones by hydrolysis with HCl in NMP. The conversion of the ketimines to ketones have been demonstrated to be a rapid and a quantitative process. The semicrystalline polymer that is obtained is in the form of a fine powder, and the particle size can be controlled by the rate of hydrolysis as well as by the agitation rate during

hydrolysis. Polymers obtained from this method has been applied to powder prepregging of composites (87).

When Farnham and Johnson attempted to synthesize PEK and PEEK using sulfolane as the solvent, they failed to obtain high molecular weight polymers due to premature crystallization of the polymer during polymerization. A major innovation on the synthesis of semicrystalline poly(arylene ether ether ketones) by the aromatic nucleophilic substitution was reported by ICI in 1975 by in which they used diphenyl sulphone as the the high boiling solvent (88). Using diphenyl sulfone as the solvent, they were able to conduct polymerizations at temperatures near the T_m of the resulting polymer and keep the polymer chains in solution for the synthesis of high molecular weight polymers. This discovery, along with using a slight excess of potassium carbonate allowed the synthesis of PEEK for the first time by the aromatic nucleophilic substitution. This is shown Scheme 12. Diphenylsulfone is a solid at room temperature and the polymer is usually isolated by coagulating the hot polymeric solution into a non solvent such as methanol. The resulting polymer is ground into a fine powder and extracted with methanol to remove the remaining DPS and then boiled in water to remove the excess potassium carbonate and the inorganic halide. The relative difficulty that is encountered with the isolation of the polymer as well as complications such as possible side reactions (89) and stability of monomers due to the high reaction temperatures is a disadvantage with this method.

Recently, a novel method for the synthesis of poly(arylene ether ketone) (PEK) has been reported which involve reaction of 4,4'-dichlorobenzophenone with sodium carbonate in the presence of silica and catalytic amount of cuprous or cupric salts using diphenylsulfone as the solvent (90,91).

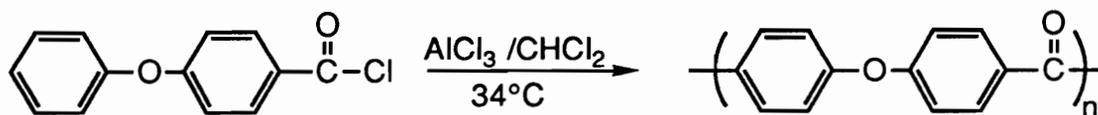


Scheme 12 Synthesis of semicrystalline poly(arylene ether ether ketones) from the reaction of 4,4'-difluorobenzophenone and hydroquinone with diphenylsulfone as the solvent (88)

The unique advantage with this approach is the ability to obtain polymers from the reaction of a less reactive and less expensive dihalide monomer (4,4'-dichlorobenzophenone).

Electrophilic substitution route has been utilized more extensively in the synthesis of semicrystalline poly(arylene ether ketones) than for the synthesis of amorphous poly(arylene ether sulfones). This process has been commonly referred to as polyacylation or polyaroylation. Early attempts to synthesize high molecular weight semicrystalline poly(arylene ether ketones) were unsuccessful due to the premature precipitation of the oligomeric species from solution. The first reported attempt was by Bonner (92) who reacted isothaloyl or terehaloyl chloride with diphenyl ether using nitrobenzene as the solvent and $AlCl_3$ as the

catalyst. Only a low molecular weight polymer was obtained which was evident by a low intrinsic viscosity ($IV \sim 0.2$). Similar results were obtained by Goodman et al. (93) who polymerized p-phenoxybenzoyl chloride using a slightly lower temperature and methylene chloride as the solvent.



Iwakura et al. (94) attempted polymerization of p-phenoxybenzoic acid using polyphosphoric acid as the solvent and obtained a moderate molecular weight polymer by protinating the carbonyls to keep the growing polymer chains in solution. With this method, it was demonstrated that the resulting polyetherketone had all para linkages. However, polymerization of aromatic dicarboxylic acids such as isophthalic acid and phthalic acid as well as aliphatic dicarboxylic acids with diphenyl ether using polyphosphoric did not result in formation of polymers. A major breakthrough was reported by Marks (95) who used liquid hydrogen fluoride as the solvent and boron trifluoride as the catalyst, with this system, a variety of high molecular weight semicrystalline poly(arylene ether ketones) were synthesized. A further advancement was made by Dahl (96) who stressed the importance of molecular weight control for the hydrogen fluoride and boron trifluoride system. The use of encapping agents such as biphenyl, p-phenoxy benzophenone and benzoyl chloride resulted in improved melt stability of the polymers. Also, inherent viscosities in the range of 0.8-1.65 were required for a proper balance between processability and useful mechanical properties.

Another route which has been reported to give high molecular weight semicrystalline poly(arylene ether ketones) was reported by Colquhoun et al.(97) who used trifluoromethanesulfonic acid as both the catalyst and the solvent for polymerization of select monomers which contained phenoxy and carboxylic groups. Using this approach, high molecular weight PEEK was synthesized by dissolving 4-(4'-phenoxy)phenoxybenzoic acid in trifluoromethanesulfonic acid at room temperature in 48 hours. However, there are limitations on the choice of monomer(s) which can be polymerized with this approach. For AB type monomers, the phenoxy end must be at least two phenylene groups removed from the benzoic acid end. For polymerization of AA BB type monomers, the dicarboxylic acid groups cannot be on the same benzene ring and the reactive aromatic group have to be at least three benzene rings and cannot contain electron withdrawing groups such as carbonyl groups. The presence of electron withdrawing groups will deactivate the phenyl groups to electrophilic attack.

So far, the system(s) which have been reported to give high molecular weight semicrystalline poly(arylene ether ketones) have utilized very acidic solvents to keep the growing polymer chains in solution during polymerization by protonating the carbonyl groups . Due to the corrosive nature of the these solvents, alternative methods are currently being investigated. Aluminum chloride route has received a renewed interest recently and Jansons et al.(98) have reported aluminum chloride in methylene chloride and dichloroethane in the presence of a Lewis base to be effective in giving high molecular weight polymers. The complex of aluminum chloride with Lewis bases such as dimethylformamide, tetramethylene sulfone, dimethyl sulfone, lithium chloride and sodium chloride is soluble in dichloromethane and the resulting complexed

solution function as a solvent or as a swelling medium for the growing polymer chains. Using this method, high molecular weight semicrystalline poly(arylene ether ketones) have been synthesized.

Recent development in the area of semicrystalline poly(arylene ether ketones) have been to find alternative ways to modify PEEK which will result in a higher T_g. The increase in T_g can be accomplished by incorporating biphenylene moities in the polymer repeat unit, but that will also cause an increase in T_m which causes difficulty in processing. Recently, reported was the synthesis and characterization of very short oligomeric species with aromatic ether ketone ketone (EKK) moities in the repeat unit which were functionalized with fluorine on each end (99). They proceeded to chain extend the oligomeric species by reacting it with hydroquinone or 4,4'-dihydroxydiphenyl sulfone with diphenyl sulfone as the solvent. With nucleophilic substitutions to synthesize polymers, ether ether interchange occurs, however, the idea behind this investigation was to diminish the probability of ether interchange by reacting only very short (n=1,2) oligomeric species. Chain extension of the oligomer (n=2) with 4,4'-dihydroxy diphenyl sulfone resulted in a polymer with increased T_g (180°C), but the T_m changed only slightly and was similar to that of PEEK (335°C). Also, the synthesis of block copolymers of PEEK/PEKK and PEKK/PES have also been reported (100,101). Since the block length of both components are very short no phase separation was observed.

2.9 Characterization of Semicrystalline Poly(Arylene Ethers)

Semicrystalline poly(arylene ethers) are polymers which along with amorphous regions are also defined by regions which are crystalline. Although some of the poly(arylene ether sulfones) are semicrystalline, it is more common for poly(arylene ether ketones) to be semicrystalline. In addition to the T_g , which corresponds to the macromolecular segmental motion of polymer chains in the amorphous region, semi crystalline polymers also display a crystallization temperature (T_c), temperature at which maximum crystallization occurs, and a crystallization melting temperature (T_m), the temperature at which the crystalline regions melt. For semicrystalline polymers, they do not flow until the temperature is above the T_m . With semicrystalline polymers, the usage temperature is extended to temperatures above the T_g , whereas, for amorphous polymers, the usage temperature is limited to below the T_g of the polymer. In Table 3, T_g and T_m values for various semicrystalline poly(arylene ether ketones) are shown. The T_g and T_m of semicrystalline poly(arylene ether ketones) are influenced by the ratio of ketones to ethers in the polymer repeat unit. As the concentration of ketone increases, the T_g and T_m also increases due to a higher extent of polar interactions between polymer chains. Likewise, as the concentration of ether increases, the T_g and T_m decreases due to ethers functioning as flexibilizers which decreases the rigidity of the polymer chains. Semicrystalline poly(arylene ethers) exhibit a much better solvent resistance than the amorphous poly(arylene ethers). Semicrystalline poly(arylene ether ketones) are not soluble in conventional organic solvents at room temperature, except in strongly acidic solvents such as sulfuric acid, triflic acid etc.. At temperatures greater than 300°C they are soluble in aromatic solvents such diphenylsulfone.

Table 3 The Tgs and Tms of various semicrystalline poly(arylene ether ketones) (40).

	Tg (°C)	Tm (°C)
	160	350
	150	315
	155	365
	155	365
	165	385

Recently, the semicrystalline poly(arylene ether ketones) have been very popular because they afford many of the desirable properties of thermosets such as high usage temperatures and very good solvent resistance, without the need for long cure cycles as required for thermosets. In addition, they still possess the critical thermoplastic behavior which allows semicrystalline poly(arylene ether ketones) be molded and remolded during the fabrication stage if the need arises, whereas, with thermosets this is not possible.

2.10 Networks

2.10.1 Time-Temperature-Transformation Diagram

One of the main characteristics of thermosets or networks are that they are insoluble, unlike amorphous thermoplastics which are readily soluble in organic solvents. Thermosets are insoluble in organic solvents, although they may swell to different extents in various solvents. Another characteristic of thermosets is that they do not flow when subjected to temperatures above T_g , this behavior has been commonly referred to as infusibility. The insolubility and infusibility limit the processability of thermosets. Thermosets include the phenolics, epoxies, some urethanes, acetylenes, maleimides, nadaimides and benzocyclobutenes.

Usually, thermosets are obtained from low molecular weight oligomers which can be easily processed. During the cure, the molecular weight increases due to the chain extension and branching reactions and this process continues until the gel point is reached. During an isothermal cure, the material undergoes various transformations and the curing cycle influences the final physical properties of the network (105). Two important transformations during a cure step are gelation and vitrification. Gelation is characterized by generation of infinite molecular weight and is dependent on reactivity, stoichiometry, and functionality of the starting materials. Prior to gelation, the material is still soluble, however, after gelation the material does not flow and is no longer processable. A gelled material consists mainly of an insoluble fraction but there may be present a very small amount of a soluble fraction which has been commonly referred to as the sol fraction. The other transformation is vitrification which occurs when the T_g of the growing network gradually increases during the cure and coincides with the cure temperature. At this point, the material is an ungelled glass, which

brings about an abrupt halt to curing due to the inability of the reactive groups to react with each other. Prior to vitrification, the cure is chemically or kinetically controlled, however, at vitrification the cure can still progress but only very slowly because the rate is diffusion controlled. Gillham (102-105) has reported the various transformations that occur during a curing process and has developed a useful diagram which is commonly known as the TTT (Time Temperature Transformation) diagram. The TTT Diagram is shown in Figure 2. The diagram was obtained by measuring the times to various states that occur during an isothermal cure at different cure temperatures using torsional braid analysis (TBA). These states are liquid, sol glass, sol/gel glass, gel glass, gel rubber, sol/gel rubber, and char. Also shown are three prominent temperatures which are T_{g0} , gel T_g , and $T_{g\infty}$. T_{g0} is the T_g of the uncured starting materials, below this temperature the material is only a soluble glass and no significant curing reactions occur below this temperature. The gel T_g is the point at which gelation and vitrification occur simultaneously. The $T_{g\infty}$ is the T_g of the fully cured network. As can be seen from the TTT diagram, curing between the T_{g0} and gel T_g only results in vitrification followed by gelation, but if the cure is conducted between gel T_g and $T_{g\infty}$, gelation occurs first followed by vitrification. At this point, the material consists of a finite molecular weight sol fraction and infinite molecular weight gel fraction. Further curing can be obtained by increasing the temperature. If the network material does not degrade at temperatures above the $T_{g\infty}$, reaction at higher temperatures is the most direct method of obtaining a fully cured material. This method is more applicable for reaction of linear rubber systems in which the fully cured network has a relatively low T_g . For high T_g systems in which reaction above the $T_{g\infty}$ leads to a thermal degradation, fully

cured material can be obtained by tailoring the time temperature cycle to reach the full cure line by curing between gel T_g and $T_{g\infty}$. The TTT diagram also shows the line corresponding to phase separation, this was obtained by combining the TBA results with cloud point measurements for a rubber modified thermoset.

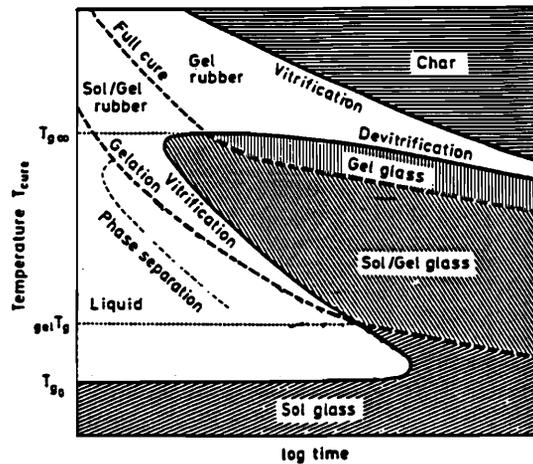


Figure 3 TTT diagram showing various states that occur during isothermal curing as a function of temperature and time (105)

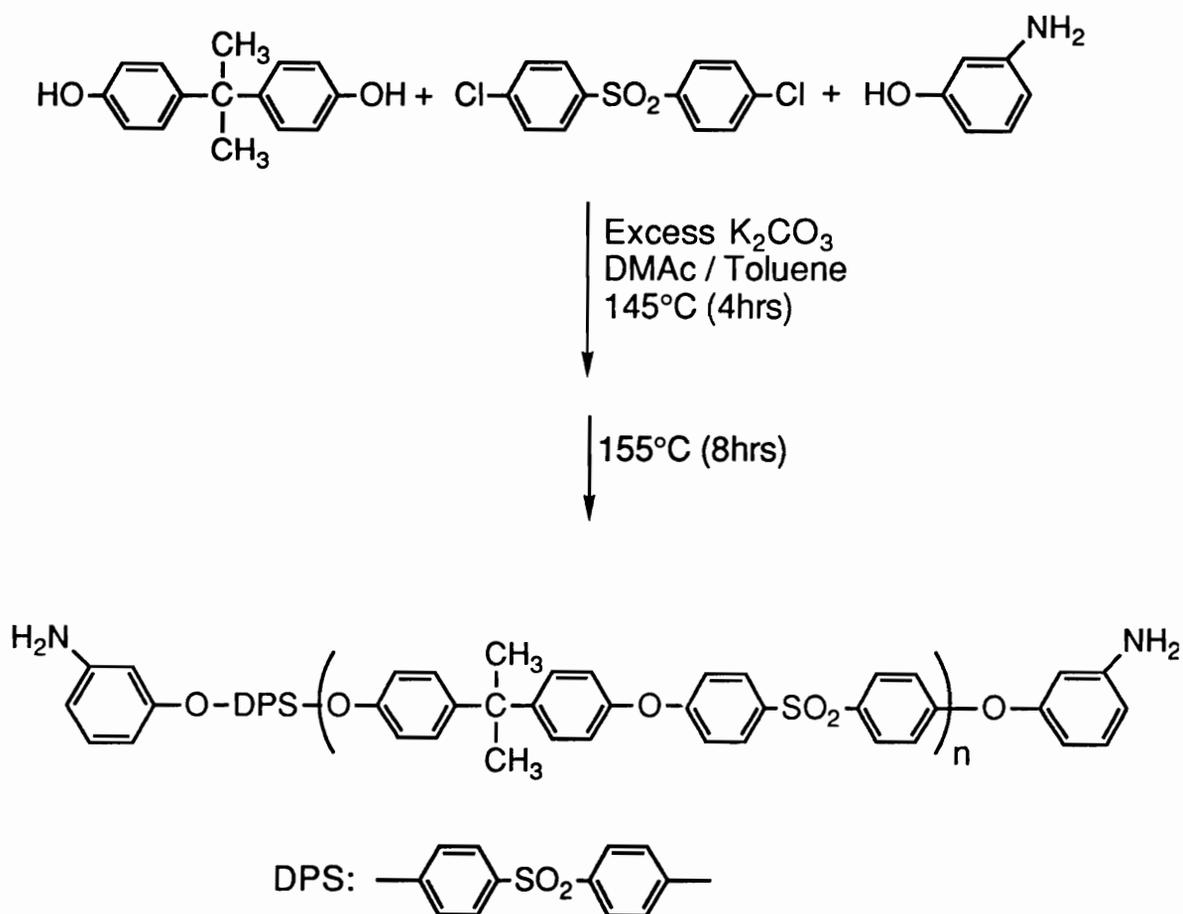
The results show that phase separation occurs prior to gelation and that the window for onset of phase separation and gelation decreases as the cure temperature increases. The cure temperature influences the morphology that develops by affecting the amount, the composition, and the distribution of dimensions of the dispersed phase and the TTT diagram provide very useful information which can be used to control the onset and the duration of phase separation.

In the area of composites, it is desirable to have a low viscosity resin for good wetting of the resin to the composite fibers. The TTT diagram can be used to control the viscosity levels and the time and temperature cycle so as to minimize the stresses associated with shrinkage of the cured resin which cause

the fibers in the composites to buckle. The TTT diagram also provide valuable information pertaining to the storage temperature and how long reactive materials can be stored without being gelled.

In short, the TTT diagram allows one to choose the temperature and the time of cure such that various states such as gelation, vitrification, and phase separation occur in a controlled manner to optimize the properties of the resulting network. Recently, a new TTT diagram for a tetrafunctional epoxy modified with poly(ether sulfone) and dicyandiamide as the curing agent has been reported (106). Using torsional braid analysis along with other characterizational methods, they were able to take into considerations other transformations such as onset of phase separation, gelation, fixation of the dimension of the phase separated structure, end of phase separation and vitrification .

Modifications of amine terminated oligomers of poly(arylene ethers) to other functional groups capable of undergoing crosslinking reactions have been a common method to obtain networks. The main focus behind research efforts with networks from poly(arylene ethers) has been to retain the attractive properties of poly(arylene ethers) while simultaneously enhancing the solvent resistance and increasing the T_g . In this area, the synthesis and modification of amine terminated poly(arylene ethers) has been extensively utilized. The synthesis of amine terminated poly(arylene ethers) involves incorporation of either meta or para aminophenol as the monofunctional endcapper (204,107). The synthesis of amine terminated poly(arylene ether sulfones) from Bisphenol-A, DCDPS and meta aminophenol using potassium carbonate route is shown in Scheme 13.

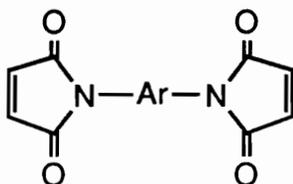


Scheme 13 Synthesis of amine terminated poly(arylene ether sulfones) from bisphenol-A and DCDPS using meta aminophenol as the endcapper (107)

The amount of the monofunctional encapper incorporated is determined by the Carothers equation which is used to calculate various molecular weights of the halogen terminated oligomers. The molecular weight of the oligomer governs the concentration of the monofunctional endcapper. As the molecular weight of the oligomer increases, the concentration of the amine decreases accordingly, so there is an inverse relationship between the molecular weight of the oligomer and the concentration of the amine. The resulting amine terminated poly(arylene ether sulfone) can be characterized by intrinsic viscosity, NMR, and by titrating the amine groups to determine the molecular weight.

2.10.2 Bismaleimides

Bismaleimides are an important class of materials that undergoes thermal free radical crosslinking reactions to yield networks. Networks from bismaleimides may display attractive properties such as good physical properties, thermal stability, and processability. The general structure of bismaleimides is shown below



The Ar may be any aromatic moiety from a monomeric unit or it can also be aromatic units on the repeat unit of a polymer. Therefore, a wide range of structures can be obtained by varying the nature of Ar. The crosslinking can be induced either thermally or by a microwave (107). An advantage with networks from bismaleimides is that no volatile by products are formed during the cure and they have been investigated as a possible candidate as a matrix resin for high performance fiber reinforced composites. The cure of bismaleimides have been investigated using electron spin resonance (ESR), nuclear magnetic resonance (NMR), and differential scanning calorimetry (DSC).(108-111). The curing of maleimides is shown in Figure 4. Due to the presence of two adjacent imide carbonyls and its electron withdrawing effect on the olefin bonds, bismaleimides undergo curing just above the crystalline melting point of the bismaleimide monomer or the T_g of the polymer. During the cure, it is believed that radicals are produced which combine with other radicals to form covalent bonds (108).

Networks from monomeric bismaleimides display a high T_g and a high modulus, but the cured network is very brittle due to the high crosslink density resulting from the relative low molecular weight of the starting material. There have been various efforts to increase the toughness of these brittle networks. One of these efforts have been to increase the molecular weight between the maleimides by incorporating oligomeric poly(arylene ethers) since these polymers have been shown to be tough and show good mechanical properties. One of the modification involves the synthesis of amine terminated poly(arylene ethers) which is then reacted with maleic anhydride to afford maleimide terminated poly(arylene ethers) (107,115). Shown in Scheme 14 are various methods for the conversion of amines to maleimides (116). In principle, every aromatic diamine or amino terminated oligomers can be used. By increasing the molecular weight between the maleimides, the crosslink density can be decreased and the resulting network can be toughened. Various amine terminated poly(arylene ethers) have been converted to the corresponding maleimides and crosslinked. Lyle et al.(107) have synthesized various oligomers of amorphous maleimide terminated poly(arylene ether ketones) and crosslinked the maleimides either by a thermal treatment or by a microwave treatment to afford tough networks. They observed that as the molecular weight between the maleimides increased, the fracture toughness of the networks also increased. Also, the thermal coefficient of expansion of the networks decreased as the molecular weight decreased due to an increase in the crosslink density. The maleimide terminated oligomers of poly(arylene ether ketones) can be directly blended with monomeric bismaleimides such as bismaleimidodiphenylmethane (117,118). By varying the blend composition, the properties of the resulting

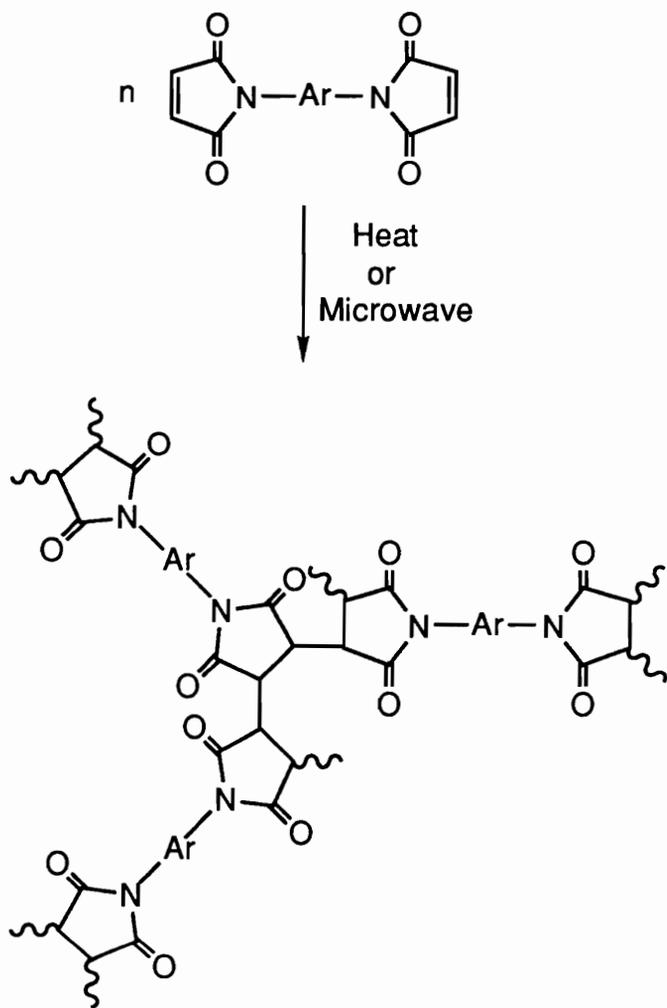
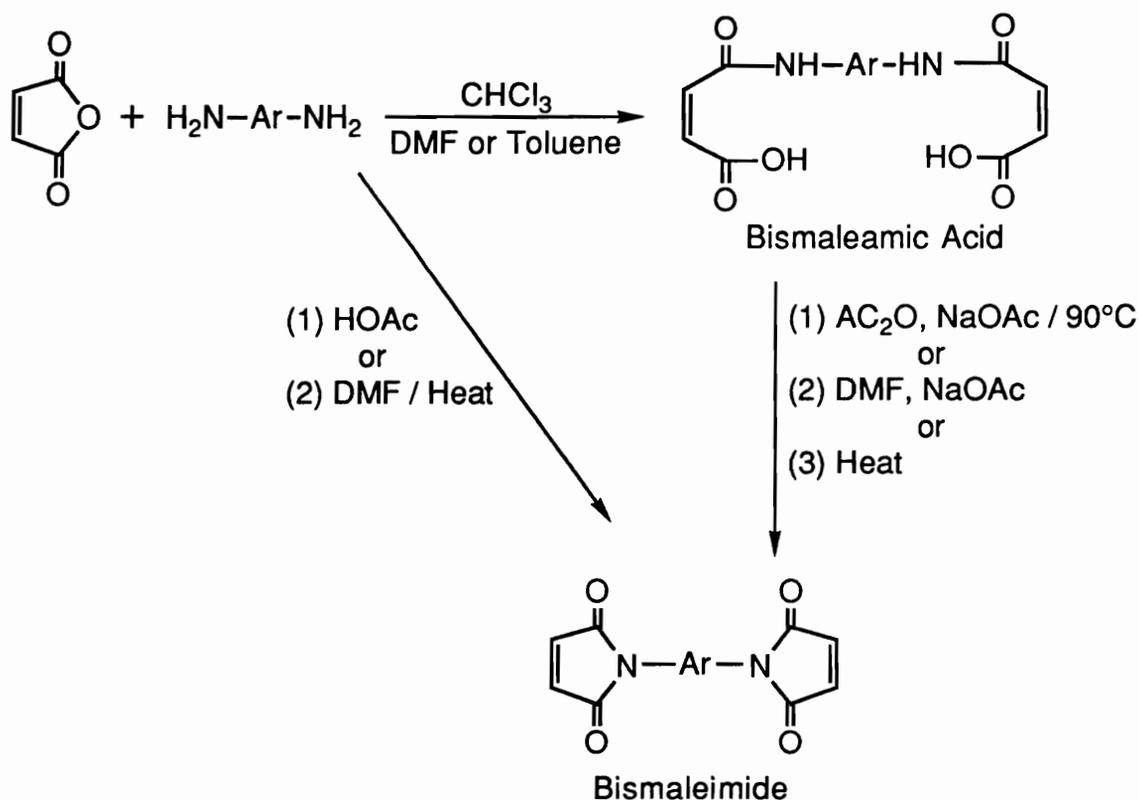


Figure 4 Network formation from the cure of maleimides



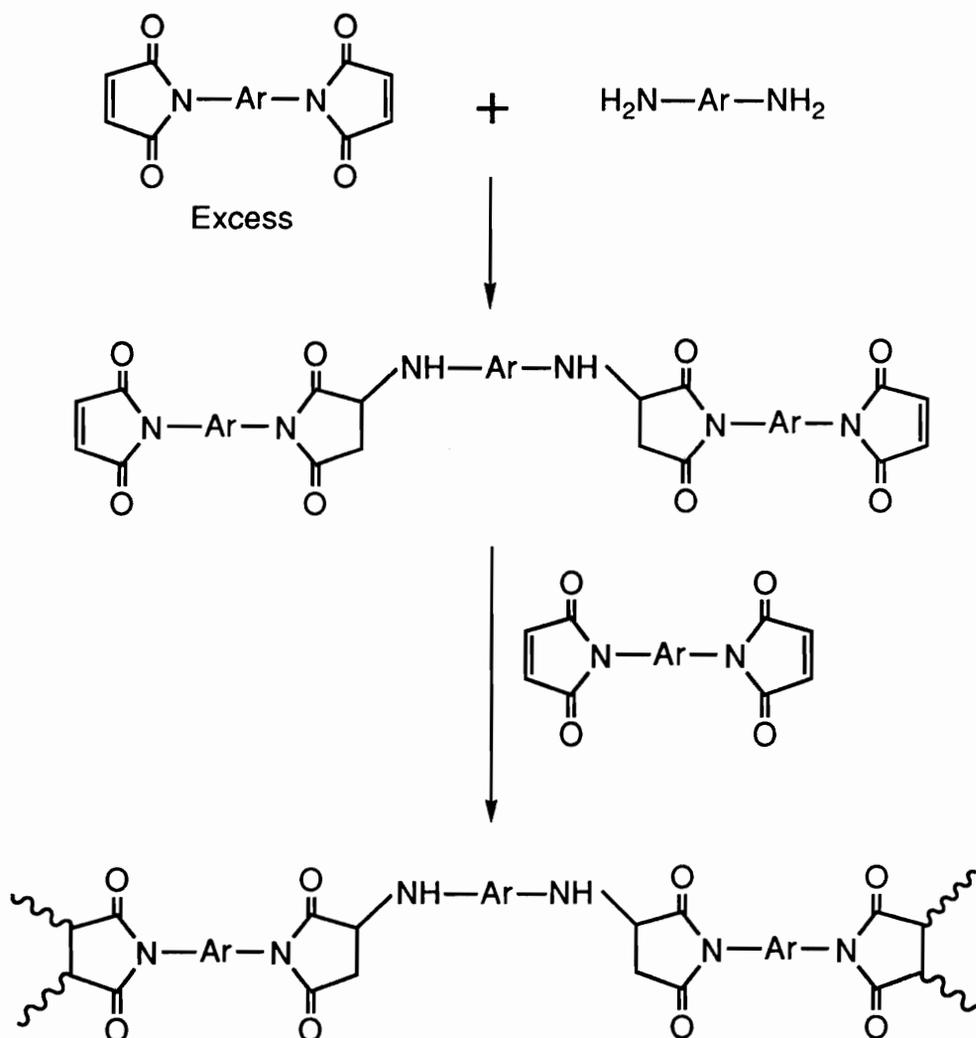
Scheme 14 Various methods available for the conversion of amines to maleimides (116)

network such as the fracture toughness, crosslinked density, and rubbery modulus can be controlled.

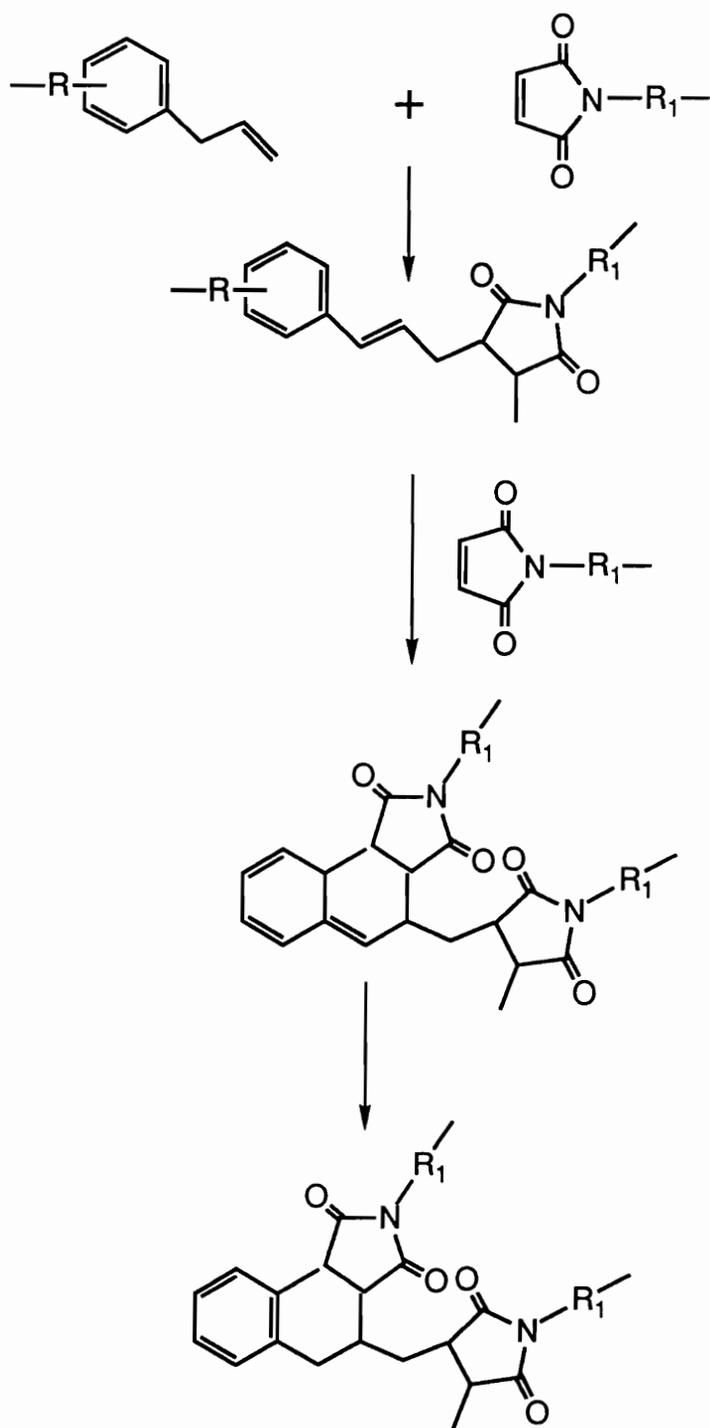
Another method which has been reported to increase the toughness of brittle maleimide networks has been to incorporate aromatic diamino compounds or amine terminated oligomers of poly(arylene ethers) with monomeric bismaleimides(119-122). In the presence of amines, maleimides may chain extend by a Michael addition reaction. The chain extended species then undergo crosslinking reactions if an excess bismaleimides is used to form networks. The reaction is shown in Scheme 15.

Another approach to toughen brittle bismaleimides has been to incorporate allylphenyl comonomers(123,124). In the presence of allylphenyl monomers, Diels Alder reactions are proposed to take place, as is shown in Scheme 16. The mechanism which has been proposed involve the allyl group reacting with the olefin bonds of maleimides which result in an ene adduct, this adduct reacts further with excess maleimides and rearomatization result in the formation of a network. The modified networks showed improved flexural strength and flexural strain with increasing comonomer concentration. The fracture toughness increased as more of the comomer was incorporated with a maximum at approximately 40 percent. The moisture absorption also decreased as the concentration of the comonomer increased, but the Tg of the modified network deacresed as more of the comonomer was incorporated. Wilkinson et al.(125) have reported toughening of commercial methylene dianiline based bismaleimide / o,o'-diallylbisphenol-A resin system with various thermoplastic modifiers. The nature of the thermoplastic modifier was varied as well as the molecular weight, end group, and the amount of the thermoplastic modifier incorporated into the resin. As the molecular weight of the thermoplastic modifier increased, the fracture toughness also increased. With respect to the thermoplastic modifier, higher Tg thermoplastics resulted in a lower fracture toughness value for the modified networks. The nature of the end groups also influenced the fracture toughness, thermoplastic with reactive amine end groups resulted in a higher fracture toughness than for those networks which were modified with unreactive end groups. The morphology of the modified network was dependent on the amount (wt%) of the thermoplastic that was incorporated. Below 15%, a two phase morphology was obtained in which micron size particles

of the thermoplastic was dispersed in the maleimide network. At approximately 15%, a phase inversion occurred and for the 20, 25 and 30 percent incorporation, a phase inverted morphology was obtained in which the thermoplastic was the continuous phase and epoxy as the discrete phase.



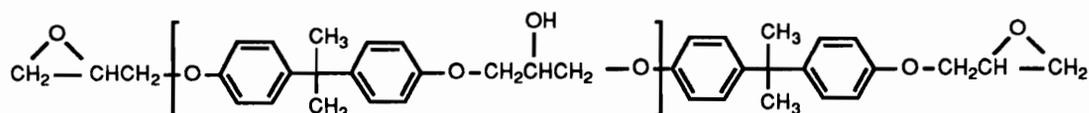
Scheme 15 Michael addition of amines with maleimides followed by network formation of maleimides (119)



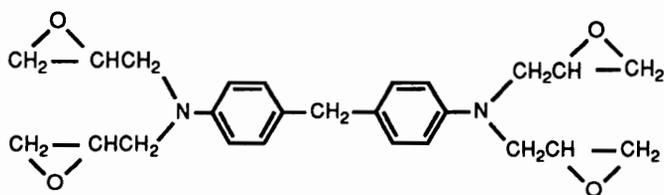
Scheme 16 Network formation from Diels Alder reaction of allylphenyls with maleimides (123)

2.10.3 Epoxies

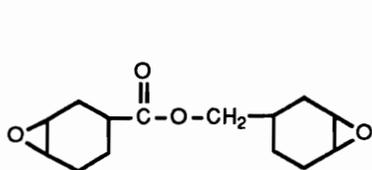
Epoxies are another class of functional group that can undergo crosslinking reactions with curing agents to afford networks. Some of the common epoxy resins that are commercially available are shown in Figure 5. Although epoxies were initially utilized as coating and adhesives, its scope of application has expanded to encapsulation of electrical and electronic components.



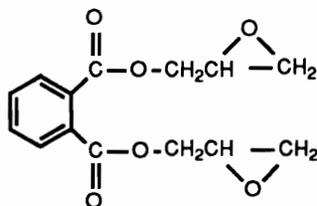
Glycidated Bisphenol-A



Glycidated Polyamine



Cycloaliphatic Resin



Glycidated Polybasic Acid

Figure 5 Commonly utilized epoxy resins (126)

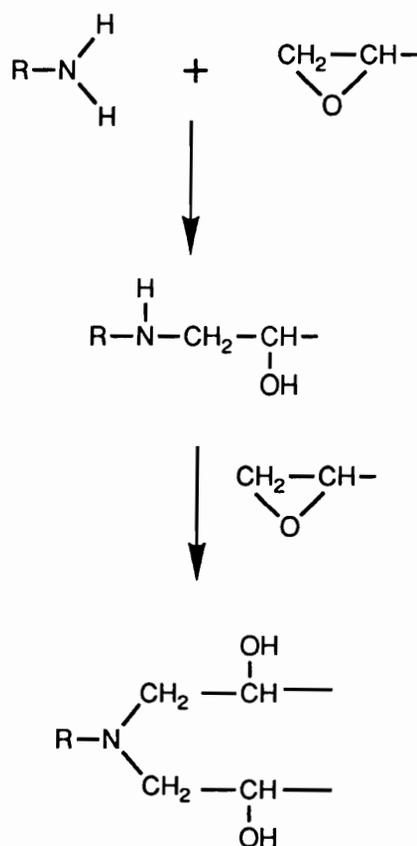
Recently, epoxies have also been investigated as a possible candidate for applications in fiber reinforced composites. Some of the attractive properties of epoxies are:

- Excellent adhesion to a variety of substrates and reinforcements
- Low shrinkage on cure
- No volatiles given off during the curing process
- Good dimensional stability
- Good chemical resistance
- Good mechanical and electrical properties

Various curing agents can be used for the curing of epoxies, common curing agents are aliphatic and aromatic amines, cyclic anhydrides, imidazoles, dicyandiamide and Lewis acid which are typically boron trifluoride complexes (126). Of these, only the amine curing agents and the mechanisms by which they participate in curing reactions will be addressed.

All aliphatic, cycloaliphatic and aromatic amines react with epoxides without the formation of by-products. Schechter et al. (127) reported that reaction of amines with epoxide ring proceeds according to Scheme 17. The initial step involves the reaction of the primary amine with the epoxide, this results in the formation of a secondary amine and a secondary alcohol. The resulting secondary amine reacts further with another epoxide to produce a tertiary amine and another secondary alcohol. The reaction of the secondary amine with epoxide is slower due to the steric hinderance about the nitrogen atom (128). The reaction between the secondary alcohol and epoxide has been shown to be negligible for most stoichiometric amine concentrations (129). Due

to a greater nucleophilicity, aliphatic amines react more rapidly with epoxides than aromatic amines. In general, linear aliphatic amines cure epoxy resins rapidly at room temperature, thus, they are the curing agent used in the epoxy or crazy glue. Cycloaliphatic amines such as piperidine are more hindered than linear aliphatic amines and react more slowly and require heat for curing. Aromatic amines react with epoxides more slowly than aliphatic and cycloaliphatic amines and usually are cured at elevated temperatures 93-177°C. Due to a lower reactivity of aromatic amines with epoxides, it is usually possible to obtain a usable solid B-stage (thermoplastic) with extended storage life. Partially cured material may have a storage life of 1-2 weeks at room temperature.



Scheme 17 Mechanism of reaction of an amine with an epoxide (127)

Despite the attractive properties of epoxy networks, they are inherently very brittle which limit their utility. Inclusion of rubber particles have been utilized to improve the toughness of epoxy networks (130-135). This is achieved by co-reacting various amounts of a oligomeric rubbery component. The most commonly utilized rubbery component is the carboxyl terminated butadiene acrylonitrile copolymer (CTBN) or the amine terminated butadiene acrylonitrile copolymer (ATBN). Initially, the rubber, epoxy, and the curing agent forms a homogeneous mixture. During the curing process, the rubber phase separates and form discrete micron particles (136-138). The modified network from the inclusion of a rubbery component has been shown to dramatically improve the fracture toughness of the epoxy network. The fracture toughness has been shown to be dependent on the testing rate (139), temperature (140), crosslink density (141), volume fraction of rubber (110), and the nature of the curing agent (142,143). Even though it is widely accepted that inclusion of rubbery particles improve the fracture toughness of epoxy networks, the mechanism(s) to account for the toughness have not been clear and there still exist controversies (144-149). Often more than one mechanism acting simultaneously have been reported to explain the toughening effect of the rubbery particles (150-151). The general concept which has been agreed by many researchers is the effect of the crosslink density or the number average molecular weight between crosslink sites $\langle M_c \rangle$. It has been demonstrated that it is the plastic deformation of the matrix such as crazing, voiding and shear yielding which may be the main source for the toughening by the inclusion of the rubber particles into the epoxy networks (141,152-154). Truong et al. (155) has demonstrated that for unmodified epoxy networks, the crosslink density can be varied by using different curing cycles.

They observed that a long cure at a low temperature resulted in a network with a low number average molecular weight between crosslinked sites. A short cure at high temperatures resulted in a network with a higher number average molecular weight between crosslinked sites which can be reduced with a subsequent cure. As the network becomes more brittle (molecular weight between crosslink site decreases), the epoxy network is less able to undergo plastic deformations. This is the reason why inclusion of rubber particles improve the fracture toughness of epoxy networks from difunctional epoxy resins, however, attempts to toughen tetrafunctional epoxy resins have proven to be much less successful due to a decreased ability of the epoxy network to undergo plastic deformation.

Although improvement in the fracture toughness has been obtained by co-reacting rubber with epoxy resins, a small amount of rubber remains in the epoxy network. This results in the lowering of the modulus and the T_g because the modulus and the T_g of the rubber modifier is much lower than the matrix. To circumvent these undesirable effects, others have incorporated engineering thermoplastic particles into epoxy networks. By modifying epoxy networks with thermoplastics, the fracture toughness can be improved without sacrificing the high modulus and the high T_g . The most commonly investigated thermoplastic blends have been poly(ether sulfones) and poly(ether imides). Bucknall and Partridge (156) initially attempted to toughen epoxy networks with poly(ether sulfones). Even though the thermoplastic phase separated during the cure, no significant improvement in fracture toughness was observed. This result was attributed to the poor adhesion between the phase separated particles and the epoxy matrix. Bucknall and Gilbert (157) investigated the incorporation of poly(ether imides) by physical blending into tetra functional epoxy resin, and they

were able to increase the fracture toughness from 0.5 to 1.42 MNm^{-3/2}. They were also able to obtain two phase morphologies with their systems. They attributed the increase in the fracture toughness to a sufficiently strong interface resulting from either van der Waals bonding, other physical interactions or a possible reaction with the epoxy resin. Hedrick et al. (158) incorporated oligomers of poly(arylene ether sulfones) (PSF) with reactive hydroxyl functional groups into bisphenol-A epoxy resin (Epon 828) and obtained a dramatic improvement in the fracture toughness of epoxy networks. The incorporation was conducted by pre-reacting the thermoplastic with the epoxy resin (Epon 828) using catalytic amount of quaternary ammonium hydroxide to obtain epoxide terminated thermoplastic. Temperature was then increased to decompose the catalyst and the stoichiometric amount of diaminodiphenylsulfone was then added as the curing agent and cured. Both the incorporated amount and the molecular weight was varied to investigate the effect on the morphology and the fracture toughness. Later Hedrick et al. (159) also demonstrated the same behavior with amine terminated oligomers of poly(arylene ether sulfones). They demonstrated that morphology and the fracture toughness was dependent on the molecular weight of the thermoplastic modifier and the amount of the modifier that was incorporated into the epoxy resin. A two phase morphology in which the thermoplastic particles were uniformly distributed in the continuous epoxy matrix was obtained when the incorporation of the thermoplastic was less than 15%(wt). The average particle size increased as molecular weight of the thermoplastic modifier increased and the frequency of the particles increased as more of the thermoplastic was incorporated into the epoxy network. When the incorporation of the thermoplastic was greater than 20%(wt), a phase inversion occurred in

which the thermoplastic became the continuous phase and the epoxy was the discrete phase.

Using SEM, DMA and optical microscopy Brown and Kim (160) investigated the morphology and the toughening mechanisms of a commercial thermoplastic modified epoxy network. They observed a similar two phase morphology in which phase inversion occurred at a certain incorporation of the thermoplastic. However, they observed a continuous increase in the fracture toughness as more of the thermoplastic was incorporated, regardless of the morphology. They attributed this behavior to different toughening mechanisms which operate at different compositions. Prior to phase inversion, toughening was attributed to the ductile tearing of the thermoplastic dispersed phase and to localized plastic yielding of the matrix. After phase inversion, the toughness was attributed to the ductile tearing of the continuous thermoplastic phase.

Another toughening mechanism that have been proposed for the toughness of thermoplastic modified epoxy networks is the ductile stretching and tearing of the phase separated thermoplastic particles and plastic deformation of the matrix around the particles (159). In the presence of phase separated particles, there are stress concentrations around the particles when a uniform tensile stress is applied. This stress concentration induces or promotes localized plastic deformation of the matrix and thereby increase the fracture toughness. Another mechanism that has been proposed is commonly referred to as the "crack pinning mechanism" and this mechanism involves the interaction between the crack front and the dispersed thermoplastic particles (160). Conditions which favor crack pinning mechanism are systems where the matrix is brittle and the particles are well bonded to the matrix and are not penetrable. As the crack front

propagates through the sample it encounters the phase separated thermoplastic particles. Since the particles are inherently very tough and ductile, the crack front bows around the particles and causes formation of secondary cracks while the main crack front is still pinned by the particles. The particles that pin the crack do not fracture themselves until the crack front is circumvented by the particle. This process of forming new secondary crack fronts not only diffuse the crack front but also requires more energy for the propagation of the crack front.

In thermoplastic modified epoxy networks, the number average molecular weight between crosslinked sites was determined to be not as important as in the rubber modified epoxy networks (161). Zengli et al. (161) have also investigated bisphenol-A polysulfone (PSF) and polyethersulfone (PES) modified difunctional and tetrafunctional epoxy resins with both diaminodiphenyl sulfone and piperidine as curing agents. They investigated the effect of molecular weight and end groups on both the morphology and the fracture toughness. The end groups they investigated were chlorine and hydroxyl end groups. When they modified diglycidyl ether bisphenol-A epoxy resin with hydroxyl terminated PES with diaminodiphenylsulfone as the curing agent, they were not able to observe phase separated PES particles. Since there was no phase separation of PES, they observed only a slight increase in the fracture toughness as function of molecular weight. They observed two phase morphologies with modification of both chlorine and hydroxyl terminated oligomers of PSF. However, epoxy networks that were modified with hydroxyl terminated PSF showed a greater fracture toughness than epoxy networks modified with chlorine terminated PSF. Also the fracture toughness was enhanced as molecular weight increased, this they attributed to the increased ductility of PSF as a function of molecular weight.

They also investigated various possible mechanisms to account for the increased fracture toughness by calculating both the change in critical strain release rate (ΔG_{1c}) and the stress distribution in the epoxy matrix around a PSF particle. The ΔG_{1c} they calculated was smaller than the experimental value, so they deduced that stretching and tearing of the PSF particles were inadequate to explain the enhancement in the fracture toughness. They also calculated the stress concentration factor around the particles and compared the calculated value to the rubber modified epoxy networks in which the plastic deformation plays a critical role increasing the fracture toughness. The value they obtained for the thermoplastic modified epoxy network was much lower than the value they obtained for the rubber modified network. Based on the results of these calculations, along with no observed effect of the cross linked density on the fracture toughness, they deduced that plastic deformation of the matrix around PSF particles may not be an important mechanism to account for the increased fracture toughness. With SEM, they also observed no significant plastic deformation around PSF particles of fractured surfaces. Based on their investigation, they stated that major mechanism for the tough ductile thermoplastic modified epoxy networks seemed to be the crack pinning mechanism and they they were able to observe strong evidences of the crack pinning mechanism using SEM.

2.10.4 Ethynyls

Phenyl ethynyls or acetylenes are another functional group which can undergo crosslinking reactions to afford networks. Recently, amorphous

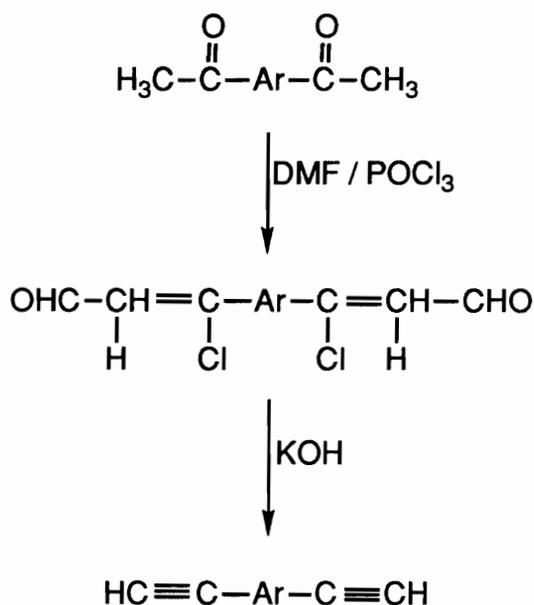
poly(arylene ether) oligomers with terminal ethynyls and substituted ethynyls have received considerable attention as a candidate for high temperature adhesives and high performance matrix resins for aerospace applications (162-167, 205). Acetylene terminated oligomers provide better solubility and processability because of the low melt viscosity. The modification of poly(arylene ethers) with terminal ethynyl groups retain the attractive properties of amorphous poly(arylene ethers) and increase the solvent resistance and the T_g. Ethynyls offer attractive features such as undergoing cure under moderate conditions without the evolution of volatiles for void free fabrication of parts. They can also be thermally induced to initiate cure without the use of catalysts and they have excellent shelf lives. Various synthetic methods for the incorporation of the reactive functional groups have been utilized and reported. First, a survey of the various methods for the syntheses of ethynyls and substituted ethynyls will be addressed followed by ways in which they have been incorporated onto various polymeric systems. Even though there are many different synthetic routes available for the synthesis of ethynyls and substituted ethynyls, only the commonly utilized synthetic method will be discussed. One of the method is the reaction of aryl acetyl functionality with a Vilsmeier reagent which is a complex of N,N-dimethyl formamide (DMF) and an acid chloride such as phosphorous oxychloride or oxalyl chloride (168,169). This results in the formation of β-chlorocinnam aldehyde which can be cleaved with a strong base such as sodium hydroxide to obtain the ethynyl group. Yields of as high as 80% have been obtained under proper conditions. The reaction scheme is shown in Scheme 18.

Another method which can be used is the reaction of aryl halides, particularly iodides with metal alkynides such as copper acetylides (170). Using

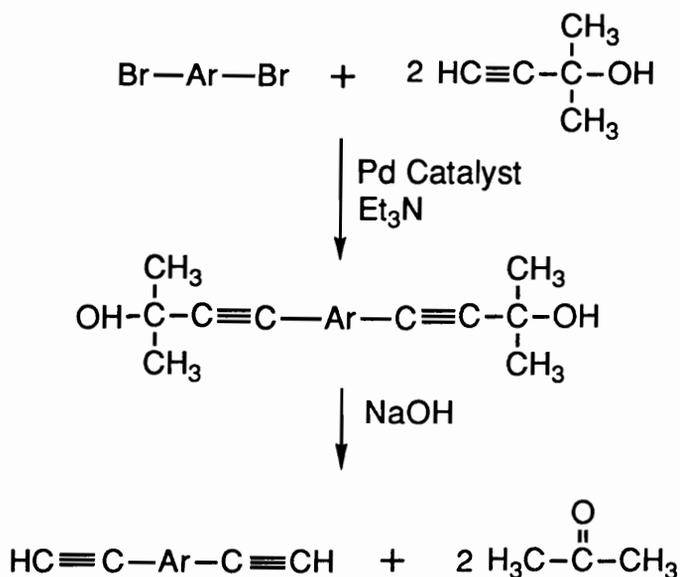
this method 90% yield has been reported for the synthesis of diphenylacetylene from the reaction of iodobenzene with copper phenylacetylide in pyridine.

A method which is commonly utilized is the palladium catalyzed reaction of organic halides with acetylenes. There are two variations to this method, one involves the reaction of aryl bromides or iodides with 2-methyl-3-butyne-2-ol to yield 3-methyl-4-aryl-3-butyne-2-ol which in the presence of a caustic will liberate the protecting group to produce the corresponding ethynyl (171-173). This is shown in Scheme 19. This is the preferred method because of the high yield in the first step which is greater than 90%. The second step to cleave the protecting group is a quantitative process but a disadvantage with this method is that compounds containing functional groups which are sensitive to a strong base such as esters or prone to degradation under basic conditions cannot be used. Ethynyls from compounds with ester functionality has been obtained by using sodium hydride as the base instead of sodium hydroxide. The other variation involves the use of trimethylsilylacetylene instead of 2-methyl-3-butyne-2-ol (174). Although this method is more expensive, this modification allows the conversion of aryl bromides which contain base sensitive functionality such as aldehydes. The resulting trimethylsilyl group can be cleaved with potassium carbonate to yield the ethynyl derivative.

The reactive ethynyls and substituted ethynyls, namely phenylethynyls have been incorporated by various means to oligomers and high molecular weight amorphous poly(arylene ethers). Incorporation of reactive groups on oligomer chain ends have been achieved by two ways. The first method involves the synthesis of various molecular weight of hydroxyl terminated oligomers which is then reacted with an aromatic acid chloride which contains the ethynyl



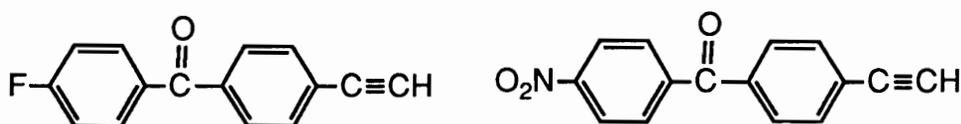
Scheme 18 Synthesis of ethynyls from reaction of aromatic acetyl groups with Vilsmeier reagent (168)



Scheme 19 Synthesis of ethynyls by palladium coupling reaction of aromatic bromides with 2-methyl-3-butyne-2-ol (171)

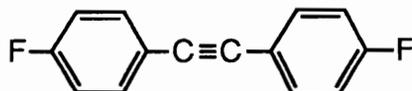
functionality such as meta or para ethynyl benzoyl chloride (175,176). This results in the formation of hydrolytically unstable ester linkages on the chain ends. In addition, this method involves the isolation of the hydroxyl terminated oligomers prior to the modification of the hydroxyls to ethynyl terminated oligomers, and a further isolation step is required after the modification. The reaction scheme is shown in Scheme 20.

The other method for the synthesis of ethynyl terminated poly(arylene ethers) utilizes a monofunctional encapper which contains the ethynyl functionality such as those shown below (177-179).

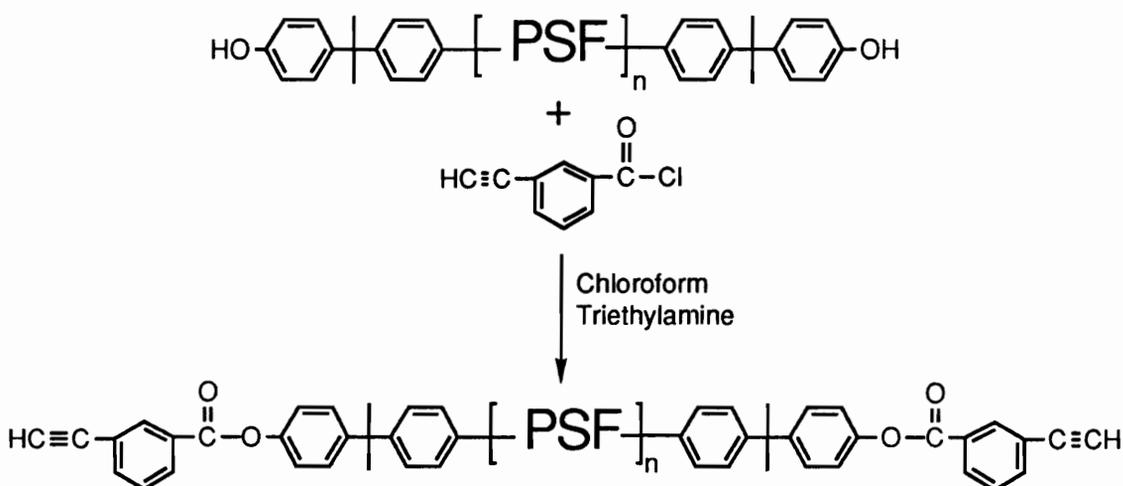


This method is simpler because the ethynyl terminated oligomers can be obtained directly after the isolation of the oligomer after polymerization. In addition, ether bonds are generated during the process which is more hydrolytically stable than the ester bonds. From model reactions, the displacement of the nitro group occurred faster than the fluorine with the phenolate of 4-isopropylphenol (178). With this method, the endcapper was introduced last after the phenolate terminated oligomers were formed in situ. Using the monofunctional ethynyl encapper, various molecular weight oligomers were synthesized, characterized and crosslinked to afford networks with better solvent resistance and higher T_gs. In addition to having ethynyls on chain ends, ethynyls have also been introduced on the backbone of amorphous poly(arylene ethers) (180). This was accomplished by the successful synthesis of a new novel monomer in which the ethynyl group was demonstrated to

sufficiently activate fluorines for aromatic nucleophilic substitution. The monomer was bis(4-fluorophenyl)acetylene.



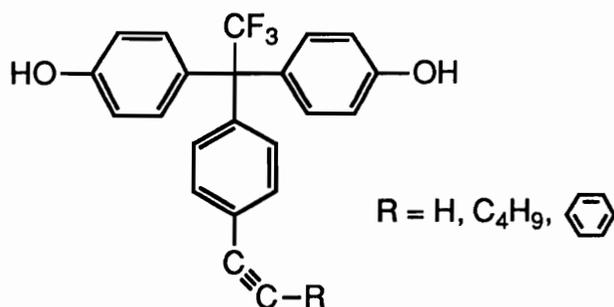
Inherent viscosity of 0.69 dl/g was obtained by reacting the above monomer with bisphenol-A. When the ethynyls were cured, a maximum exotherm for the crosslinking occurred at 380°C.



Scheme 20 Conversion of hydroxyl terminated polysulfone to an ethynyl derivative (175)

Others have reported on the synthesis of pendant ethynyls on the backbone of amorphous poly(arylene ethers) (181-183). An example involves the synthesis of a bisphenol monomer which contains the ethynyl functionality (183). Homopolymerization with difluorobenzophenone resulted in inherent viscosity of 0.38 dl/g when R was a phenyl. When R was H or C₄H₉ gel formation was observed, however, this problem was alleviated by conducting copolymerizations in which 10 and 30% of the ethynyl containing bisphenol was

reacted with another bisphenol (hexafluoro bisphenol-A) and difluorbenzo phenone.

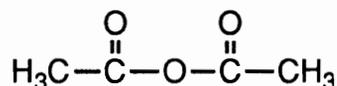


The exotherm for the curing of the ethynyls and substituted ethynyls were reported to occur at 265°C for the ethynyl, 300°C for the hexynyl and 370°C for the phenyl ethynyl from DSC measurements conducted at 20°C per minute.

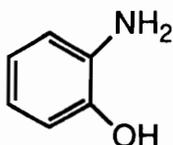
The mechanism of the crosslinking of the ethynyls is complex and still is not fully understood, the insoluble nature from the cure make identification of the products difficult. From the initial investigation into the cure mechanism and products, it was believed that cyclotrimerization of the ethynyls to generate the aromatic moiety was the main product (184), however, it was later demonstrated that cyclotrimerization only accounted for approximately 30% of the products (185,186). Based on the curing of a monomer bis(4-ethynylphenyl) ether, double bonded conjugated structures were the principle components and a free radical initiated mechanism was proposed (187). Others have reported various other reaction mechanism and products such as diacetylenes from the coupling of the ethynyls (Glazer coupling) and the formation of enynes (Strauss coupling) (188,199). Aromatic products from Diels-Alder reactions such as tetramers, naphthalenes and conjugated polyenes have also been reported (190,191). In addition, electrophilic addition of the ethynyl group to an aromatic moiety has also been reported (188,192).

3.0 EXPERIMENTAL

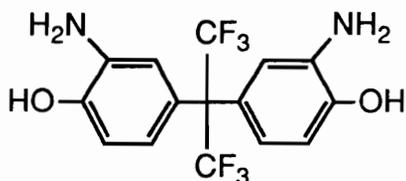
3.1 Chemical Structure and Physical Properties of Monomers, Solvents and Reagents



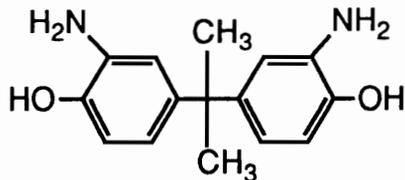
Supplier: Fisher
Name: Acetic Anhydride
Empirical Formula: $\text{C}_4\text{H}_6\text{O}_3$
Molecular Weight: 102.09 g/mol
Bp: 139°C (1atm)
Density: 1.08 g/ml



Supplier: Aldrich
Name: o-Aminophenol 2-Aminophenol
Empirical Formula: $\text{C}_6\text{H}_7\text{NO}$
Molecular Weight: 109.13 g/mol
Mp: 174-177°C



Supplier: Central Glass Company of Japan
Name: 2,2'-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane
Empirical Formula: $\text{C}_{15}\text{H}_{12}\text{F}_6\text{N}_2\text{O}_2$
Molecular Weight: 366.26 g/mol
Mp: 244-245°C



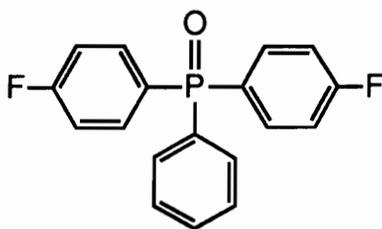
Supplier: Synthesized

Name: 2,2'-Bis(3-amino-4-hydroxyphenyl)propane

Empirical Formula: $C_{15}H_{18}N_2O_2$

Molecular Weight: 258.32 g/mol

Mp: 256°C



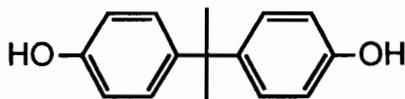
Supplier: Synthesized according to reference (74).

Name: Bis(4-fluorophenyl)phenylphosphine oxide

Empirical Formula: $C_{18}H_{13}F_2PO$

Molecular Weight: 314.27 g/mol

Mp: 124-126°C



Supplier: Dow Chemical Company

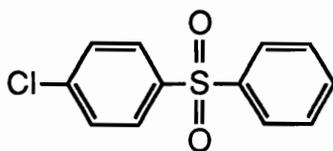
Name: Bisphenol-A 2,2'-Bis(4-hydroxyphenyl)propane

4,4'-Isopropylidenediphenol

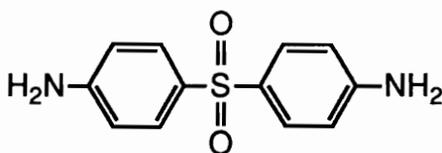
Empirical Formula: $C_{15}H_{16}O_2$

Molecular Weight: 228.27 g/mol

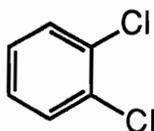
Mp: 158-159°C



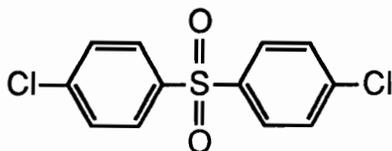
Supplier: Aldrich
Name: 4-Chlorophenyl phenylsulfone
Empirical Formula: $C_{12}H_9ClSO_2$
Molecular Weight: 252.72 g/mol
Mp: 90-94°C



Supplier: Aldrich
Name: 4,4'-Diaminodiphenylsulfone 4-Aminophenylsulfone
Empirical Formula: $C_{12}H_{12}N_2SO_2$
Molecular Weight: 248.30 g/mol
Mp: 175-177°C



Supplier: Fisher
Name: o-Dichlorobenzene 1,2-Dichlorobenzene
Empirical Formula: $C_6H_4Cl_2$
Molecular Weight: 147.01 g/mol
Bp: 180.5°C (1atm)
Density: 1.30 g/mol



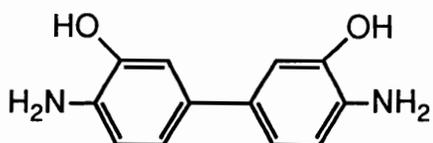
Supplier: Amoco

Name: 4,4'-Dichlorodiphenylsulfone (DCDPS) Bis(4-chlorophenyl)sulfone

Empirical Formula: $C_{12}H_8Cl_2SO_2$

Molecular Weight: 287.17 g/mol

Mp: 145-148°C



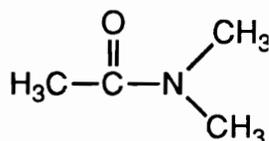
Supplier: Krichev

Name: 2,2'-Dihydroxybenzidine 4,4'-Diamino-3,3'-Dihydroxy Biphenyl

Empirical Formula: $C_{12}H_{12}N_2O_2$

Molecular Weight: 216.24 g/mol

Mp: 292°C (dec)



Supplier: Fisher

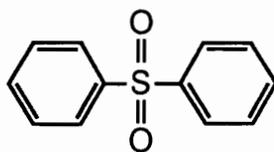
Name: N,N'-Dimethylacetamide (DMAc)

Empirical Formula: C_4H_9NO

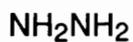
Molecular weight: 87.12 g/mol

Bp: 165°C (1atm)

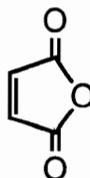
Density: 0.937 g/ml



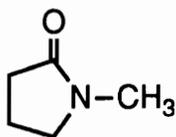
Supplier: Aldrich
Name: Diphenylsulfone Phenylsulfone 1,1'-Sulfonylbisbenzene
Empirical Formula: $C_{12}H_{10}SO_2$
Molecular Weight: 218.27 g/mol
Mp: 128-129°C
Bp: 378-379°C



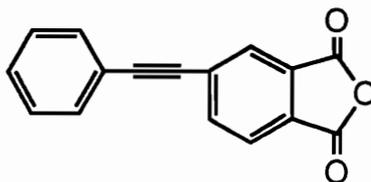
Name: Hydrazine
Empirical Formula: H_4N_2
Molecular Weight: 32.05 g/mol
Bp: 113.5°C (1atm)
Density: 1.021 g/ml



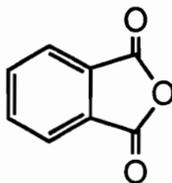
Supplier: Aldrich
Name: Maleic Anhydride 2,5-Furandione
Empirical Formula: $C_4H_2O_3$
Molecular Weight: 98.06 g/mol
Mp: 52.8°C



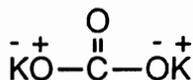
Supplier: Fisher
 Name: N-Methylpyrrolidone (NMP) N-Methylpyrrolindone
 Empirical Formula: C_5H_9NO
 Molecular Weight: 99.13 g/mol
 Bp: 202°C (1atm)
 Density: 1.033 g/ml



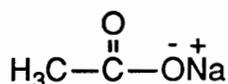
Supplier: Synthesized according to reference (193)
 Name: 4-Phenylethynylphthalic Anhydride
 Empirical Formula: $C_{16}H_8O_3$
 Molecular Weight: 248.23 g/mol
 Mp: 146-148°C



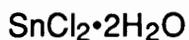
Supplier: Aldrich
 Name: Phthalic Anhydride 1,3-Isobenzofurandione
 Empirical Formula: $C_8H_4O_3$
 Molecular Weight: 148.11 g/mol
 Mp: 130.8°C



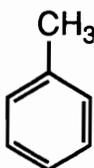
Supplier: Fisher
 Name: Potassium Carbonate
 Empirical Formula: K_2CO_3
 Molecular Weight: 138.21 g/mol



Supplier: Fisher
Name: Sodium Acetate
Empirical Formula: $\text{C}_2\text{H}_3\text{NaO}_2$
Molecular Weight: 82.04 g/mol



Supplier: Aldrich
Name: Tin (II) Chloride Dihydrate
Empirical Formula: $\text{H}_4\text{O}_2\text{Cl}_2\text{Sn}$
Molecular Weight: 225.63 g/mol
Mp: 37.7°C (dec.)
Bp: 652°C



Supplier: Fisher
Name: Toluene Methylbenzene
Empirical Formula: C_7H_8
Molecular Weight: 92.13 g/mol
Bp: 110.6°C (1atm)
Density: 0.866 g/ml

3.2 Purification of Monomers, Solvents and Reagents

Acetic Anhydride: Distilled from calcium hydride and stored under nitrogen in a round bottom flask with a rubber septa.

o-Aminophenol: This compound was purified by refluxing in diethyl ether for ~5 hours. The collected off white product was crystallized from charcoal treated ethanol. It was necessary to repeat the process more than once to yield a very pure compound. Alternative method to crystallization was sublimation at a reduced pressure.

2,2'-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane: This monomer was purified by crystallization from ethanol (95%) and the resulting crystals were filtered and washed with diethyl ether and dried in a vacuum oven at ~100°C for 8 hrs. The product obtained was a fluffy white material

2,2'-Bis(3-amino-4-hydroxyphenyl)propane: This compound was very difficult to purify. The best method to obtain a very pure material was to ensure a high degree of purity for the *2,2'*-Bis(3-nitro-4-hydroxyphenyl) propane prior to the reduction. This compound has been reported in the literature to be crystallizable from ethanol, however, the solubility of this compound was very small and enormous volume of solvent was required.

Bis(4-fluorophenyl)phenylphosphine oxide (DFTPPO): Purified according to reference (74).

Bisphenol-A: This monomer was received in a monomer grade and was used without further purification, however, this monomer can be crystallized using toluene. Unlike DCDPS, this monomer was slower to develop crystals and was not as difficult to filter out the activated carbon.

4-Chlorophenyl phenylsulfone: This compound was purified by crystallization using either toluene or diethylether, using the latter solvent required a larger volume of solvent to obtain a homogeneous solution.

4.4'-Diaminodiphenylsulfone (DDS): Used as received, however, it can be crystallized from deoxygenated methanol.

o-Dichlorobenzene: Distilled from calcium hydride at a reduced pressure and stored under nitrogen in a round bottom flask with a rubber septa.

4.4'-Dichlorodiphenylsulfone (DCDPS): DCDPS was received in a monomer grade and no further purification was required, however, the monomer was dried in a vacuum oven at 80°C for 8 hours prior to use. This monomer can be purified using charcoal treated toluene, depending on the color of the homogeneous solution. Crystallization of this monomer was very rapid and it is advantageous to use small granules of charcoal instead of the fine powder for easier filtration. However, if the fine powder is used, glass fiber filter paper with smaller pores than the conventional filter paper (Fisher) can be used instead of celite to remove the charcoal. The resulting crystals were collected and dried in a vacuum oven at 80°C for 8 hours to remove the excess solvent, if large needles were obtained it was grinded and dried again to remove a trace amount of solvent.

2.2'-Dihydroxybenzidine: This compound was purified by forming the amine hydrochloride salt which was conducted by suspending the compound in a minimum amount of warm water (~60-70°C) and adding concentrated HCl dropwise until an intensive homogeneous brown solution was obtained. The charcoal treated solution was filtered and the resulting solution was cooled to

room temperature. Crystals were observed at this point, however, if crystals were not observed which often occurred if excess water was used, more concentrated HCl was added dropwise until a slight cloudy solution was observed. Soon thereafter, formation of crystals were observed. The collected crystals were dissolved in a minimum amount of water at ~60-80°C, treated with charcoal, filtered and sodium acetate was added until o-aminobisphenol precipitated from the solution. The precipitated product was filtered and washed with a copious amount of water followed by minimal amount of chilled ethanol and dried in a vacuum oven at ~100°C for 8 hours. The appearance of the resulting product was light pink which can turn brown upon exposure to light for an extended period of time (even during the drying stage in the vacuum oven), so the container with the product should be covered with aluminum foil during the drying stage.

N,N'-Dimethylacetamide(DMAc): This solvent was distilled from calcium hydride at a reduced pressure and stored under nitrogen in a round bottom flask with a rubber septa.

Diphenylsulfone: This compound was purified by crystallization from charcoal treated acetone, filtered, and dried in a vacuum oven.

Hydrazine: Used as received.

Maleic Anhydride: This compound was easily purified by sublimation at a reduced pressure.

N-Methylpyrrolidone (NMP): Distilled from calcium hydride using reduced pressure and stored under nitrogen in a round bottom flask with a rubber septa.

4-Phenylethynylphthalic Anhydride: Purified according to reference (193).

Phthalic Anhydride: Similar to maleic anhydride, this compound was purified by sublimation at a reduced pressure.

Potassium Carbonate: Used as received, however, it was dried in a vacuum oven at ~100°C/8hrs to remove moisture prior to use.

Sodium Acetate: Used as received.

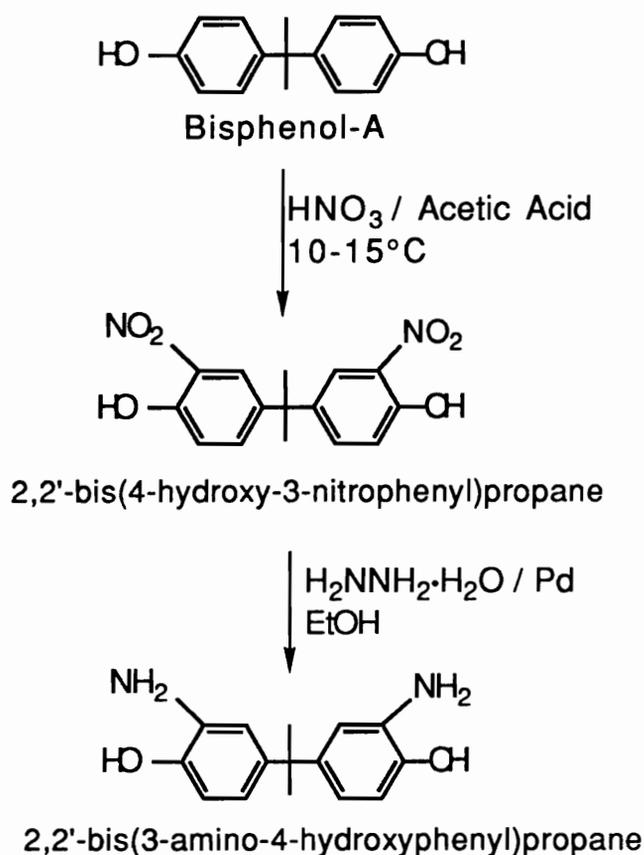
Tin Chloride Dihydrate: Used as received.

Toluene: Used as received.

3.3 Synthesis of Monomers and Polymers

3.3.1 Synthesis of 2,2'-Bis(3-Amino-4-Hydroxyphenyl)Propane

The 2,2'-bis(3-amino-4-hydroxyphenyl)propane was synthesized by nitration of bisphenol-A to obtain 2,2'-bis(4-hydroxy-3-nitrophenyl)propane which was then reduced using hydrazine and ethanol to yield 2,2'-bis(3-amino-4-hydroxyphenyl)propane. The scheme is shown in scheme 21.



Scheme 21 Synthesis of 2,2'-bis(3-amino-4-hydroxyphenyl)propane via nitration and reduction of bisphenol-A

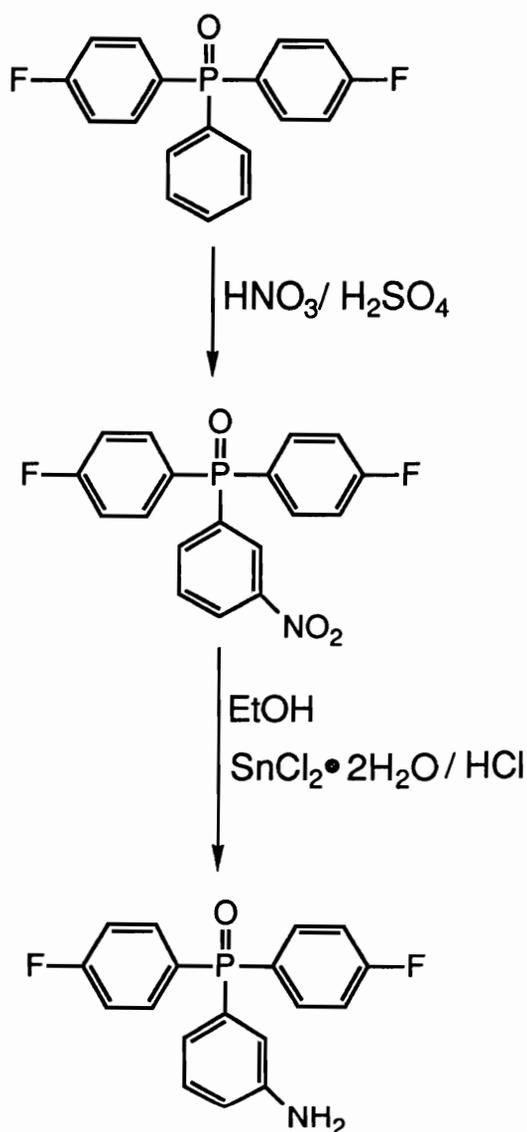
Nitration of bisphenol-A to obtain 2,2'-bis(4-hydroxy-3-nitrophenyl)propane was conducted using the following procedure. To a 500ml four neck round bottom flask equipped with a mechanical stirrer, a nitrogen inlet, a thermometer, and a addition funnel was added 50g (0.2190 moles) of bisphenol-A and washed with 150ml acetic acid. The reactants inside the flask were stirred at room temperature until most of the bisphenol-A dissolved. At this point, a ice/water mixture was placed under the flask until the temperature inside the flask decreased to approximately 10°C, temperature lower than 5°C will cause the mixture to solidify due to a relative low freezing point of acetic acid. At this point,

a mixture of 45g nitric acid (0.5038 moles) in 50 ml acetic acid was introduced dropwise and the overall temperature was maintained between 10-15°C. When the addition of nitric acid / acetic acid mixture was complete (~1.5 hr), the ice/water bath was removed and the resulting dark burgundy solution with precipitated product was allowed to equilibrate to room temperature for approximately 45 minutes. The solution was cooled to about 10°C and filtered and the filtrate was then precipitated into ice water mixture. The crude product was dissolved in diethyl ether and washed repeatedly with water until a neutral solution was obtained. Diethyl ether was removed and 85% yield of the crude 2,2'-bis(nitro-4-hydroxyphenyl) propane was obtained. The resulting product was crystallized (3 -4 times) with acetic acid and dried in a vacuum oven at 80°C for 8 hours. The crystallized product had a melting point of 133-135°C.

The nitro groups were reduced to the amines by the following procedure. To a 1000 ml four neck round bottom flask equipped with a mechanical stirrer, a nitrogen inlet, thermometer, addition funnel and a condenser was added 19.88 g (0.0625 moles) of 2,2'-bis(nitro-4-hydroxy phenyl) propane along with 0.99 g (5 wt%) of 10% Pd/Carbon and washed with 200ml of ethanol. The mixture was slowly heated and when the temperature reached about 45°C, 24 ml (0.5000 moles) of hydrazine was added dropwise. When the addition was complete, the mixture was refluxed for additional 3 hours. The resulting mixture was filtered through celite and washed with 200 ml hot ethanol. The first crop of white crystals were collected and a second crop of white crystals were collected by reducing the concentration of the filtrate. The total yield of 2,2'-bis(3-amino-4-hydroxyphenyl) propane from 2,2'-bis(3-nitro-4-hydroxyphenyl) propane was 48% (7.80 g) and the melting point was 249°C.

3.3.2 Synthesis of 3-Aminophenyl-bis(4-fluorophenyl)phosphine Oxide (Amino DFTPPO)

The synthesis of bis(4-fluorophenyl)-3-aminophenylphosphine oxide (Amino DFTPPO) was synthesized by nitration of bis(4-fluorophenyl)phenyl phosphine oxide (DFTPPO) to obtain bis(4-fluorophenyl)-3-nitrophenylphosphine oxide (Nitro DFTPPO) which was then reduced using $\text{SnCl}_2 \cdot \text{HCl}$ with ethanol to yield amino DFTPPO. The reaction scheme is shown in Scheme 22. The 2,2'-bis(4-hydroxy-3-nitrophenyl)propane was synthesized using the following procedure. To a 500ml four neck round bottom flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and an addition funnel was added 22.79g (0.0725 moles) of DFTPPO and 200ml H_2SO_4 . The contents were stirred at room temperature until a homogeneous solution was obtained. Then the flask was immersed in a ice water bath until the temperature inside the flask reached approximately 5°C . At this point, a solution of 7.51g (0.0834 moles) of HNO_3 and 28ml H_2SO_4 in an addition funnel was introduced dropwise. When the addition was complete, the ice water bath was removed and stirred for another half hour. The reaction mixture was then slowly poured into 3000ml of water and ice. The precipitate was filtered and washed with a copious amount of water. It was then dissolved in chloroform, filtered and washed with water two times, once with a aqueous solution of sodium bicarbonate, and then finally with a saturated sodium chloride solution. The chloroform layer was separated and dried with magnesium sulfate and removal of chloroform resulted in approximately 90% yield of the crude product which was a yellow material with a melting point of $146\text{-}148^\circ\text{C}$. This material was used without further purification for the reduction of the nitro groups to the amines.



Scheme 22 Synthesis of amino DFTPPO from bis(4-fluorophenyl)phenyl phosphine oxide by nitration and reduction

Reduction of nitro DFTPPO was carried out in 95% ethanol with tin chloride dihydrate and hydrochloric acid. To a 1000 ml four neck round bottom flask equipped with a nitrogen inlet, mechanical stirrer, condenser, and a thermometer was added 21.42g (0.0596 moles) of nitro DFTPPO and 306ml of ethanol. A heating mantle was used to induce a gentle reflux of ethanol. Then, tin chloride

dihydrate and the HCl were added in three portions 18g (0.0798 moles) of tin chloride dihydrate and 33ml (0.3690 moles) of HCl with each addition. After the third addition, the solution was refluxed for another two hours. The heating mantle was then removed and the solution was cooled to room temperature. The solution was transferred to a round bottom flask and ethanol was removed under reduced pressure. The resulting solution was made alkaline using an aqueous solution of sodium or potassium hydroxide. The alkaline solution was poured into 3000ml of water and ice and allowed to stand at room temperature overnight. The SnCl_4 which is a by-product from the reaction will slowly dissolve in the basic media. The resulting off white solid product was filtered and washed with a copious amount of water and dried in a vacuum oven at 80°C overnight. After drying, 15.37g (0.0467 moles) of the product was obtained, a yield of 78%. The crude product was purified by repeated Kugelrohr distillation and the capillary melting point of the resulting material was $157\text{-}159^\circ\text{C}$.

3.3.3 Synthesis of a Random Copolymers of Poly(arylene ether sulfones) and Poly(arylene ether phosphine oxides) with Pendant Amines

For the most part, one to one stoichiometry of the aromatic bisphenol and activated dihalide monomers was used throughout the investigation. The objective was to synthesize high molecular weight copolymers and vary the concentration of the amines along the backbone to investigate the structure property relationships of polymers and networks resulting from the modification of the pendant amines. An example of a calculation used for the synthesis of a high molecular weight copolymer from the polymerization of DCDPS and bisphenol-A with 10 mol% incorporation of Amino DFTPPO shown below .

$$5.0000 \text{ g Bisphenol-A} / 228.27 \text{ g/mol} = 2.190 \times 10^{-2} \text{ moles}$$

$$(2.190 \times 10^{-2} \text{ moles}) (0.90) (287.17 \text{ g/mole}) = 5.6601 \text{ g DCDPS}$$

$$(2.190 \times 10^{-2} \text{ moles}) (0.10) (314.27 \text{ g/mole}) = 0.6883 \text{ g Amino DFTPPO}$$

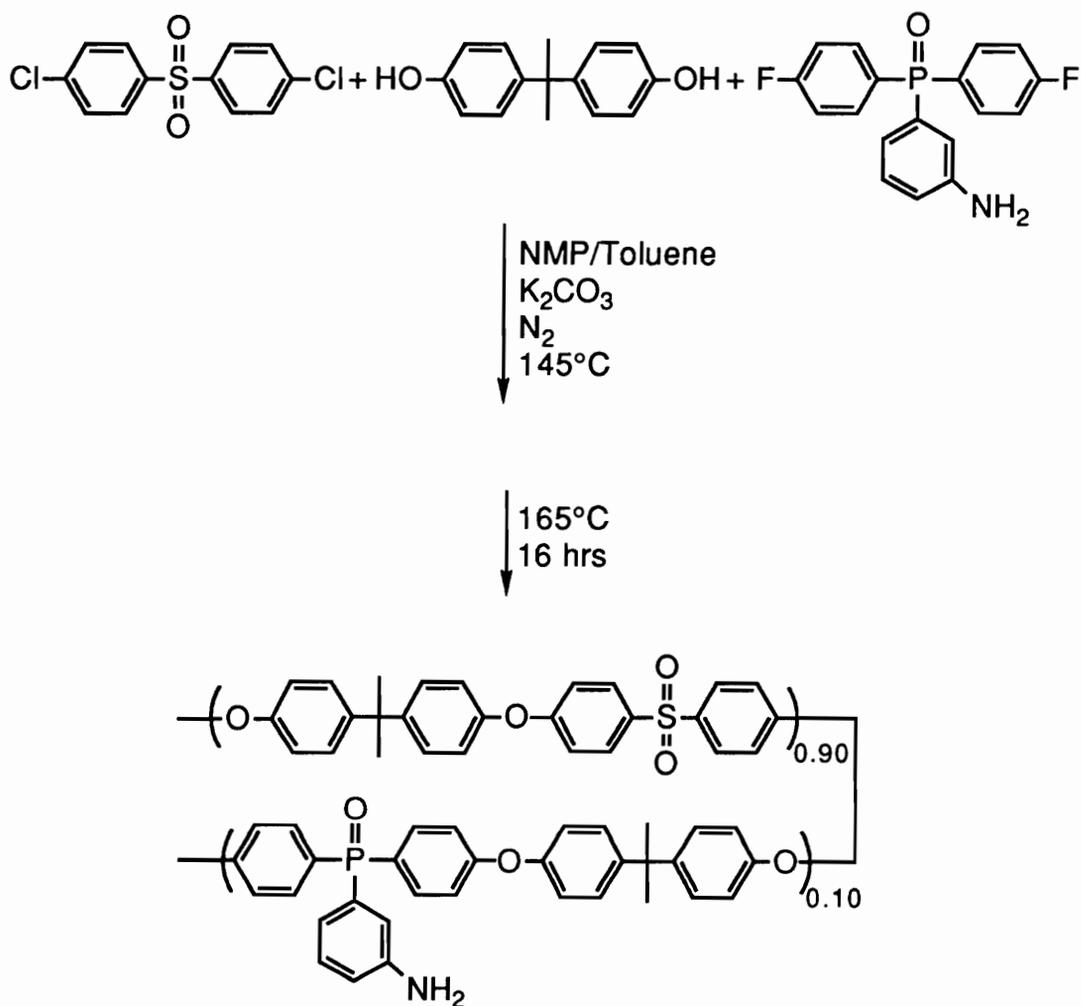
$$(5.0000 + 5.6600 + 0.6883) \text{g} / 0.20 = 57 \text{ ml NMP}$$

$$(57)(0.50) = 28 \text{ ml Toluene}$$

$$(2.190 \times 10^{-2} \text{ moles}) (1.15) (138.21 \text{ g/mole}) = 3.4808 \text{ g K}_2\text{CO}_3$$

The polymerization was conducted using a 20% solids content which was calculated from the total amount of the monomers that were used. The amount of toluene was based on a 50:50 ratio relative to the amount of NMP, and 15 mole% excess of potassium carbonate was used based on the amount of bisphenol-A. The reaction conditions used for the synthesis of various copolymers are shown in Scheme 23. The polymerization was conducted according to the following procedure. To a four neck 250ml round bottom flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and a dean stark trap was added 5.0000g (2.19×10^{-2} moles) of bisphenol-A, 5.6601g (1.97×10^{-2} moles) of DCDPS, 0.6883g (2.19×10^{-3} moles) of amino DFTPPO that were carefully weighed on teflon coated weighing pans along with 3.4808g (2.518×10^{-2} moles) of K_2CO_3 under a constant purge of nitrogen. The monomers and potassium carbonate were washed with 57 ml of NMP and 28 ml of toluene for a quantitative transfer of the reactants. Initially, the polymerization was conducted at 145°C for approximately four hours to azeotrope off the water. Then the temperature was raised to 165°C for an additional sixteen hours. The viscous solution was then filtered, neutralized with acetic acid and coagulated into a large

excess (5-10 times) of methanol and water (80:20). The polymer was filtered and dried in a vacuum oven at 80°C for 8 hours. The dried polymer was redissolved in chloroform and coagulated into excess methanol and dried in a vacuum oven at 80°C for another 8 hours.



Scheme 23 Synthesis of a random copolymer from DCDPS and bisphenol-A with 10 mole% incorporation of amino DFTPPO

3.3.4 Curing of Epoxy Resins with Pendant Amines

Before discussing the procedure used for the epoxy cure with pendant amines and a aromatic diamine curing agent, a sample calculation will be provided which was used to determine the amount of polymer, epoxy resin, and the curing agent. The sample calculation is for the 10 wt% loading of a high molecular weight copolymer from the reaction of 90 mole% DCDPS, 10 mole% amino DFTPPO and 100 mole% of bisphenol-A.

Molecular Weight of Epon 828 = 380.0 g/mole

Molecular Weight of 4,4'-DDS = 248.3 g/mole

For determination of Epon 828 and DDS weight fractions

$$[248.3 + 2(380.0)] \text{ g/mole} = 1008.3 \text{ g/mole}$$

$$\text{DDS Wt. Fraction} = 248.3 \text{ g/mole} / 1008.3 \text{ g/mole} = 0.2463$$

$$\text{Epon 828 Wt. Fraction} = 760.0 \text{ g/mole} / 1008.3 \text{ g/mole} = 0.7537$$

Calculation for a 40.00 gram total resin with 10 wt% loading of polymer

$$(40.00)(0.10) = \mathbf{4.00 \text{ g}} \text{ of polymer}$$

$$4.00\text{g} / 4964 \text{ g/mole} = 8.056 \times 10^{-4} \text{ moles of polymer}$$

$$(8.056 \times 10^{-4} \text{ moles})(380\text{g/mole}) = 0.3061\text{g Epon 828}$$

$$40.00 \text{ g mixed resin} - (4.00 \text{ g polymer} + 0.3061\text{g Epon 828}) = 35.69 \text{ g}$$

$$\text{Amount of DDS} = 35.69 \text{ g} \times 0.2463 = \mathbf{8.7898 \text{ g}}$$

$$\text{Amount of Epon 828} = 35.69 \times 0.7538 = 26.9041 \text{ g}$$

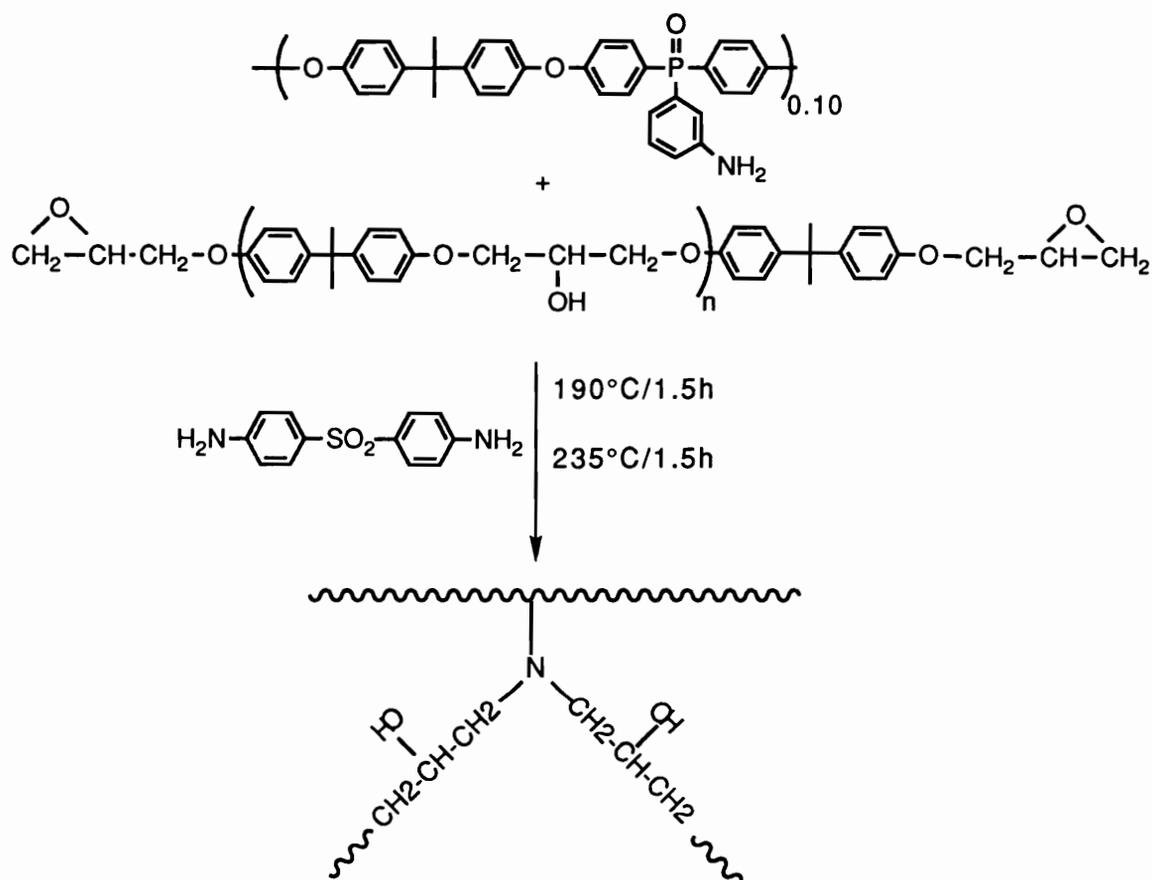
$$\text{Total amount of Epon 828} = (26.9041 + 0.3061)\text{g} = \mathbf{27.2102 \text{ g}}$$

$$\begin{aligned} \underline{\text{Total Amount}} &= 27.2102\text{g Epon 828} + 4.0000\text{g Polymer} + 8.7898\text{g DDS} \\ &= \mathbf{40.0000\text{g Mixed Resin}} \end{aligned}$$

First, the weight fractions for DDS and Epon 828 are determined based on their molecular weights. Next, the amount of the desired mixed resin is multiplied by the desired wt% loading of the polymer. This affords the amount of polymer for the correct wt% loading. Dividing by the molecular weight (from the titration of the amines) of the polymer yields moles of polymer; next, the stoichiometric amount of epoxy resin needed to react with the pendant amines was obtained. From the total amount of mixed resin, the calculated amount of polymer and the stoichiometric amount of Epon 828 needed to react with the pendant amines was subtracted. Based on this value, the amount of the DDS curing agent and the stoichiometric amount of Epon 828 that will react with DDS was calculated by multiplying by their respective weight fractions. The total amount of Epon 828, DDS, and the polymer should be the amount of the desired mixed epoxy resin.

Curing was conducted by adding Epon 828 and the pendant amino copolymer to a 150ml two neck round bottom flask equipped with a mechanical stirrer and a nitrogen inlet connected by a rubber hose to a vacuum pump. Initially, the contents were stirred at 110°C (oil bath temperature) until a homogeneous solution was obtained. This took between 0.5-1.5 hour depending on the molecular weight of the polymer and the amount of the polymer that was incorporated. Vacuum was applied throughout the process to degass the system and a silicone oil bath was used to regulate the temperature. Once a homogeneous solution was obtained, a stoichiometric amount of 4,4'-diaminodiphenylsulfone (DDS) was added and the temperature was raised to 135°C. Upon dissolution of DDS, the homogeneous solution was then transferred to a preheated RTV silicone mold, covered with a 0.01 ml teflon sheet and weighted down. The curing was done in a convection oven at 190°C for 1.5h

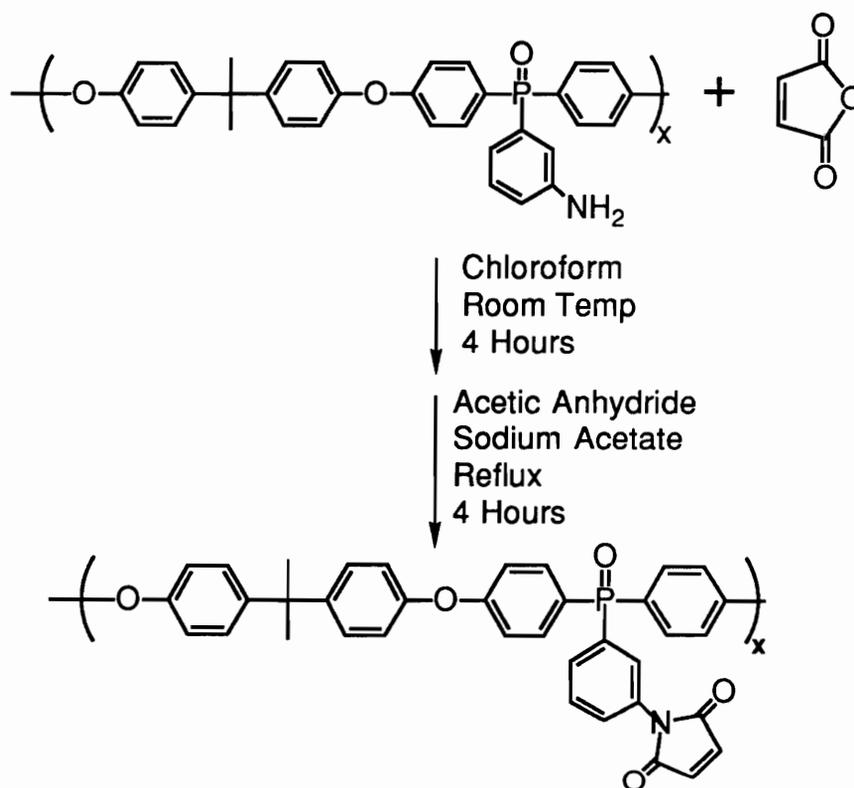
and then post cured at 235°C for an additional 1.5h. The curing scheme which was used is shown in Scheme 24. Only the repeat unit with the pendant amines is shown, the other repeat which is not shown would be from the reaction of bisphenol-A and the other activated dihalide monomer (DCDPS).



Scheme 24 Curing of Epon 828 with pendant amines on a copolymer of a poly(arylene ether sulfone) and poly(arylene ether phosphine oxide) using 4,4'-DDS as the curing agent

3.3.5 Conversion of Pendant Amines to Maleimides

The conversion of pendant amines to maleimides was carried out according to the following procedure and the reaction scheme is shown in Scheme 25. Again, only the repeat unit with the pendant amines is shown, in this case, the subscript on the repeat unit would be 0.10.



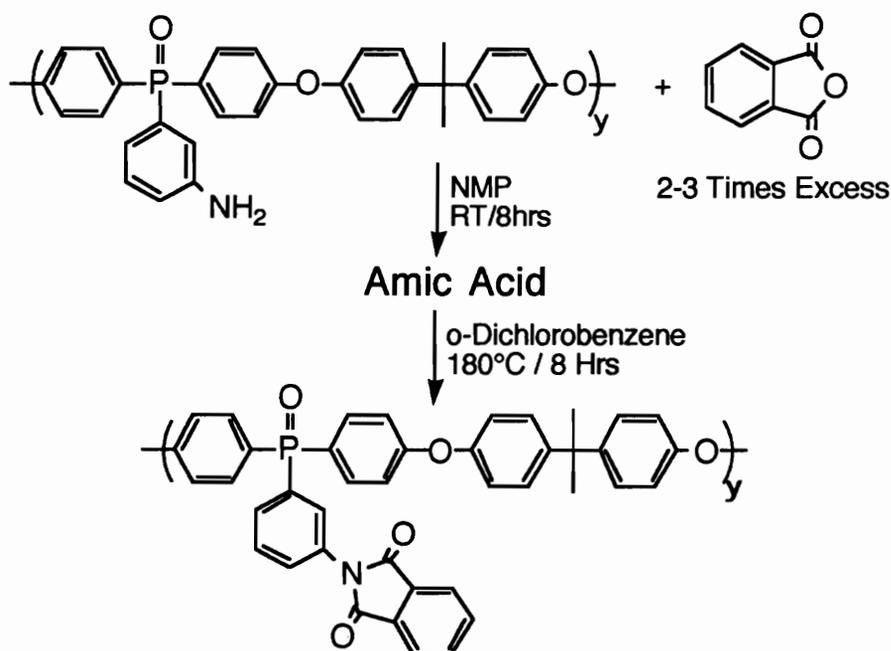
Scheme 25 Conversion of pendant amines to maleimides

To a four neck 500ml round bottom flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and a condenser was added 13.8g (0.0030 moles) of the high molecular weight copolymer (polysulfone and poly(arylene ether phosphine oxide) (PEPO)) with 10 mole% pendant amines along with 276ml of chloroform. The contents were stirred at room temperature until a homogeneous yellow solution was obtained. Once homogeneous, 0.59g (0.0060 moles) of

maleic anhydride was added. This solution was stirred at room temperature for an additional 4 hours. Then 5.19ml (0.0550 moles) of acetic anhydride along with 0.45g (0.0055 moles) of sodium acetate were added and refluxed for another four hours. The yellow homogeneous solution was then coagulated into excess methanol and dried in a vacuum oven at 80°C for 8 hours. The pendant maleimides were then thermally cured at 250°C for 3 hours and then post cured at 280°C for an additional hour.

3.3.6 Conversion of Pendant Amines to Phthalimides

The conversion of pendant amines to phthalimides was carried out using the following procedure and the reaction scheme is shown in Scheme 26.



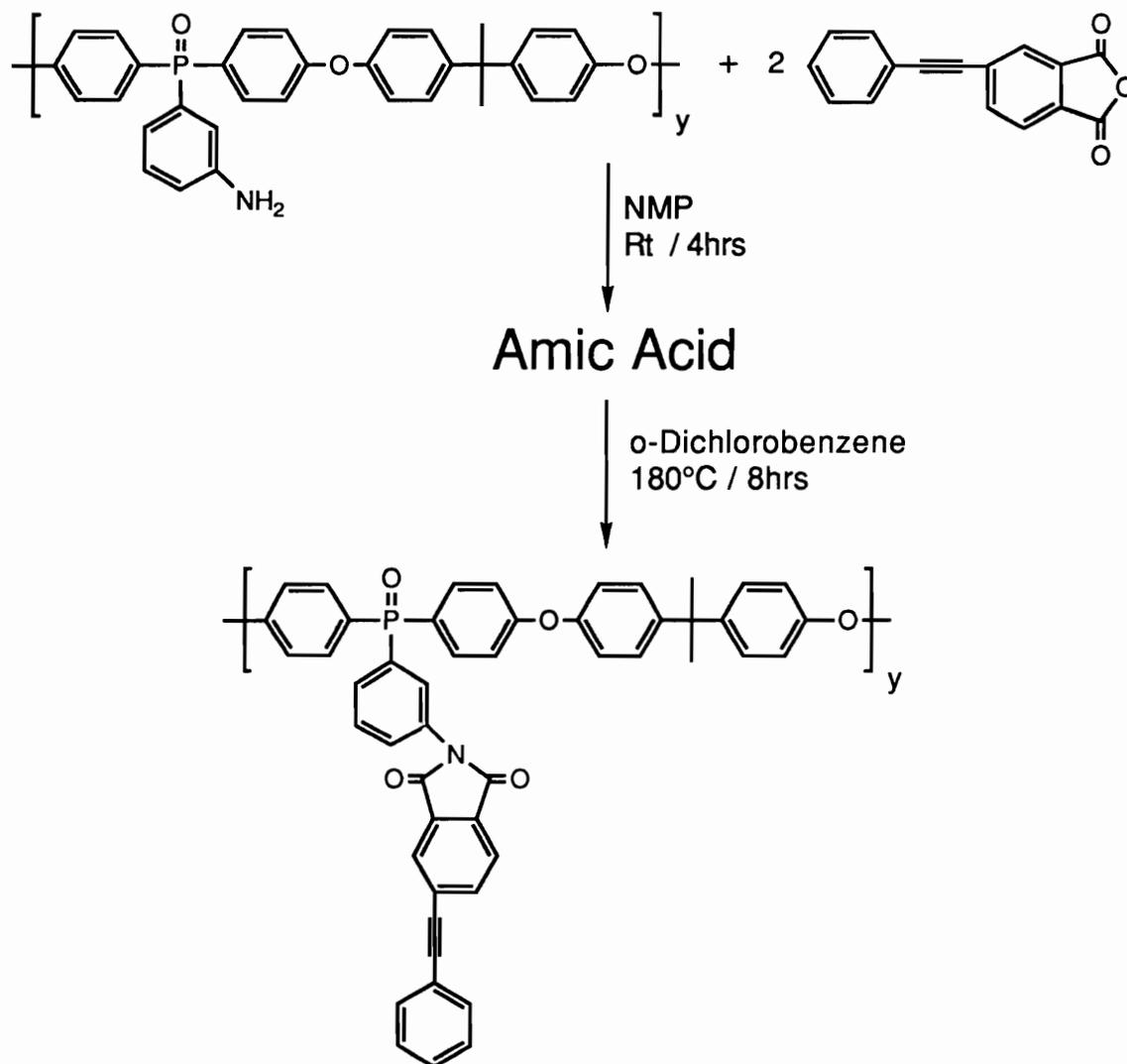
Scheme 26 Conversion of pendant amines to phthalimides

To a four neck 250ml round bottom flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and a reverse dean stark trap was added 5.00g (1.00×10^{-3} moles) of the copolymer of polysulfone and PEPO with 10 mole% of pendant amines along with 29ml of NMP. The contents were stirred at room temperature until a homogeneous solution was obtained. Once homogeneous, 0.4475g (3.02×10^{-3} moles) of phthalic anhydride was added. This solution was stirred at room temperature for an additional 8 hours. Then 6 ml o-dichloro benzene was added and the temperature was increased to 185-190°C for 8 hours. The resulting solution was then coagulated into excess methanol and dried in a vacuum oven at 80°C for 8 hours.

3.3.7 Conversion of Pendant Amines to Phenylethynylphenylimides

The following procedure was used for the conversion of pendant amines on poly(arylene ether phosphine oxides) (PEPO). To a four neck 250ml round bottom flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and a reverse dean stark trap was added 5.50g (1.16×10^{-3} moles) of PEPO with 10 mole% of pendant amines along with 55 ml (10 wt% solids) of NMP. The contents were stirred at room temperature until a homogeneous solution was obtained. Once homogeneous, 0.5770 g (2.32×10^{-1} moles) of 4-phenylethynylphthalic anhydride was added. This solution was stirred at room temperature for 4 hours. Then 11 ml of o-dichlorobenzene was added and the temperature was increased to 185-190°C for 8 hours. The resulting solution was then coagulated into excess methanol and dried in a vacuum oven at 80°C over

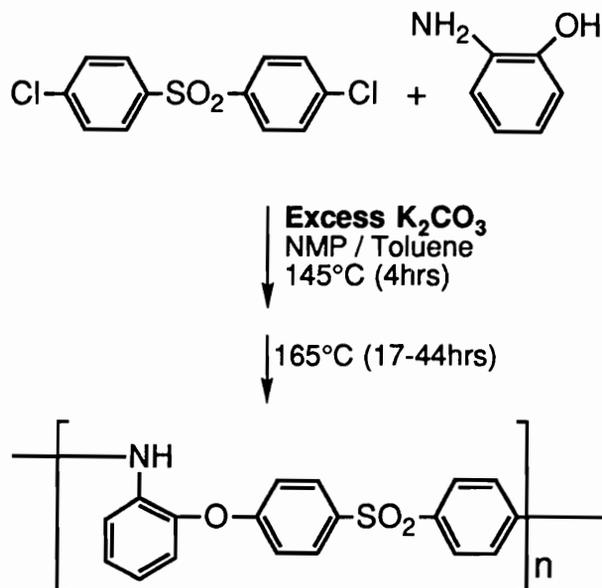
night. The resulting polymer was then thermally cured at 350°C/30min to afford networks. The reaction scheme is shown in Scheme 27.



Scheme 27 Conversion of pendant amines to phenylethynylphenyl imides

3.3.8 Stoichiometric Nucleophilic Polymerization of o-Aminophenol (OAP) and DCDPS

Stoichiometric polymerization of OAP and DCDPS was conducted similar to the synthesis of random high molecular weight polymers according to Scheme 28.



Scheme 28 Stoichiometric polymerization of o-aminophenol and DCDPS

Thus 5.0000g (1.741×10^{-2} moles) of DCDPS and 1.9000g (1.741×10^{-2} moles) of OAP along with 1.5040g (2.176×10^{-2} moles) of potassium carbonate was added to a 100ml four neck round bottom flask equipped with a nitrogen inlet, mechanical stirrer, thermometer, and a dean starke trap along with 31ml of NMP and 16ml of toluene. Initially, the polymerization was conducted at $145^\circ C$ for four hours to azeotrope off the water. Then the temperature was raised to $165^\circ C$ for an additional seventeen hours. The solution was then filtered, neutralized with acetic acid and coagulated into a large excess (5-10 times) of methanol and

water (80:20), filtered, and dried. It was redissolved in THF and coagulated into excess methanol and dried in a vacuum oven at 80°C for another 8 hours.

Two experimental parameters were investigated, one being the excess amount of potassium carbonate and the other variable was the reaction time. With respect to the potassium carbonate, a 25% excess was added regardless of whether OAP was treated as a monofunctional monomer or a difunctional monomer. In the calculation above, OAP was treated as a monofunctional monomer, the initial assumption was that the aromatic amine would not require potassium carbonate for reaction with DCDPS. A difunctional treatment of OAP would require twice the amount of potassium carbonate calculated above. The other parameter was the total reaction time which was varied from 21 hours to 48 hours.

3.3.9 Stoichiometric Polymerization of o-Aminophenol and 5,000 \langle Mn \rangle Chlorine Terminated Polysulfone

One to one polymerization of OAP and 5K chlorine terminated bisphenol-A DCDPS polysulfone was conducted using a similar procedure and reaction condition as the previously mentioned OAP and DCDPS. The number average molecular weight for the chlorine terminated polysulfone was obtained from proton NMR by determining the integrated ratio of the aromatic protons ortho to the chlorine to the isopropylidene protons in the repeat unit. The polymerization was conducted by adding 5.0000g (9.299×10^{-4} moles) of 5K chlorine terminated polysulfone and 0.1015g (9.299×10^{-4} moles) of OAP into a 100ml four neck round bottom flask equipped with a nitrogen inlet, thermometer, mechanical stirrer, and a dean stark trap. The reactants were washed with 26ml of NMP and

13ml of toluene. Initially, the reaction was conducted at 145°C for 4 hours and then raised to 165°C for another 17 hours. The resulting solution was filtered, neutralized with acetic acid, and then coagulated into methanol and water (80:20). After drying, a second precipitation from a chloroform solution into methanol was performed.

3.4 Model Reaction of 2,2'-Bis(3-Amino-4-Hydroxyphenyl) Hexafluoro propane and 4-ChloroPhenyl Phenylsulfone

The model study was conducted using one mole of 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane and two moles of 4-chlorophenyl phenylsulfone. Into a 100ml four neck round bottom flask equipped with a nitrogen inlet, thermometer, mechanical stirrer, and a dean stark trap was added 2.0000g of 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane and 2.7598g (1.092×10^{-2} moles) of 4-chlorophenyl phenylsulfone along with 24ml of DMAc and 12ml of toluene. The reaction was azeotroped at 145°C for four hours and then the temperature was increased to 155°C for 12 hours. The solution was then filtered, neutralized with acetic acid and DMAc was removed under a reduced pressure. The product was dried in a vacuum oven at ~ 100°C for 8 hours.

3.5 Characterization

3.5.1 Dynamic Mechanical Analysis (DMA): DMA characterization plots were obtained using a Perkin Elmer DMA-7. The samples analyzed in the extension mode were films with approximate dimensions of 0.6 x 5 x 6mm. Samples

analyzed using the three point bend mode had approximate dimensions 2 x 6 x 15mm. A heating rate of 5°C/min. and a frequency of 1Hz were used.

3.5.2 Differential Scanning Calorimetry Measurements were made using a Perkin Elmer DSC-7 with a heating rate of 10°C/min. The sample sizes were in the range of 5- 15mg.

3.5.3 Fracture toughness Fracture toughness measurements were conducted in accordance with ASTM D-5045-91 (E-399-90) test method. Between 8-12 samples with rectangular dimensions of 3.2mm x 6.5mm x 38mm were analyzed. The samples were notched at the center to a depth of approximately 0.5mm using a reciprocating saw. Then a sharp crack was cryogenically initiated using a razor blade dipped in liquid nitrogen. Care was taken to ensure that the crack propagated evenly down the center of the notch. The pre-cracked specimens were then loaded on a three-point bend fixture and the load to failure was obtained using an Instron (Model 1123). The crosshead speed used was 0.05 inch/min.

3.5.4 Gel Permeation Chromatography (GPC) GPC's were performed using Waters 150-C ALC/GPC with a differential refractive index and viscosity detectors. The concentration was 3 mg/ml in NMP. The Permugel columns in the range of 100Å to 10⁶ Å were used as the separation system with a flow rate of 1 ml/min. at 60°C.

3.5.5 Fourier Transform Infrared Spectroscopy (FTIR): FTIR spectra were obtained with a Nicolet MX-1 instrument. Polymeric samples were very thin films cast from dilute solutions of chloroform onto a glass substrate. Initially, they were

air dried by covering the sample with a crystallizing dish, allowing a small opening at the bottom for a gradual evaporation of chloroform. When the presence of solvent was no longer visible, it was transferred to a vacuum oven. The sample was dried at room temperature for ~0.5-1 hour and then heated to ~80-100°C for an additional 0.5-1hr. Monomers were analyzed by mixing ~10:1 ratio of KBr to sample and obtaining a KBr pellet.

3.5.6 Intrinsic Viscosities Intrinsic viscosities were measured at 25°C in Ubbelohde viscometers with chloroform or NMP as the solvent.

3.5.7 Nuclear Magnetic Resonance (NMR) The proton and carbon NMR spectra was obtained using a Varian Unity 400 MHz instrument. The samples were dissolved in deuterated chloroform or dimethylsulfoxide that contained 0.05% tetramethylsilane (TMS) and all of the peaks were referenced relative to TMS peak at 0 ppm.

3.5.8 Percent gelation The percent gelation of cured networks were determined by soxhlet extractions in chloroform for 3-4 days. The samples were then dried in a vacuum oven until a constant weight was obtained. The percent gelation was then calculated by using the following formula

$$\% \text{ gelation} = ((\text{initial weight} - \text{weight after extraction}) / \text{initial weight}) \times 100$$

3.5.9 Scanning Electron Microscopy (SEM) The morphology of the fractured surfaces was investigated by scanning electron microscopy (SEM) using the International Scientific Instruments Model SX-40 SEM. Samples were mounted

on aluminum substrates with silver paint and the fractured surfaces were sputter coated with about 100Å of gold prior to analysis.

3.5.10 Thermogravimetric Analysis Measurements were made using a Perkin Elmer Thermogravimetric Analyzer TGA-7 with a heating rate of 10°C/min.

3.5.11 Potentiometric Titration Potentiometric titrations for aromatic amines on monomers and polymers were performed using an MCI GT-05 automatic titrator. Samples were dissolved in 60 ml chloroform and 10 ml acetic acid and then titrated with HBr (0.025N) in acetic acid. The end point was detected by a maximum in the first derivative of the potential. The sample size was such that each analysis required between 2-4 ml of titrant. For amine terminated polymers, the targeted molecular weight can be used to determine the appropriate sample size. Likewise, for titration of polymers with pendant amines, the approximate molecular weight per amine can be calculated based on the amount of the monomers that were charged into the reaction flask. A sample calculation based on 10 mole% of amino DFTPPO polymerized with 90 mole% DCDPS and 100 mole% bisphenol-A will be provided as an example. From the amount of each monomer charged into the reaction flask, their respective moles can be obtained by dividing by their molecular weights. The moles of monomers used for this sample calculation are

0.0153 moles of amino DFTPPO

0.1380 moles of DCDPS

0.1533 moles of bisphenol-A

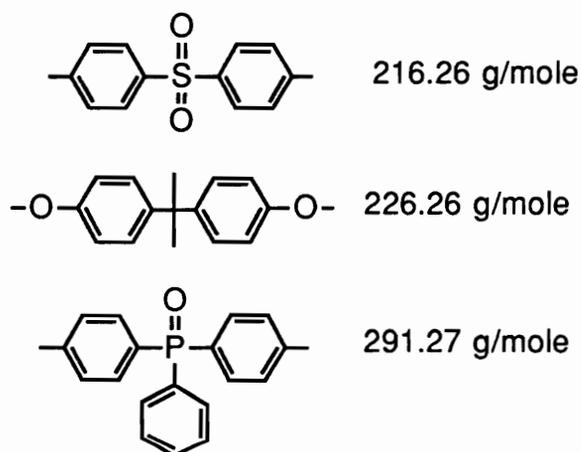
The procedure involves dividing by the moles of amino DFTPPO and when this is done, the following numbers are obtained.

$$0.0153 \text{ moles}/0.0153 \text{ moles} = 1.000$$

$$0.1380 \text{ moles}/0.0153 \text{ moles} = 9.020$$

$$0.1533 \text{ moles}/0.0153 \text{ moles} = 10.02$$

The number average molecular weight per amine group was then calculated by taking these numbers and multiplying by the molecular weight of the monomer in the repeat unit. For activated dihalide monomers, this would be the molecular weight without the halogens, and for the bisphenol this would be the molecular weight without the phenolic protons. These are shown below



Finally, the number average molecular weight per amine was obtained by executing the following mathematical operation:

$$\begin{aligned}
 \langle M_n \rangle / \text{amine} &= 1(\text{amino DFTPPO}) + 9.02(\text{DCDPS}) + 10.02(\text{bisphenol-A}) \\
 &= [1(291.27) + 9.02(216.26) + 10.02(226.26)] \text{ g/mole} \\
 &= 4509 \text{ g/mole}
 \end{aligned}$$

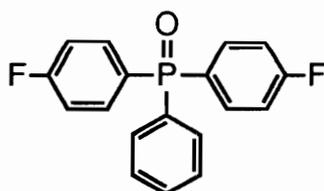
The experimental value from the titration of the amines for this particular sample yielded a value of 4965 g/mole, eg. ~5,000 g/mole.

4.0 RESULTS AND DISCUSSION

4.1 Synthesis and Characterization of 3-Aminophenyl-Bis(4-Fluorophenyl) Phosphine Oxide (Amino DFTPPO)

In the synthesis of amine terminated poly(arylene ethers), addition of a calculated small amount of either meta or para aminophenol may be added as the monofunctional endcapper (204,107,116). Even though the endcapper contains both the amine functionality as well as the phenol, it is the phenolate that exclusively undergoes the aromatic nucleophilic substitution reaction and not the amine. The type of monomers which were investigated for the incorporation of pendant amines onto the backbone of poly(arylene ether)s was directed toward monomers which contained both the amine functionality as well as another reactive difunctionality which could polymerize to afford a poly(arylene ether) backbone with the incorporation of the pendant amines.

Previously in our laboratory, we have demonstrated that bis(4-fluorophenyl)phenylphosphine oxide (DFTPPO) can be polymerized with various aromatic bisphenols to yield high molecular weight poly(arylene ethers) (74). The structure of the DFTPPO monomer is shown below



There are three phenyl rings bonded to the phosphine oxide and since the phosphine oxide is a weak electron withdrawing group, nitration of DFTPPO should occur predominantly meta to the phosphine oxide on the pendant phenyl ring. Nitration of DFTPPO was successfully conducted using a mixture of nitric and sulfuric acid in sulfuric acid. As discussed in the experimental section,

nitration went smoothly to give mainly the mono nitro substituted product. In addition to the mono nitro substitution, a small amount (<2%) of dinitro and trinitro substituted products were also obtained which are shown in Figure 6.

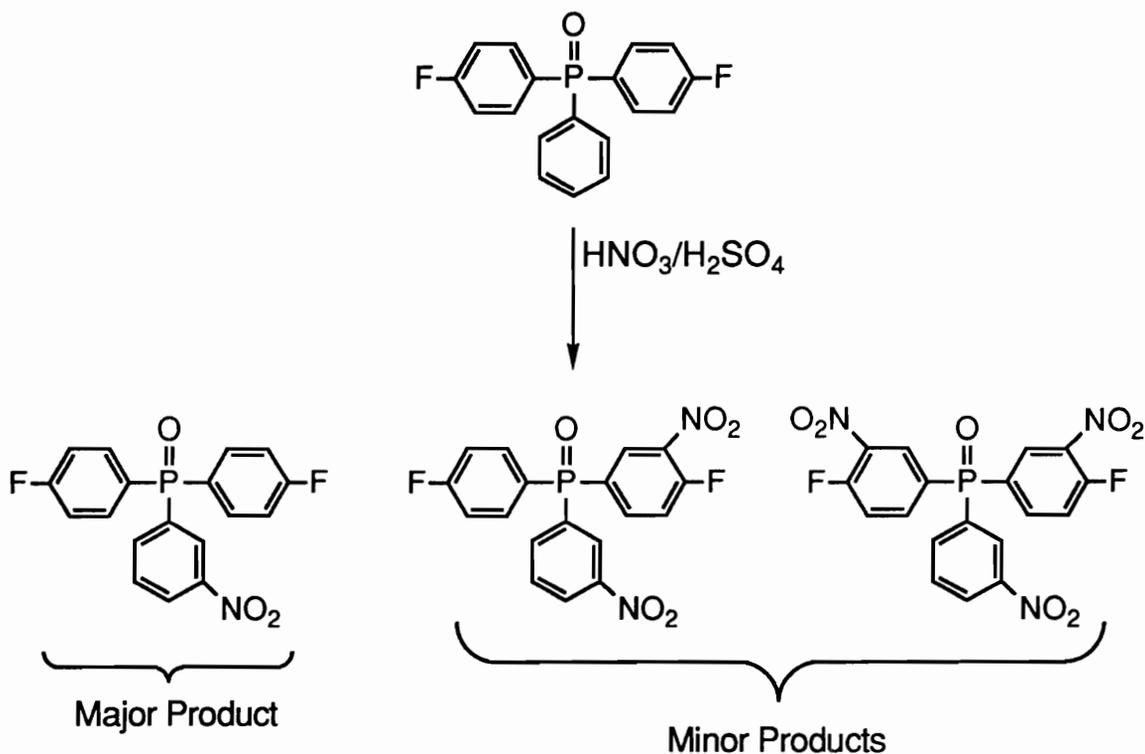
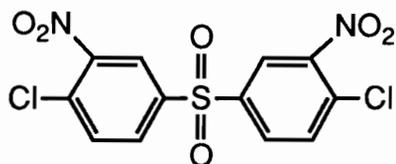


Figure 6 Products obtained from nitration of bis(4-fluorophenyl)phenylphosphine oxide with nitric and sulfuric acid

The major product from the nitration of DFTPPO was the substitution of a nitro group on the pendant phenyl ring meta to the phosphine oxide, the addition of a second nitro group is very unlikely and requires a more severe reaction condition. The other minor products are nitration on the two phenyl rings in which the nitro was ortho to the halogen and meta to the phosphine oxide. Other experimental evidence to support this has been the reported nitration of bis(4-chlorophenyl)

sulfone (DCDPS) with nitric and sulfuric acid to obtain the bis(4-chloro-3-nitrophenyl) sulfone(195,196).



Since sulfone deactivated the aromatic rings toward nitration to a greater extent than the phosphine oxide, nitration was conducted at a slightly higher temperature (~60-80°C).

The yield of the minor products from the nitration of DFTPPO was influenced by the amount of excess nitric acid added and by how long the reaction mixture was allowed to equilibrate at room temperature after the addition of the nitrating mixture. For the nitration of DFTPPO, a fifteen percent molar excess of nitric acid was added, based on mono nitration; increasing the amount of excess nitric acid favored the formation of multiple nitrated products. After the addition of the nitrating mixture, the reaction mixture was allowed to equilibrate at room temperature for about 30 minutes. Increasing the reaction time also favored multiple nitrations.

The crude product from the nitration of DFTPPO was isolated by precipitation of the reaction mixture into excess ice water. This often resulted in a tacky yellow material which adhered to the filter paper. Product isolation could be obtained by dissolving in chloroform and filtering the mixture followed by repeated washings with water and then removing the dried chloroform to afford a yield of ~ 85-90%. Alternatively, the crude product could be isolated by dissolving in a minimum amount of ethanol followed by filtration and precipitation into a large quantity of ice water. With the latter method, caution must be

exercised to make sure that the amount of ethanol was the absolute minimum amount, otherwise, precipitation into water only resulted in a yellow homogeneous solution.

Purification of the nitro product was difficult, even though crystals could be obtained from different solvents such as ethanol, chloroform, and solvent mixtures of THF/haxane, this did not remove the impurities. The method which was found to be successful was repeated kulgerohr distillations followed by precipitation into hexane from chloroform. The typical yield with this method was rather low and in most cases about 50% . The IR spectrum of the purified nitro product from a KBr pellet is shown in Figure 7 and assignments of some of the major peaks are shown in Table 4.

Table 4 Major IR peak assignments of bis(4-fluorophenyl)-3-nitrophenyl phosphine oxide (nitro DFTPPO)

Functional Group	Wavenumber (cm ⁻¹)
Aromatic C-H	3051
Nitro	1532
Aromatic C=C	1588 1497
Phosphine Oxide	1187
C-F	1159
P-Aromatic Carbon	1141 991

The prominent nitro absorbance was observed as a strong peak at 1532 cm^{-1} as well as absorbances due to the phosphine oxide and the carbon bonded to phosphorus. The proton NMR was an additional experimental evidence for the obtainment of nitro DFTPPO and the proton NMR of nitro DFTPPO in deuterated chloroform is shown in Figure 8. The assignment for the peaks were based on the contribution of functional groups and their effect on the chemical shift of a monosubstituted benzene. The shift values for the phosphine oxide were not available and a ketone group was used instead. Even though the exact values for the calculated chemical shifts did not correlate well with the experimental values, the general trend from the calculated values were used to assign the protons on the NMR. The protons ortho to the nitro were deshielded the most and was observed furthest downfield. The peaks in the aromatic region were slightly further downfield than the aromatic protons of an unsubstituted benzene (7.27 ppm) due to the presence of the phosphine oxide and the nitro electron withdrawing groups. Complex splitting patterns were observed for the aromatic protons and this was due to the splitting by the phosphorus which has the same nuclear spin as hydrogen.

The carbon NMR of nitro DFTPPO in deuterated chloroform is shown in Figure 9. The peak assignments were calculated based on substituent effect of substituted aromatic benzoid compounds. Although the shift factors for the fluorine and the nitro groups were available. The shift factors for the phosphine oxide could not be obtained, these values for the phosphine oxide was derived from the chemical shifts for the different carbons of triphenyl phosphine oxide. The base value of 128.5 was subtracted from the chemical shifts of different carbons of triphenyl phosphine oxide and these shift values were used for the

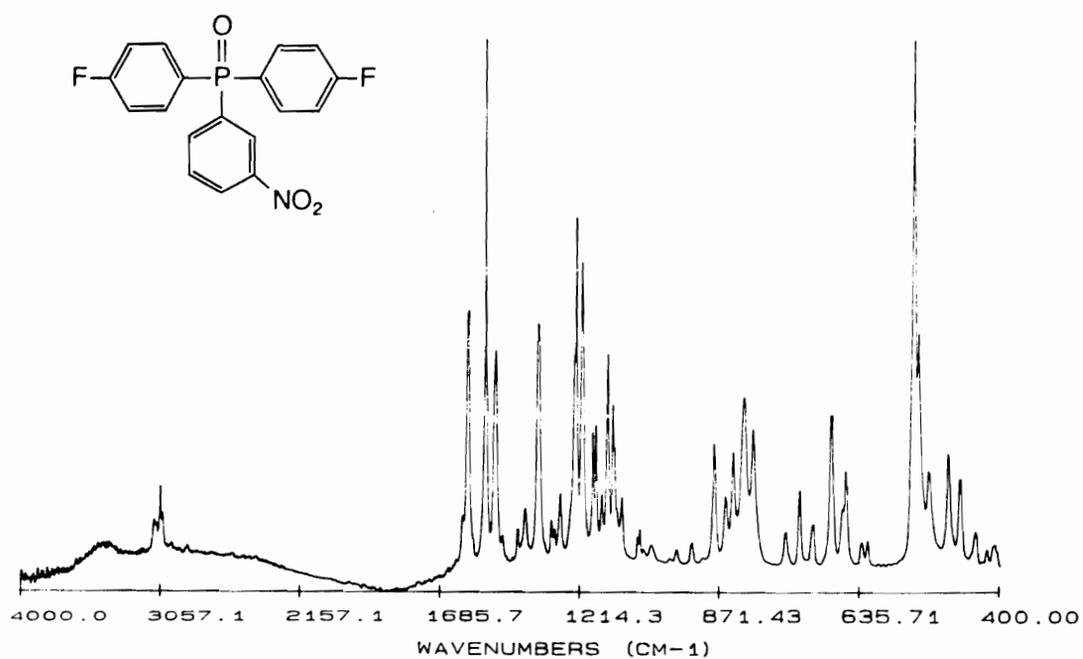


Figure 7 FT-IR of bis(4-fluorophenyl)-3-nitrophenylphosphine oxide from KBr pellet

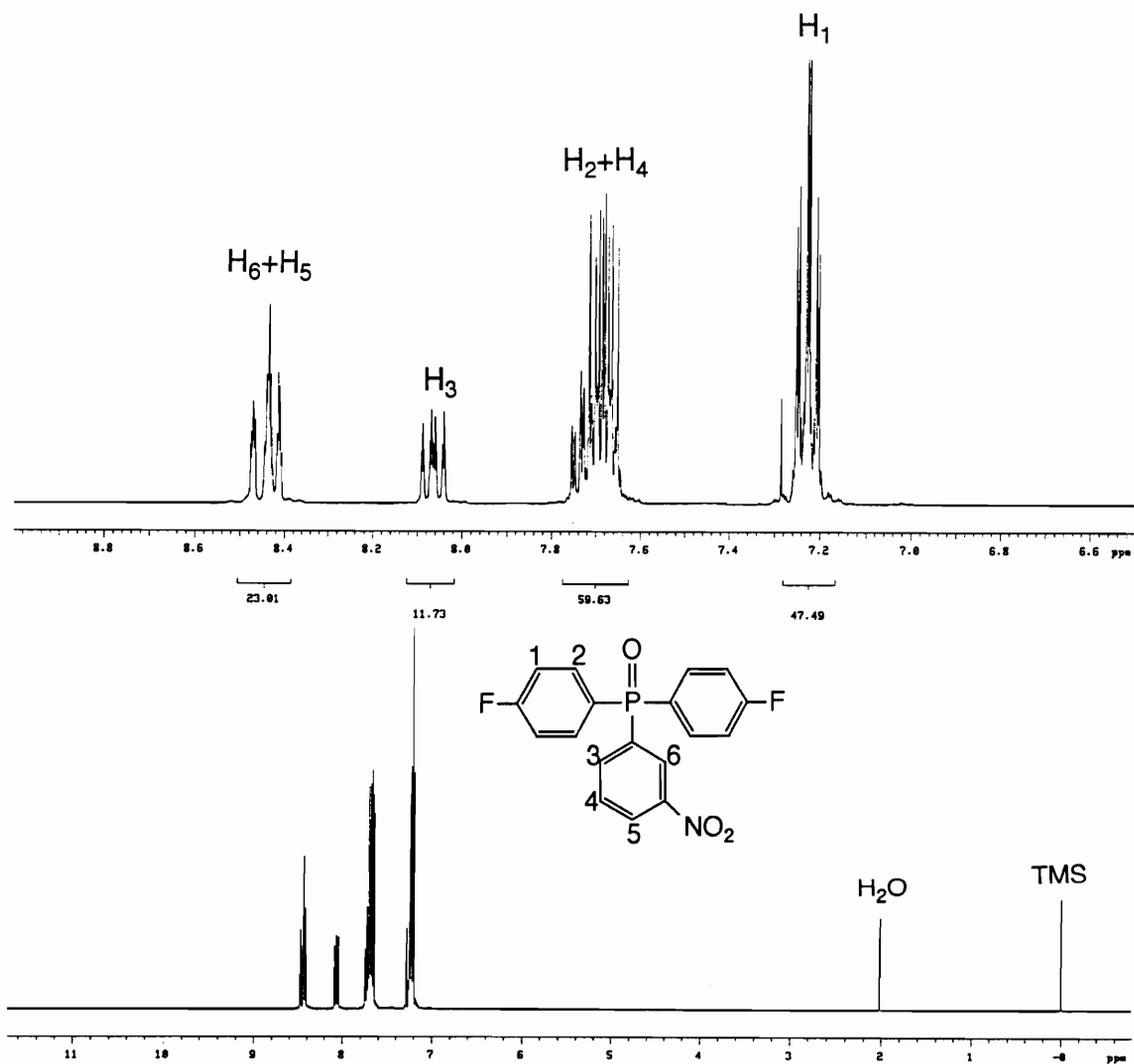


Figure 8 Proton NMR of bis(4-fluorophenyl)-3-nitrophenylphosphine oxide in deuterated chloroform

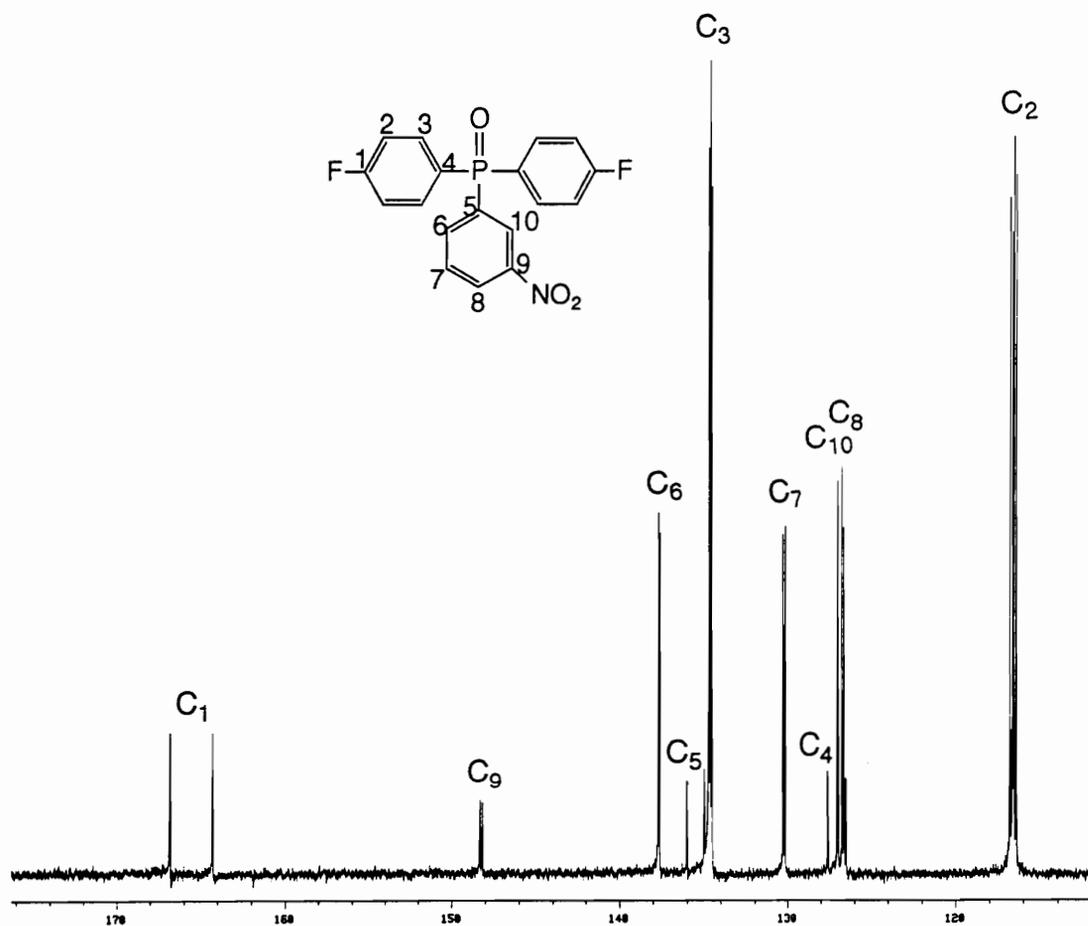


Figure 9 Carbon NMR of bis(4-fluorophenyl)-3-nitrophenylphosphine oxide in deuterated chloroform

calculations. The shift values for the phosphine oxide, nitro, and fluorine which were used for the calculation are shown in Table 5. Starting with a base value of 128.5 ppm, appropriate numerical values were subtracted or added depending on the relative position of carbon of interest to other functional groups. A comparison of the calculated and the observed chemical shifts for the different carbons of nitro DFTPPO is shown in Table 6. In general, very good agreements between the calculated and the actual values were obtained.

The crude nitro product could either be reduced to the amine without a further purification or it could be purified and then reduced. Either way, the yield of the purified amine was ~40-50%. The reduction was conducted using tin chloride dihydrate/HCl in ethanol. Even though reduction could also be conducted using palladium and hydrogen gas, the appearance of the resulting amino DFTPPO was better using the former. The yield of the crude amino DFTPPO was ~78% and the most effective method for the purification of amino DFTPPO was by repeated kulgerrohr distillations. The IR of amino DFTPPO from a KBr pellet is shown in Figure 10. Upon conversion of the nitro to the amine, appearance of new peaks for the amine was observed at 3212 and 3318 cm^{-1} . The proton NMR of amino DFTPPO in deuterated chloroform is shown in Figure 11. A broad singlet at 3.9 ppm was observed for the amine and the experimental value of 6.7 was obtained for the ratio of the peak integrations of the amine to the aromatics as compared to 6.0 for the theoretical value. In the aromatic region, the four protons ortho to the phosphine oxide was observed furthest down field at 7.65 ppm followed by the protons ortho to the fluorine at 7.15 ppm. The two ortho protons to the amine in the pendant phenyl ring was observed most upfield at 6.85 ppm due to the influence of the amine. Titration for the amine was also

Table 5 Carbon chemical shifts of functional groups used for calculation of different carbons of nitro DFTPPO

Functional Group	C1	C2	C3	C4
$\begin{array}{c} \text{O} \\ \\ \text{---P---} \end{array}$	7.1	3.8	0.3	3.7
F	35.1	-14.4	0.9	-4.4
NO ₂	20.6	-4.3	1.3	6.2

Table 6 Comparison of calculated and the observed chemical shifts for the different carbons of nitro DFTPPO

Carbon Assignment	Calculated (ppm)	Observed (ppm)
1	167.3	166.4
2	114.4	116.3
3	133.2	134.9
4	131.2	127.9
5	136.9	136.1
6	138.5	137.9
7	130.1	130.2
8	127.9	127.0
9	149.4	148.3
10	128.0	127.3

very useful for the identification of amino DFTPPO and the molecular weight of 327g/mol was obtained from the average of three titrations as compared to the theoretical value of 329 g/mol.

4.2 Synthesis and Characterization of Aminated PSF/PEPO Copolymers

There were various reasons for the synthesis of amino DFTPPO for the incorporation of amines onto the backbone of poly(arylene ethers). Like the *m*-aminophenol in which the amine is meta to the phenol, in amino DFTPPO, the amine is also meta to the phosphine oxide. Since it was known previously that the amine in the presence of other phenolates does not react with activated halides, we felt that this monomer could be a successfully reacted with aromatic bisphenols for the incorporation of pendant amines.

The copolymerizations of amino DFTPPO with DCDPS and bisphenol-A were conducted according to the reaction condition in Scheme 23. The polymerizations were conducting using NMP and toluene in a 2 to1 ratio and a 15% excess of potassium carbonate relative to the bisphenol was added. The initial reaction temperature was at 145°C for approximately 5 hours and then at 165°C for additional sixteen hours. With the copolymerization of amino DFTPPO, since this monomer contains both the amine and the activated dihalides, the amines are no longer restricted to be only on polymer chain ends. The other advantage of having the amine as a part of a monomer is that one can precisely control the extent of amination along the polymer backbone. With the pendant amines, the concentration of the amines along the backbone can be varied independently of the molecular weight. Since polymer properties are better for

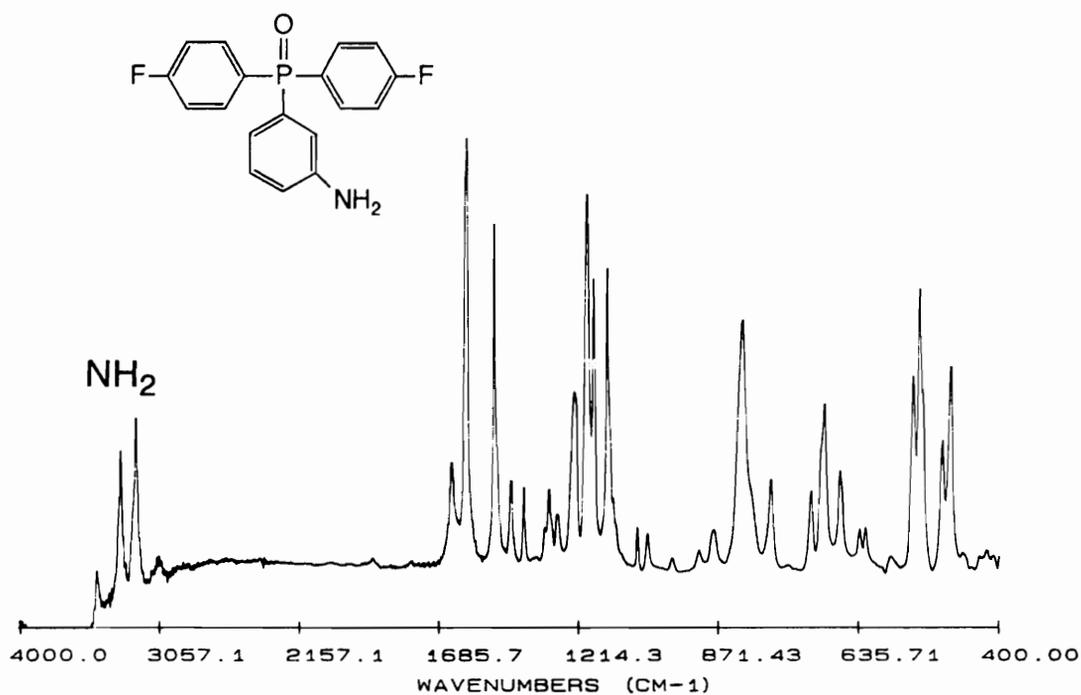


Figure 10 FT-IR of 3-aminophenyl-bis(4-fluorophenyl)phosphine oxide from KBr pellet

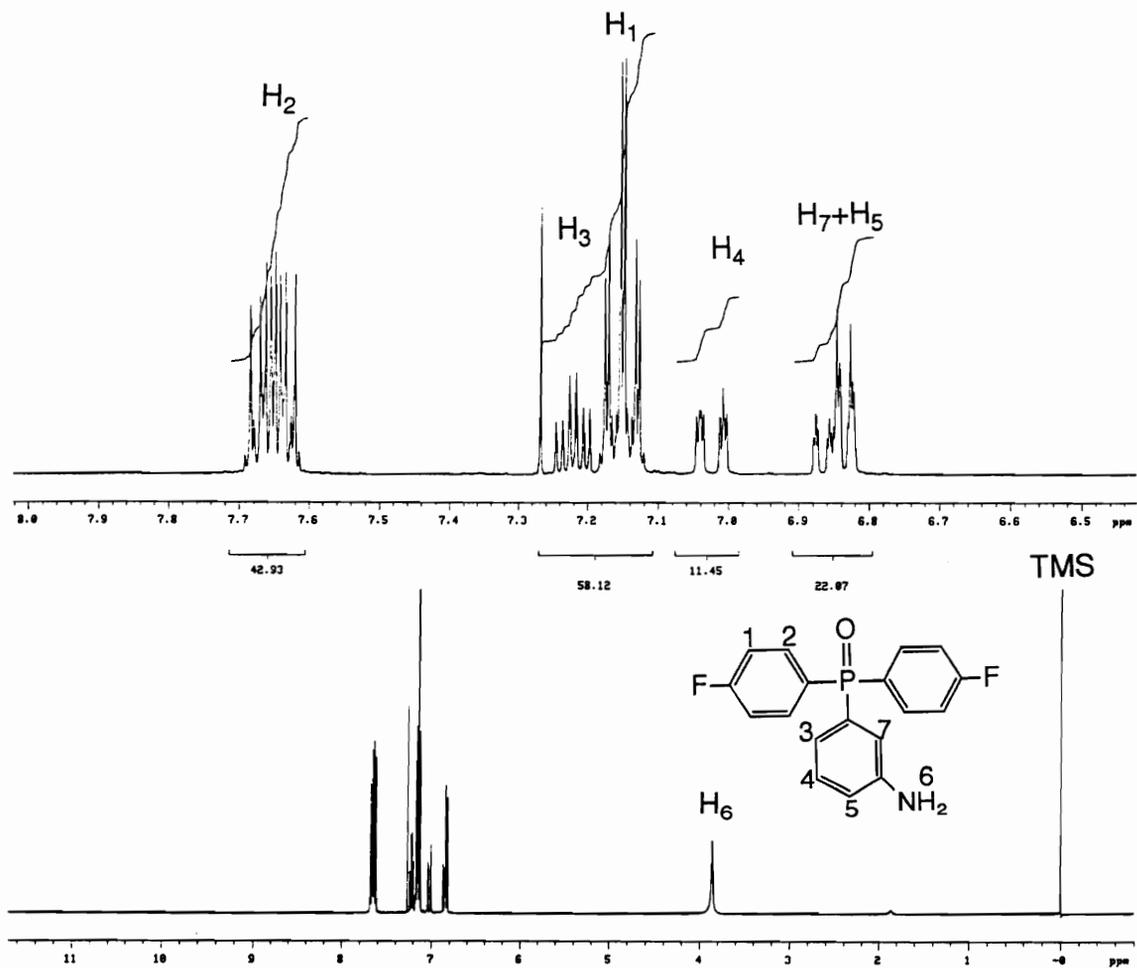


Figure 11 Proton NMR of 3-aminophenyl-bis(4-fluorophenyl)phosphine oxide in deuterated chloroform

the relative high molecular weight polymers, the synthesis of high molecular weight polymers with a different degree of amination along the polymer backbone was conducted. In all of the copolymerizations, a 1:1 ratio of the activated dihalide monomers to the bisphenol-A was used. In table 7 are the intrinsic viscosity and the titration results which were obtained for the copolymerizations of amino DFTPPO, DCDPS, and bisphenol-A.

Table 7 Intrinsic viscosity and titration results of aminated copolymers from amino DFTPPO DCDPS and bisphenol-A

Amino DFTPPO (Mole%)	$[\eta]_{\text{CHCl}_3}^{25^\circ\text{C}}$ (dl/g)	Titration (g/mole)	
		Calculated	Obtained
Control	0.89	-----	-----
10	0.61	4509	4965
20	0.45	2286	2525
30	0.41	1547	1566

The concentration of amino DFTPPO monomer incorporated was varied from 0 to 30 mole%. For the 10 mole% incorporation of amino DFTPPO, the following mole percents of the monomers were added: 10 mole% of amino DFTPPO, 90 mole% of DCDPS, and 100 mole% of bisphenol-A. The control was the homopolymer from the polymerization of DCDPS and bisphenol-A. The intrinsic viscosities of these copolymers ranged from 0.41 to 0.61 dl/g which indicated that high molecular weight copolymers were obtained with varying degree of

amination on the polymer backbone. Titrations for the amines were conducted by dissolving the samples in chloroform and titrating with HBr in acetic acid. The appropriate sample sizes were prepared from the calculation of the number average molecular weight based on the amount of amino DFTPPO monomer charged into the reaction flask relative to the other monomers. As more of amino DFTPPO was incorporated on the polymer backbone, the number average molecular weight per amine decreased from 4965 g/mole for the 10 mole% incorporation of amino DFTPPO to 1566 g/mole for the 30 mole% incorporation. The comparison of the calculated number average molecular weights per amine and the actual values obtained from the titration results showed good agreements.

Proton NMR was a very useful method to characterize the aminated copolymers. Shown in figure 12 is a proton NMR in deuterated chloroform of the 30 mole% incorporation of amino DFTPPO. The presence of four aromatic protons ortho to the phosphine oxide was observed at 7.6 ppm along with the two protons ortho to the amine at 6.8 ppm. Also a broad singlet at 3.9 ppm was observed from the two amine protons. A further experimental evidence for the incorporation of amino DFTPPO monomer onto the polymer backbone was also obtained by carbon NMR. Shown in Figure 13 is a carbon NMR for the 30 mole% incorporation of amino DFTPPO. In addition to the carbon peaks from the other comonomers, the presence of carbon peaks from amino DFTPPO was also observed.

The proton NMR was used as one of the methods to determine the actual incorporation of amino DFTPPO onto the polymer backbone. This was obtained from the ratio of the integration of the four aromatic ortho protons to the

phosphine oxide at 7.6 ppm to the aliphatic isopropylidene protons at 1.7 ppm. The results from the proton NMR were slightly higher than expected, but this was due to the inclusion of the chloroform peak in the aromatic region, however, the general correlation of higher percent incorporations as more amino DFTPPO was added was observed. A better agreement between the expected and the actual incorporation of amino DFTPPO was obtained from the titration results. Thus for the incorporation of 10, 20, and 30 mole% of amino DFTPPO, titration values of 9, 18, and 30% incorporation was obtained. This indicated a quantitative or a nearly quantitative incorporation of amino DFTPPO onto the polymer backbone. These results are shown in Table 8.

Table 8 Comparison of incorporation of amino DFTPPO by proton NMR and amine titration for poly(arylene ether sulfone) copolymers

Amino DFTPPO Charged (mole %)	Actual Incorporation of Amino DFTPPO (%)	
	H NMR	Titration
10	13	9
20	----	18
30	33	30

An FT-IR of 30 mole% incorporation of amino DFTPPO is shown in Figure 14. The major peak assignments are shown in Table 8. The absorbances due to the primary aromatic amine from amino DFTPPO was observed at 3380 and 3466 cm^{-1} , along with absorbances from bisphenol-A and DCDPS.

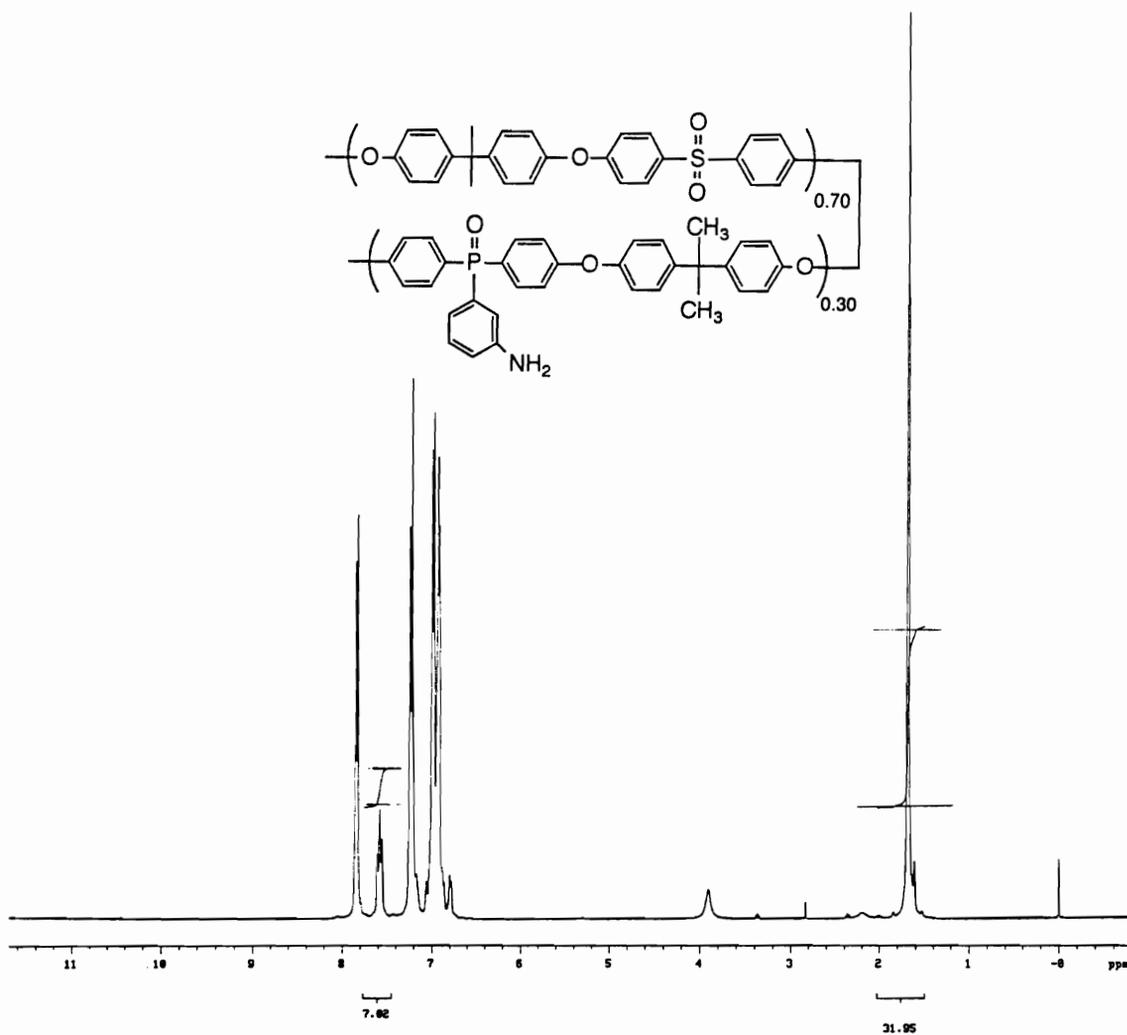


Figure 12 Proton NMR of 30 mole% aminated PSF/PEPO copolymer in deuterated chloroform

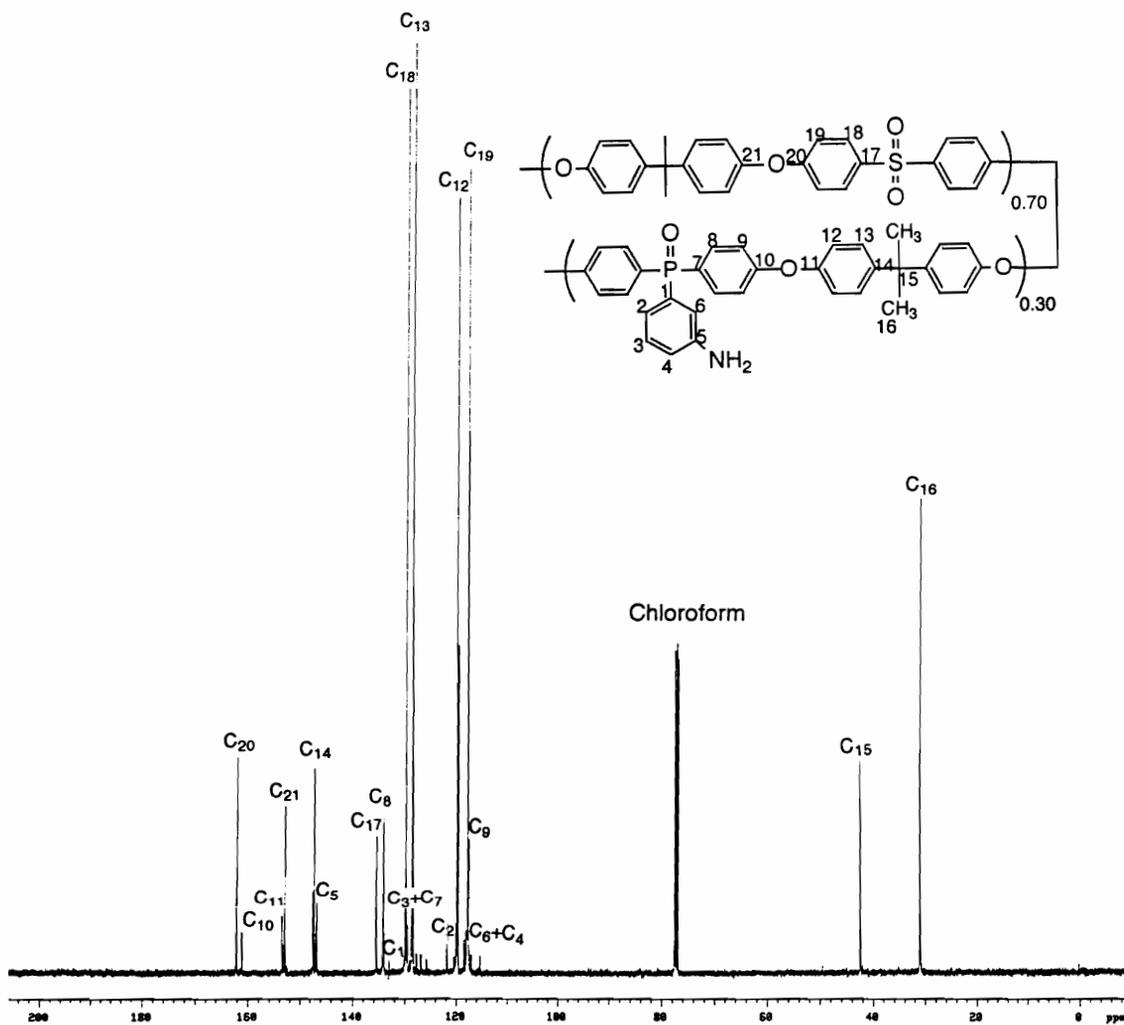


Figure 13 Carbon NMR of 30 mole% aminated PSF/PEPO copolymer in deuterated chloroform

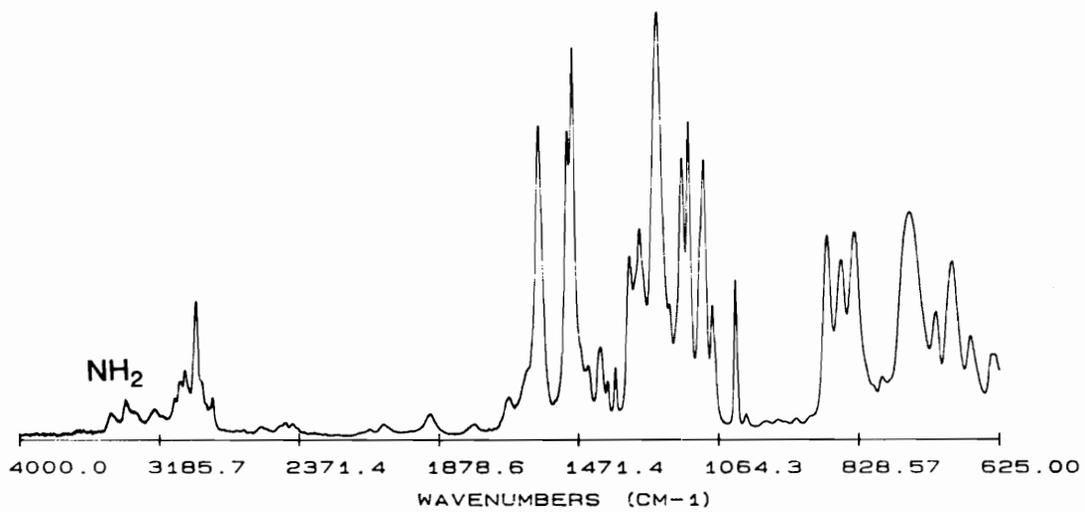


Figure 14 FT-IR of 30 mole% aminated PSF/PEPO copolymer of a cast film from chloroform solution

Table 9 FT-IR functional group assignments of 30 mole% aminated PSF/PEPO copolymer

Functional Group	Assignment (cm ⁻¹)
Aromatic Amine	3466 3380
Aromatic C-H	3038 3071
Isopropylidene C-H	2972 2873 1363
Aromatic C=C	1587 1495 1489
Aromatic C-O-C	1245
SO ₂	1324 1297 1172 1152
C-S	717 691
C-H of p-substituted phenyl	836
P-Aromatic carbon	1436 991

4.3 Higher Incorporation of Pendant Amines

Incorporations of higher concentrations of the amines were also attempted, for this series, the incorporation of amino DFTPPO monomer was 33, 42, and 100 mole% respectively. The other monomers were DCDPS and bisphenol-A. For the 100% incorporation, this was a homopolymer obtained by reacting one to one stoichiometry of amino DFTPPO and bisphenol-A. The polymerization conditions were the same as those for the copolymers discussed previously. The results obtained for the higher mole% incorporation of amino DFTPPO are shown in Table 10.

Table 10 Characterization of higher mole% amino DFTPPO containing poly(arylene ether sulfone) copolymers

Amino DFTPPO Charged (mole%)	Titration		Incorp. by Titration (%)	$[\eta]_{\text{CHCl}_3}^{25^\circ\text{C}}$ (dl/g)
	Calculated (g/mole)	Obtained (g/mole)		
33	1403	1480	31	0.56
42	1106	1172	40	0.47
100	518	521	99	0.36

The number average molecular weight per amine decreased from 1480 g/mole for the 33 mole% incorporation to 521 g/mole for the 100 mole% incorporation. From the titration results, the actual amount of the amine incorporated correlated very well with the intended values. The intrinsic viscosity was 0.56 dl/g for the 33 mole% and decreased to 0.36 dl/g for the 100 mole% which is interpreted as

meaning that relative high molecular weight polymers were obtained for the higher incorporated amount of amino DFTPPO. However, the observed trend of a decreased intrinsic viscosity value as more of amino DFTPPO was incorporated should be addressed in future studies.

There are several possible explanations to account for the decrease in the intrinsic viscosity as more of amino DFTPPO was incorporated. The first possibility may be the purity of the third monomer, since DCDPS and bisphenol-A are very pure monomers, as was demonstrated by obtaining an intrinsic viscosity of 0.89 dl/g from the polymerization of these two monomers. With respect to the purity of amino DFTPPO, great care was taken to ensure that this monomer was very pure and the polymerizations were conducted within a day of obtaining the purified amino DFTPPO.

Another possible explanation for the decrease may be that the amine may have participated in a side reaction, which disrupted the one to one stoichiometry required for high molecular weight polymers. Naturally, one would question the possibility of the amine reacting with activated halides. The probability of the amine participating in a side reaction may have increased as more amino DFTPPO was added and this possibility was investigated using carbon NMR. A carbon NMR of the homopolymer from amino DFTPPO and bisphenol-A with all of the peaks assigned is shown in Figure 15. The main peak of interest was the carbon bonded to the aromatic amine which was observed as a shoulder at 147 ppm. If the amine reacted with the activated halide within the detection limits of the NMR, the appearance of a new peak should have been observed downfield from 147 ppm due to the effect of the sulfone in the para position. As can be seen, no new peaks were observed. The titration results also support the carbon

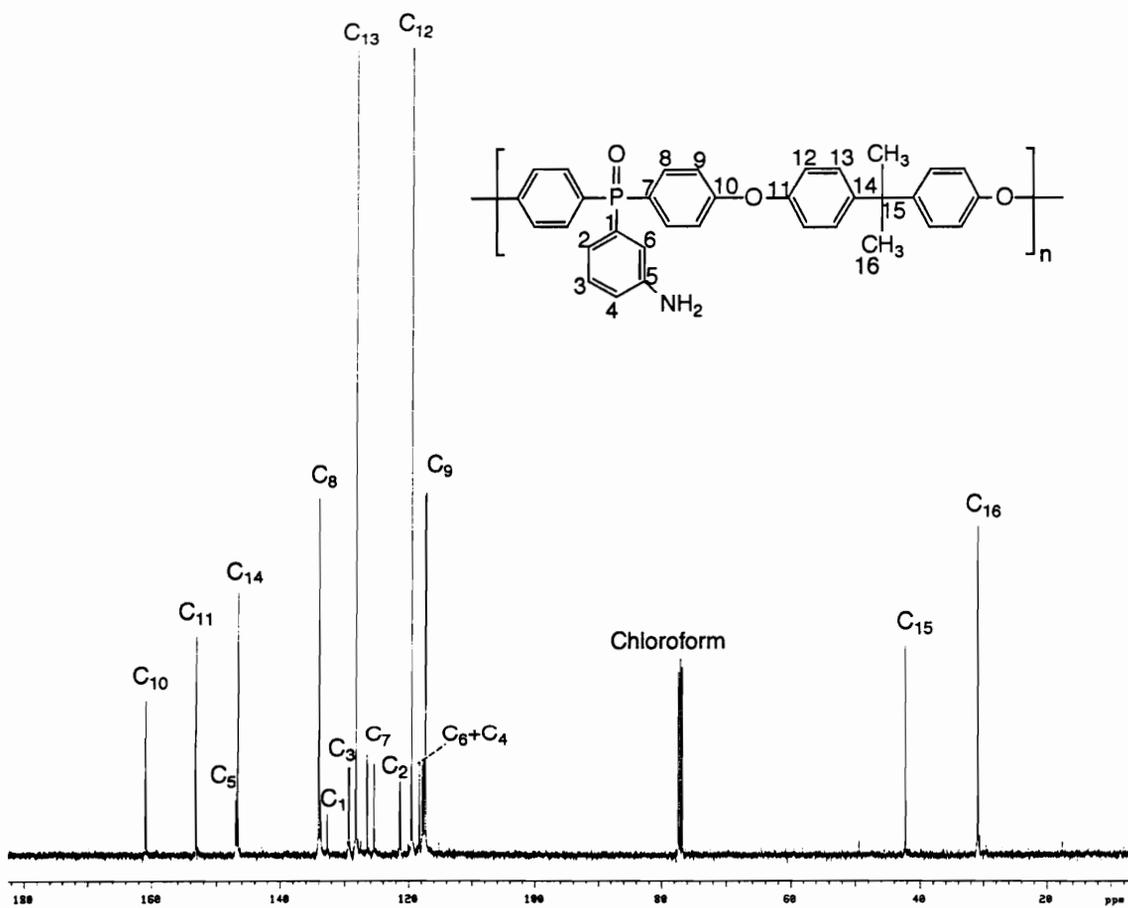


Figure 15 Carbon NMR of aminated polymer from stoichiometric reaction of amino DFTPPO and bisphenol-A

NMR conclusion. Comparison of the calculated number average molecular weight per amine (518 g/mole) and the actual value from the titration (521 g/mole) showed a very good agreement. Thus, from the carbon NMR and the titration results, the reaction of amine with activated halide probably does not account for the decrease in the intrinsic viscosity.

The other possible reason for the decreased intrinsic viscosity as more amino DFTPPO was added may be that the reaction rate decreases as the concentration of the amine increased. Thus, there may have been a greater extent of hydrogen bonding with the phenolates which could decrease their nucleophilicity. During the polymerization, not all of the phenolates are generated at once, instead, there is a gradual in situ formation of phenolates which then react with activated halides. The phenols in the reaction mixture can hydrogen bond with the phenolates which decrease the reactivity of the associated phenolate. However, as more of the phenols are converted to phenolates and react with the activated halides, the concentration of phenols available to hydrogen bond with phenolates decrease and the overall rate of polymerization increases with time. With a higher concentration of amino DFTPPO in the reaction mixture, the amines may also hydrogen bond with the phenolates and reduce the reactivity of the phenolates. The exception in this case is that since the amine does not react with the activated halide, the concentration of the amine remains constant during the polymerization.

The last explanation to account for the decrease in the intrinsic viscosity as more amino DFTPPO was reacted may simply be due to a decreased reactivity of amino DFTPPO. Phosphine oxide is a relatively weak electron withdrawing group, comparable to a ketone in 4,4'-difluorobenzophenone (DFB).

This is why only fluorine can be used as the halide to obtain high molecular weight polymers. With amino DFTPPO, the amine is meta to the phosphine oxide, and even though the amine does not have a strong influence on the phosphine oxide there may still be a slight deactivation by the electron donation from the amine to the pendant phenyl ring. This effect would decrease the reactivity of amino DFTPPO which would be more pronounced once one of the two fluorine sites has been displaced.

4.4 Thermal Characterization of Aminated PSF/PEPO Copolymers

The glass transitions (T_g) of the pendant amine copolymers are shown in Table 11. A moderate increase in the T_g was observed as more amino DFTPPO was incorporated, 193°C for the 10 mole% incorporation to 228°C for the 100 mole% incorporation. The increase in T_g was due to presence of the triaryl phosphine oxide moiety, but more importantly, the increase in the T_g was probably due to the presence of amines along the polymer backbone which can participate in intermolecular hydrogen bonding with phosphine oxides and sulfones which would result in a stiffer polymer chain. The presence of a single T_g as shown in Figure 16 indicated that the copolymers from amino DFTPPO, DCDPS, and bisphenol-A were statistical and not block copolymers and the difference in the reactivity of the phenolate toward DCDPS and amino DFTPPO was not significant under the polymerization conditions. In Figure 17 is a thermogravimetric analysis (TGA) of three aminated copolymers which were 32, 42, and 100 mole% incorporation of amino DFTPPO monomer polymerized with DCDPS and bisphenol-A. The thermograms were obtained in air at a heating rate of 10°C/min. As can be seen, these aminated copolymers showed

comparable thermo-oxidative stabilities and did not show any appreciable weight loss until about 480°C. The main feature of the incorporation of triaryl phosphine oxide moiety into the polymer backbone was the presence of char yields up to a temperature of 800°C. The amount of the char yield at 800°C was greater for the polymer/copolymer with higher incorporation of amino DFTPPO. Therefore, the char yield was highest for the 100 mole% followed by 42 and 33 mole% incorporation of amino DFTPPO.

Table 11 Comparison of Tgs for the bisphenol-A copolymers as function of the charged amount of amino DFTPPO

Amino DFTPPO Charged (mole %)	$[\eta]_{\text{CHCl}_3}^{25^\circ\text{C}}$ (dl/g)	Tg (°C)
PSF Control	0.89	190
Bis-A PEPO Control	1.09	201
10	0.61	193
20	0.45	196
30	0.41	199
33	0.56	206
42	0.47	207
100	0.36	228

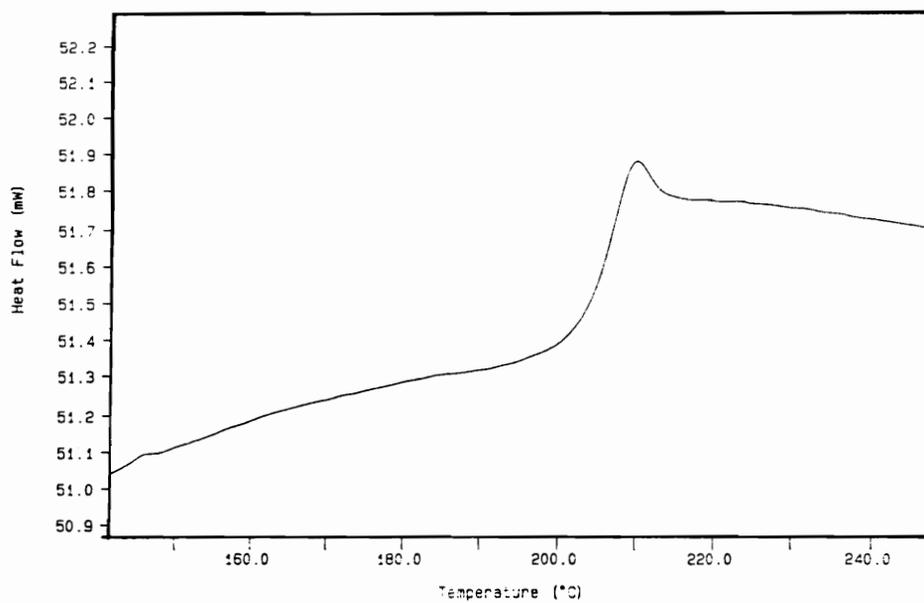


Figure 16 DSC of 30 mole% aminated PSF/PEPO copolymer

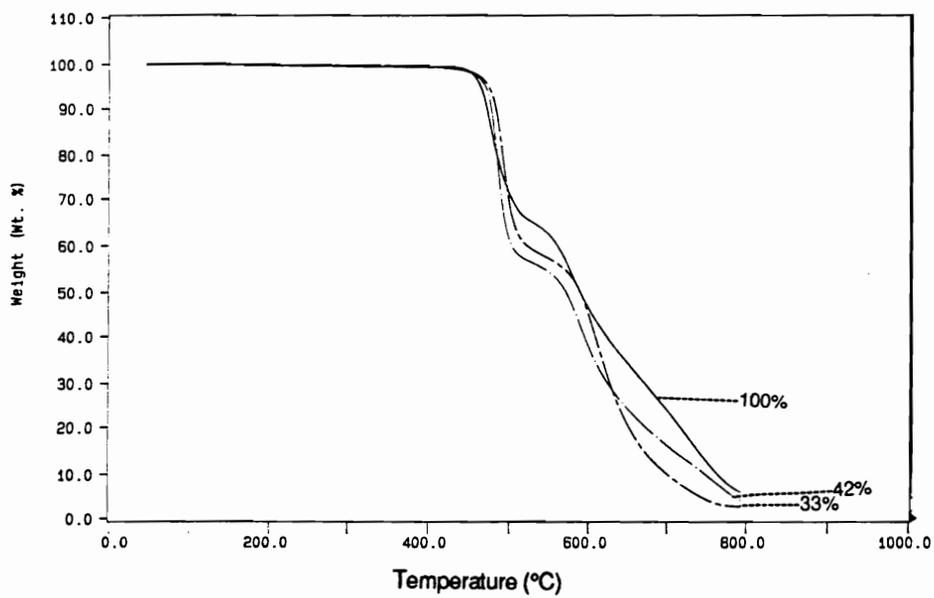


Figure 17 TGA behaviors of 33, 42 and 100 mole% aminated polymers

The effect of performing the analysis in air and in nitrogen for the 100 mole% amino DFTPPO incorporation is shown in Figure 18. A dramatic difference was observed in the thermal stability of the same material in two different atmospheres. The stability as a function of temperature was much better in a nitrogen atmosphere than in air. Since the most application of polymers are in air and not in nitrogen, the thermogram obtained in air is a better measure to predict the thermo-oxidative stability of polymeric materials. The TGA analysis in air which demonstrated the effect of pendant amines on the thermo-oxidative stability is shown in Figure 19. One is a thermogram of a high molecular weight homopolymer from a balanced polymerization of amino DFTPPO and bisphenol-A and the other polymer was a high molecular weight polysulfone from DCDPS and bisphenol-A. The polysulfone which does not contain any amines showed a better initial weight loss stability than the polymer with pendant amines. The earlier thermal degradation with pendant amine polymer was due to the presence of amines which oxidized in air at higher temperatures. Also, the polysulfone was completely degraded at about 680°C, whereas, the presence of phosphine oxide from the incorporation of amino DFTPPO resulted in about 10% retention of its initial weight, probably as a partially oxidized phosphorus containing char (75).

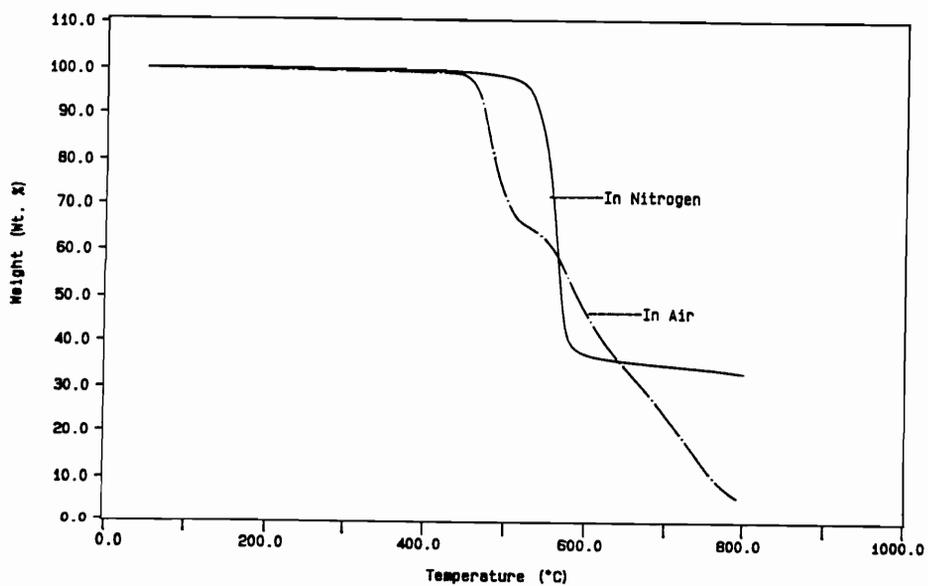


Figure 18 TGA in air and nitrogen of aminated polymer from stoichiometric reaction of amino DFTPPO and bisphenol-A

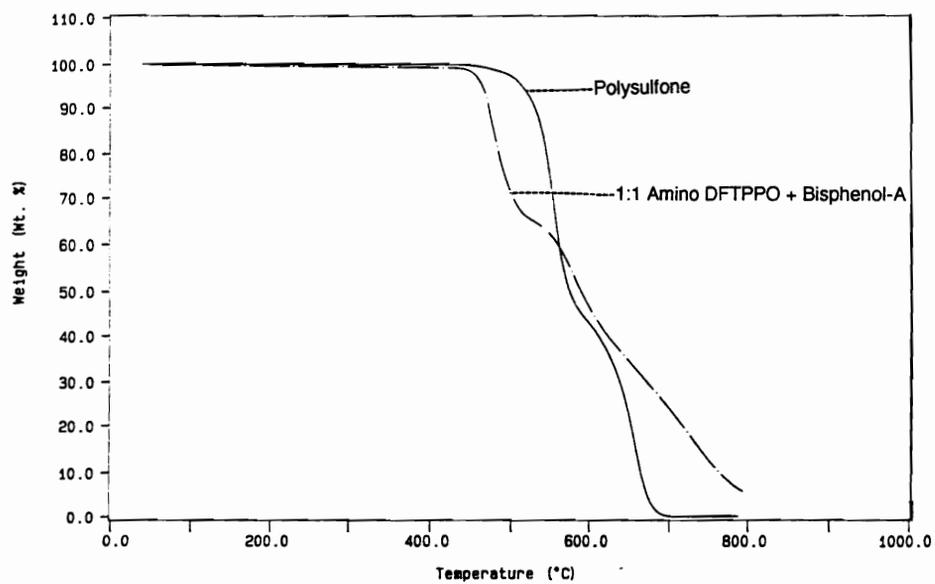
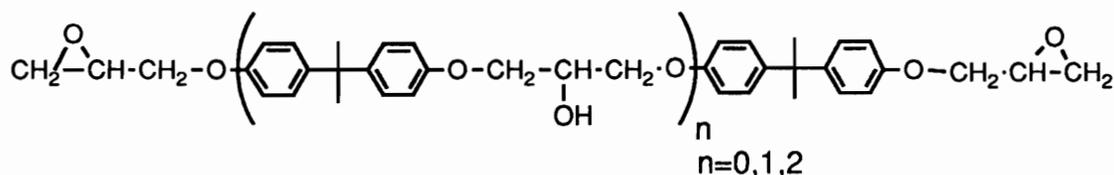


Figure 19 TGA in air of polysulfone control and 100 mole% PEPO

4.5 Modification of Epoxy Networks with Pendant Amine Copolymers

The successful synthesis of statistical aminated copolymers from step polymerization of amino DFTPPO, DCDPS, and bisphenol-A was demonstrated in the previous section. One goal for these reactive thermoplastic copolymers was to improve the fracture toughness of the brittle epoxy networks. The structure of commercially available Epon 828 is shown below and it was utilized as a model epoxy. The stoichiometric curing agent, or "hardener" was 4,4'-diaminodiphenylsulfone (DDS).



Epon 828

Previously, controlled molecular weights of the amine terminated polysulfones have been demonstrated to increase the fracture toughness of brittle epoxy networks (159, 206). One of the variables that influenced the fracture toughness of the thermoplastic modified epoxy networks was the molecular weight of the thermoplastic. As the molecular weight of the amine terminated polysulfones increased, the fracture toughness of the modified epoxy networks also increased. The other variable was the amount of the thermoplastic that was incorporated, since as the amount of the thermoplastic modifier increased, the fracture toughness of the modified epoxy network also improved. Figure 20 shows a two phase morphology that is generated by simply physically blending 15 weight percent of a commercial Udel polysulfone into the epoxy network.

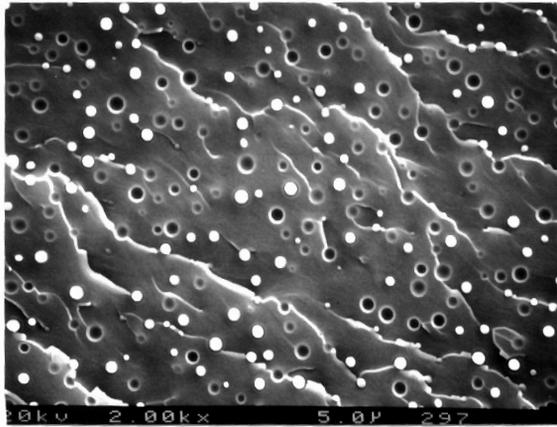
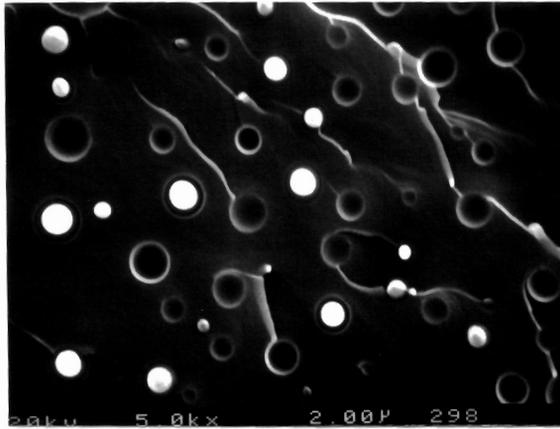


Figure 20 SEM of epoxy network modified with 10 wt% incorporation of Udel

The non-reactive commercial Bisphenol-A based poly(arylene ether sulfone) is initially soluble in the epoxy resin, however, as the cure progresses it phase separates from the epoxy matrix and forms discrete particles. It is widely believed that these discrete ductile particles enhance the fracture toughness of the modified epoxy networks, although chemical resistance is impaired. In the case with Udel, even though a two phase morphology was obtained, only a slight improvement in the fracture toughness was observed (156). This may be due to poor adhesion between the phase separated particles and the epoxy matrix. By incorporating reactive amine terminated polysulfones into epoxies, a similar two phase morphology and a dramatic increase in the fracture toughness was reported (159). The increase in the fracture toughness was attributed to the good adhesion between the polysulfone particles and the epoxy matrix as a result of the reaction of the amines with the epoxy resin.

In this investigation, high molecular weight random copolymers from the reaction of amino DFTPPO, DCDPS, and bisphenol-A with various amine concentrations on the polymer backbone were incorporated into the epoxy networks in an effort to improve the fracture toughness. The characterizations of the pendant amine copolymers of PSF/PEPO utilized in this investigation are shown in Table 12. As discussed before, a slight increase in the T_g was observed as the concentration of the amine on the polymer backbone increased. An exception was a slightly higher T_g for the 5 mole% aminated copolymer which had a T_g of 197°C as compared to 193°C for 10 mole% aminated copolymer. This was probably due to a much higher intrinsic viscosity for the 5 mole% aminated copolymer (1.00 dl/g) as compared to the 10 mole% which had a intrinsic viscosity of 0.61 dl/g. The overall intrinsic viscosities ranged from 0.41

dl/g for the 30 mole% aminated copolymer to 1.00 g/dl for the amination of 5 mole%. The number average molecular weight per amine was lower for the higher aminated copolymers than it was for copolymers with a lower concentration of the pendant amine. These values ranged from 1,566 g/mole for the 30 mole% aminated copolymer to 42,598 g/mole for the 1.0 mole% aminated copolymer.

Table 12 Characterization of the aminated copolymers from amino DFTPPO, DCDPS, and bisphenol-A used for the toughening of epoxy networks

Samples	Cure Site (Mole%)	$[\eta]_{\text{CHCl}_3}^{25^\circ\text{C}}$ (dl/g)	Tg (°C)	<Mn>/Amine (g/mole)
Amino PSF/PEPO	30.0	0.41	199	1,566
Amino PSF/PEPO	20.0	0.45	196	2,525
Amino PSF/PEPO	10.0	0.61	193	4,965
Amino PSF/PEPO	5.0	1.00	197	9,324
Amino PSF/PEPO	2.5	0.45	191	16,699
Amino PSF/PEPO	1.0	0.45	191	42,598

Various concentrations of the aminated copolymers were incorporated into the epoxy network in an effort to investigate the influence of concentration on the fracture toughness (K_{1c}) and on the generated morphology. In most cases, the

amount of the thermoplastic modifier which was utilized ranged from 5 to 25 weight percent (wt%) for each composition; however, copolymers with a very high viscosity or a high concentration of the amine limited the preparation of some compositions. The thermoplastic modified epoxy networks were prepared by adding the appropriate amount of the copolymer to the Epon 828 resin until a viscous homogeneous solution was obtained. During this process, it is probable that chain extension occurred between the pendant amines and the epoxides. The curing agent (4,4'-DDS) was added last to minimize the viscosity buildup prior to the network formation. The cycle that was used to cure all of the epoxy networks was 190°C for 1.5 hour, followed by a "post cure" at 235°C for another 1.5 hours.

4.6 Effect of the Incorporation of Various Amount of Aminated Copolymers on Morphology and Fracture Toughness of Epoxy Networks

The fracture toughness results from the curing of epoxy networks with 10, 20, and 30 mole% aminated copolymers at various weight fractions are shown in Table 13. The control was the epoxy network from Epon 828 and 4,4'-DDS. The fracture toughness of the control was $0.75 \text{ MNm}^{-3/2}$, for the 5, 10, and 15 weight percent loadings of the 30 mole% aminated copolymer, the fracture toughness was 0.75, 0.66, and $0.65 \text{ MNm}^{-3/2}$ respectively. Essentially, no increase or even a slight decrease in the fracture toughness was observed. For the various weight percent loadings of the 20 mole% aminated copolymer, the fracture toughness increased only slightly from 0.85 to $0.88 \text{ MNm}^{-3/2}$. A similar trend in the fracture toughness was also observed for the different weight percent loadings of the 10 mole% aminated copolymer.

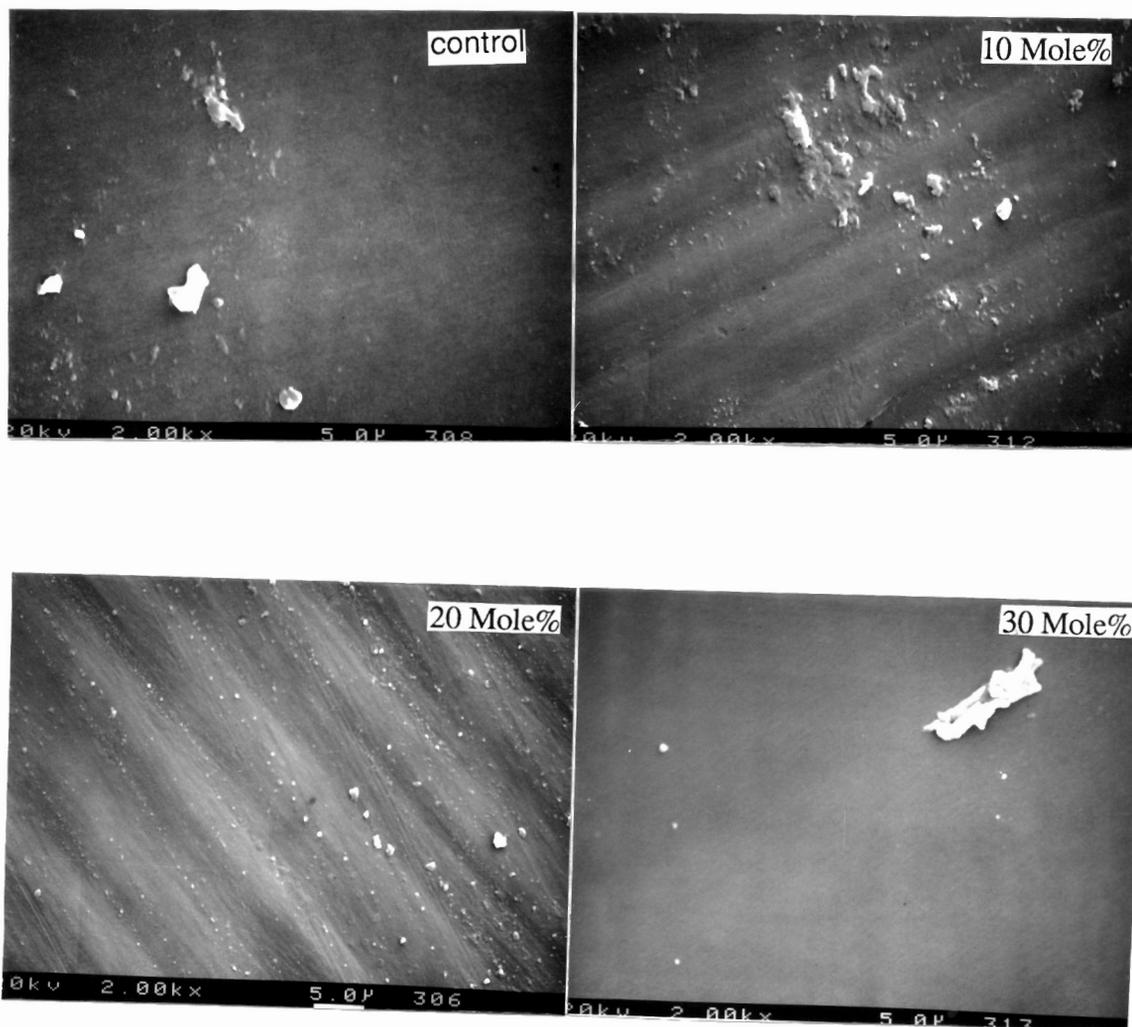


Figure 21 SEM of the control and 10 wt% of 10, 20, and 30 mole% aminated PSF/PEPO copolymer

The fractured surfaces of all the samples from the various weight percent loadings of 30, 20, and 10 mole% aminated copolymers were transparent. The scanning electron micrographs (SEM) of the control and 10 weight percent loadings of 10, 20, and 30 mole% aminated copolymers are shown in Figure 21.

Table 13 Influence of cure site and weight fraction on fracture toughness (K_{1c}) of Epon 828 and 4,4'-DDS networks modified with aminated PSF/PEPO copolymers

Samples	Cure Site (mole%)	Incorp. (wt%)	Fracture Toughness ($MNm^{-3/2}$)
Control	---	---	0.75 ± 0.08
(Udel)		10	0.84 ± 0.08
Amino PSF/PEPO	30.0	5	0.75 ± 0.07
		10	0.66 ± 0.05
		15	0.65 ± 0.16
Amino PSF/PEPO	20.0	5	0.85 ± 0.06
		10	0.88 ± 0.01
		15	0.88 ± 0.12
Amino PSF/PEPO	10.0	5	0.75 ± 0.06
		10	0.84 ± 0.12
		15	0.85 ± 0.04
		20	0.89 ± 0.06

From the SEMs, the presence of phase separated particles were not observed, these results supported the very little or no increase in the fracture toughness of these modified epoxy networks. The number average molecular weight per amine for these copolymers ranged from about 4,965 g/mole for the 10 mole% aminated copolymer to 1,566 g/mole for the 30 mole% aminated copolymer. The high concentration of amines in the copolymers produced a homogeneous system with the epoxy which did not phase separate. The results from dynamical mechanical analysis (DMA) also indicated a single phase morphology for the aminated copolymers which had a relatively high concentrations of the pendant amines on the polymer backbone.

As the concentration of the amine on the polymer backbone decreased to 5 mole%, a moderate improvement in the fracture toughness was observed and the results are shown in Table 14. Thus, for the 5 and 10 weight percent loadings of the 5 mole% aminated copolymer, the fracture toughness was 0.96 and 1.11 MNm^{-3/2}. Attempts to incorporate higher weight percent loadings of this polymer was not successful due to the very high viscosity (1.00 dl/g) of this copolymer. The fracture surfaces of these samples were opaque, however, the SEMs of these samples did not indicate the presence of a second phase. The SEMs for the 5 and 10 weight percent loadings of a 5 mole% aminated copolymer are shown in Figure 22. The fractured surfaces of these samples were rough which indicated a slight extent of stretching and tearing that occurred as the sample was being fractured. With DMA, a single phase was observed for the 5 weight percent loading, however, a slight shoulder indicative of a second phase was observed for the 10 weight percent loading of the 5 mole% aminated

Table 14 Fracture toughness of modified epoxy networks from Epon 828 and 4,4'-DDS with a physical blend (UDEL) or with an aminated (5%) PSF/PEPO copolymer

Samples	Cure Site (mole%)	Incorp. (wt%)	Fracture Toughness (MNm ^{-3/2})
Control	---	---	0.75±0.08
(Udel)		10	0.84±0.08
Amino PSF/PEPO	5.0	5 10	0.96±0.06 1.11±0.21

copolymer. The DMA which show the $\tan \delta$ behaviors of the 5 and 10 weight percent loadings of 5 mole% aminated copolymer is shown in Figure 23. **As the concentration of the pendant amine decreased even further to 2.5 mole% along the copolymer backbone, a dramatic increase in the fracture toughness was observed and these results are shown in Table 15.** The fracture toughness for the various weight percent loadings of a 2.5 mole% aminated copolymer ranged from 0.86 MNm^{-3/2} for the 5 weight percent loading to 2.28 MNm^{-3/2} for the 25 weight percent loading, this was almost a three fold improvement in the fracture toughness over the unmodified control (Epon 828 and 4,4'-DDS). Shown in Figure 24 are the SEMs for the different weight percent loadings of the 2.5 mole% aminated copolymer.

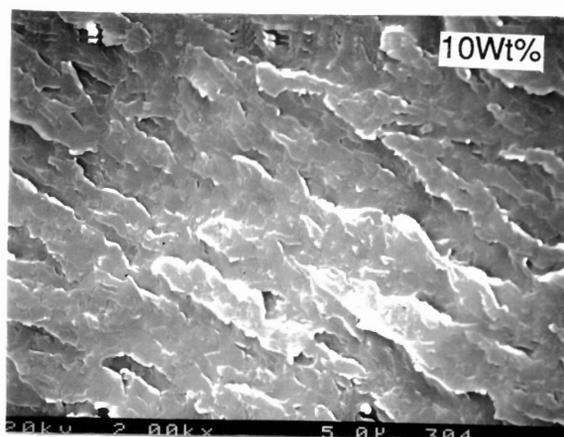
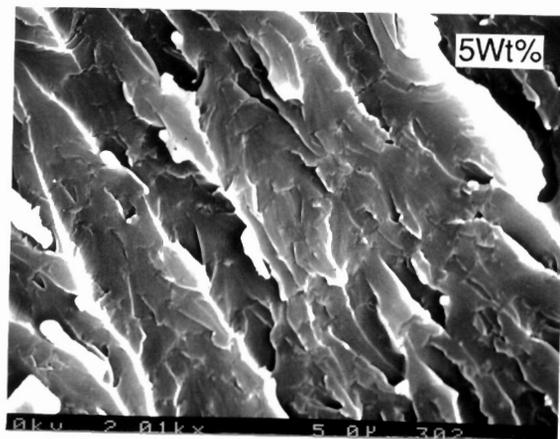


Figure 22 SEM of 5 and 10 wt% of 5 mole% aminated PSF/PEPO copolymer into epoxy networks

Table 15 Fracture toughness of modified epoxy networks from Epon 828 and 4,4'-DDS with 2.5 and 1.0 mole% aminated PSF/PEPO copolymer

Samples	Cure Site (mole%)	Incorp. (wt%)	Fracture Toughness (MNm ^{-3/2})
Control	---	---	0.75±0.08
(Udel)		10	0.84±0.08
Amino PSF/PEPO	2.5	5	0.86±0.08
		10	0.92±0.06
		15	1.19±0.10
		20	2.05±0.17
		25	2.28±0.43
Amino PSF/PEPO	1.0	5	0.89±0.15
		10	0.99±0.13
		15	1.51±0.25
		20	2.15±0.18
		25	2.55±0.14

The SEMs of these samples showed the development of two phase morphologies which changed as the composition of the thermoplastic modifier was varied. For the 5 weight percent loading, the presence of uniformly dispersed polysulfone particles on the order of a micron were observed in the continuous epoxy network. With 10 weight percent loading, the number and the size of the particles increased. Between 15 and 20 weight percent loading, a phase inversion occurred and a coarse honeycomb type morphology was

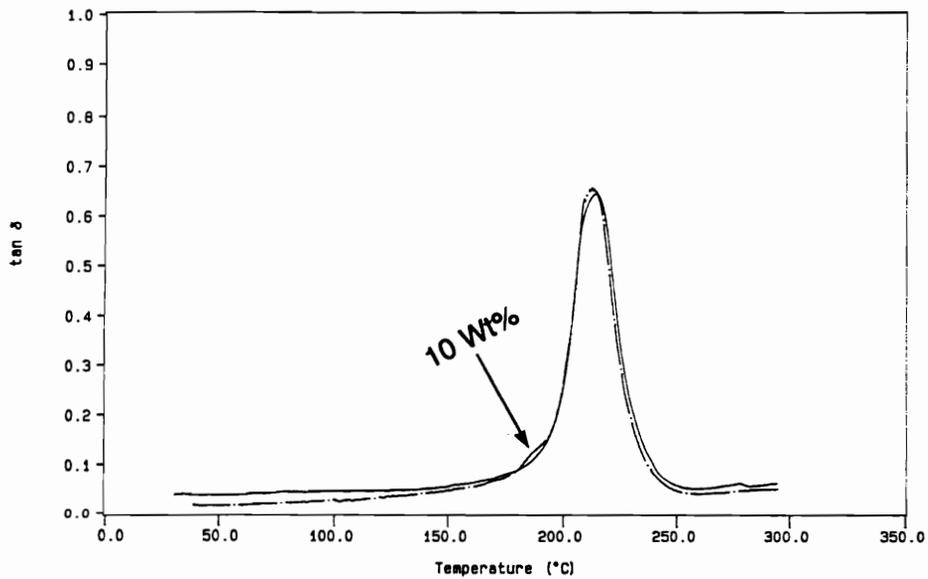


Figure 23 DMA $\tan \delta$ of 5 and 10 wt% of 5 mole% aminated PSF/PEPO copolymer into epoxy networks

observed for the 20 weight percent loading. With a phase inverted morphology, the thermoplastic was now the continuous phase which surrounded the discrete epoxy particles. As can be seen from the fracture toughness results, the dramatic increase in the fracture toughness was obtained when the concentration of the thermoplastic modifier was such that phase inversion occurred. With a 25 weight percent loading, a more defined honeycomb type of morphology was observed. The solvent uptake in chloroform of the modified epoxy networks with 5, 10, 15, 20, and 25 weight percent loadings of a 2.5 mole% aminated copolymer is shown in Figure 25. This solvent uptake was conducted by immersion of the specimen in chloroform and periodically measuring the increase in weight as a function of time. Notice the relative small increase in weight for the 5, 10, and 15 weight percent loadings in which the epoxy network surrounded the thermoplastic particles. However, after the phase inversion, the swelling resistance decreased dramatically which was probably due to a relatively large molecular weight between crosslink sites of the thermoplastic continuous phase. Therefore, phase inverted materials will swell to a greater extent than materials in which the thermoplastic particles are discrete. A DMA showing the $\tan\delta$ of the epoxy network modified with a 25 weight percent loading of 2.5 mole% aminated copolymer and the unmodified control is shown in Figure 26. A two phase morphology was clearly evident by the presence of another peak in the modified epoxy which is not present in the unmodified control. Decreasing the concentration of the pendant amine on the polymer backbone even lower to 1 mole% resulted in only a slight improvement in the fracture toughness as compared to the 2.5 mole% aminated copolymer. Shown in Figure 27, the morphologies for the various weight percent loadings of a 1.0 mole% aminated

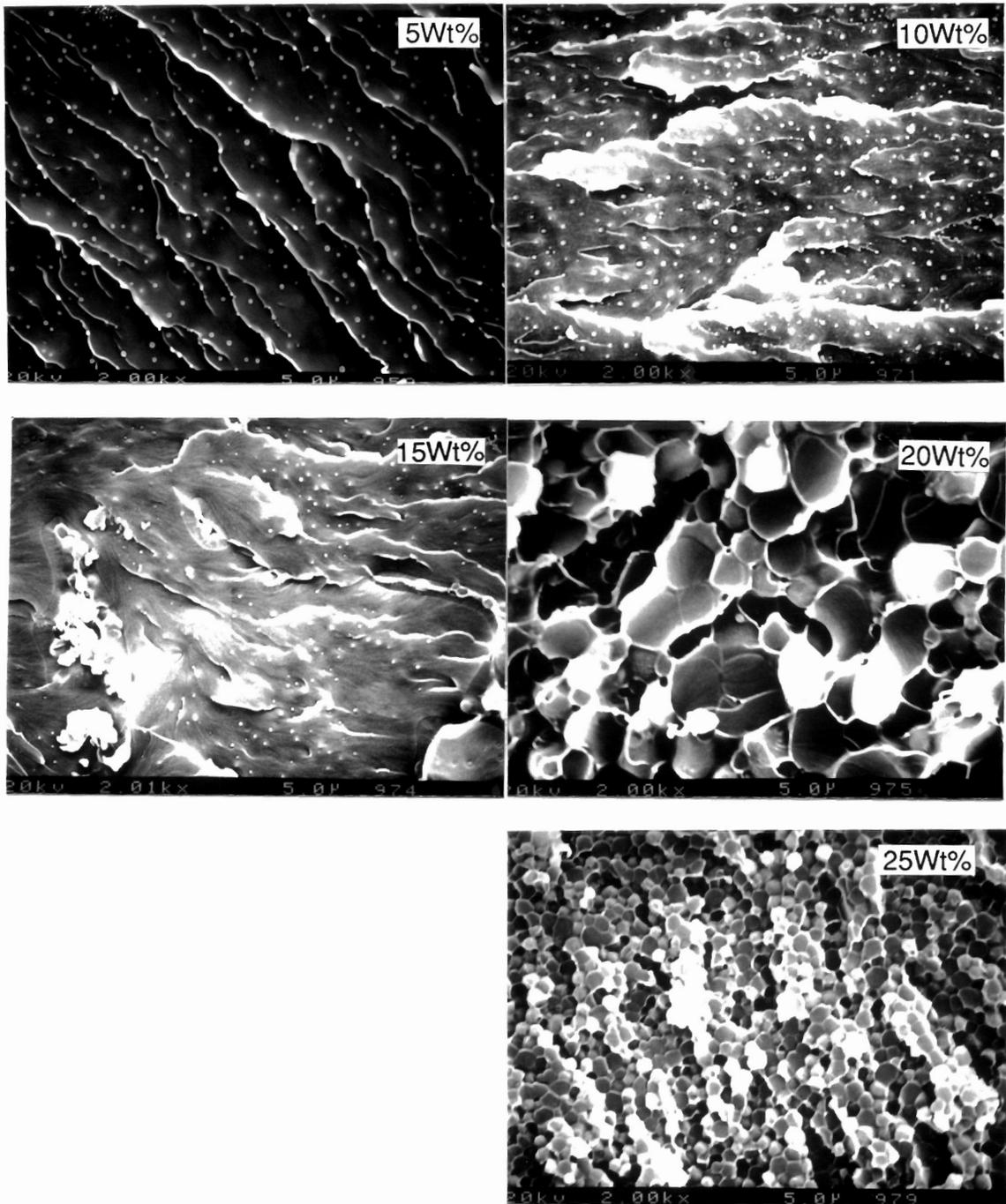


Figure 24 SEM of 5, 10, 15, 20 and 25 wt% of 2.5 mole% aminated PSF/PEPO copolymer into epoxy networks

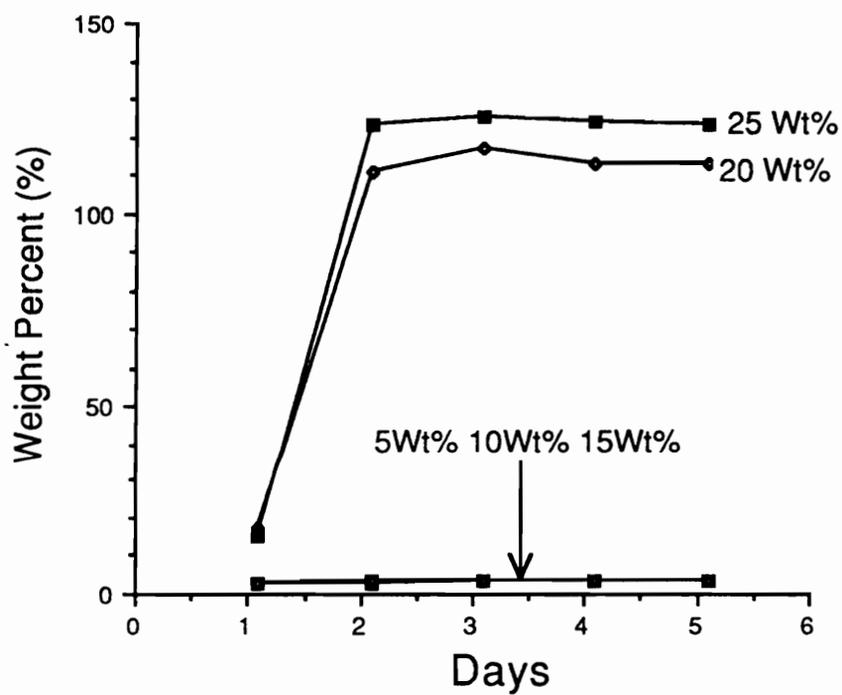


Figure 25 Influence of thermoplastic concentration in toughened epoxy networks on chloroform swelling (2.5 mole% amine groups)

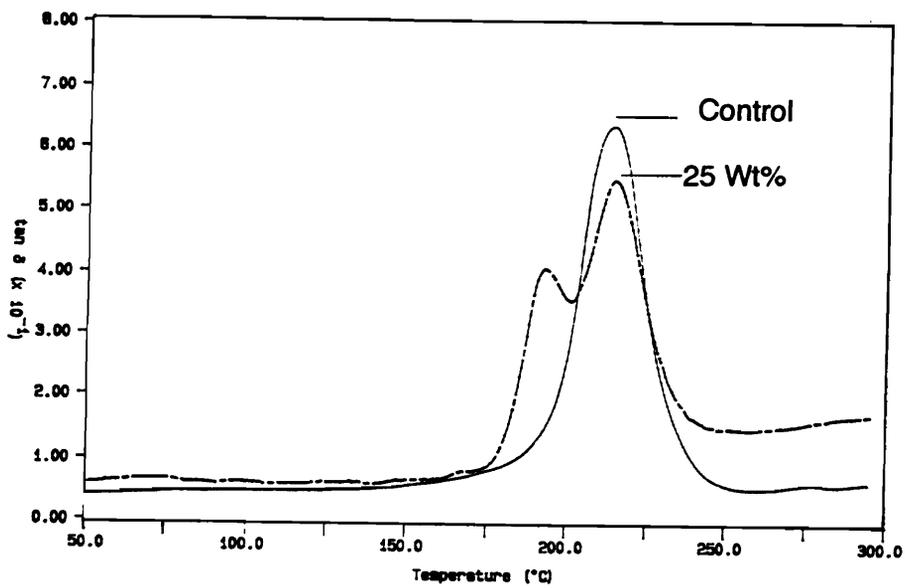


Figure 26 DMA $\tan\delta$ of the control and epoxy network modified with 25 wt% of 2.5 mole% aminated PSF/PEPO copolymer

copolymer were also similar to the morphologies obtained with 2.5 mole% aminated copolymer. However, a dramatic difference in the solvent resistance for the epoxy networks modified with the 1.0 and 2.5 mole% aminated copolymers was observed. Comparison of the solvent uptake in chloroform for the 15 weight percent loading of 2.5 and 1.0 mole% aminated copolymer is shown in Figure 28. The epoxy network modified with a 1.0 mole% aminated copolymer showed a greater extent of swelling than the epoxy network modified with a 2.5 mole% aminated copolymer.

This comparison of the solvent uptake is shown in Figure 28. The decreased solvent resistance of the epoxy networks modified with the 1.0 mole% aminated copolymers may be due to the statistical distribution in the copolymer, which produced some polymer chains that are not aminated. The DMAs of the fractured samples analyzed on a three point bend mode for the epoxy networks modified with a 15 weight percent incorporation of 1.0 and 2.5 mole% aminated copolymers as provided in Figure 29. Notice that the $\tan\delta$ for both samples display a small shoulder which indicated the presence of two phases as was confirmed by SEM. The maximum of the $\tan\delta$ for the network modified with 1.0 mole% aminated copolymer was observed at a slightly lower temperature than the epoxy network modified with the 2.5 mole% aminated copolymer, this may be due to a lower crosslink density for the epoxy network modified with the 1.0 mole% aminated copolymer which will result in a lower T_g .

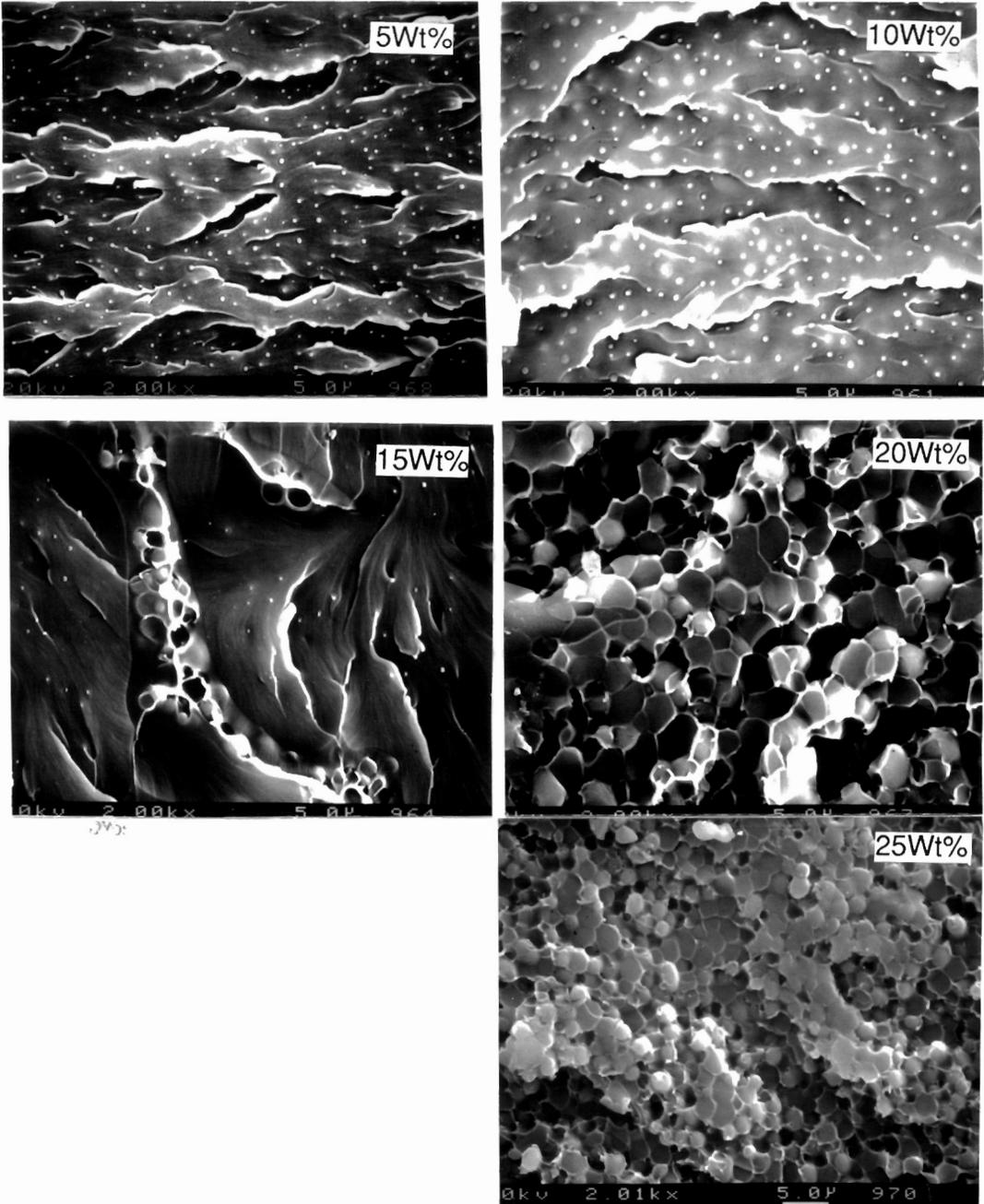


Figure 27 SEM of 5, 10, 15, 20 and 25 wt% of 1.0 mole% aminated PSF/PEPO copolymer into epoxy networks

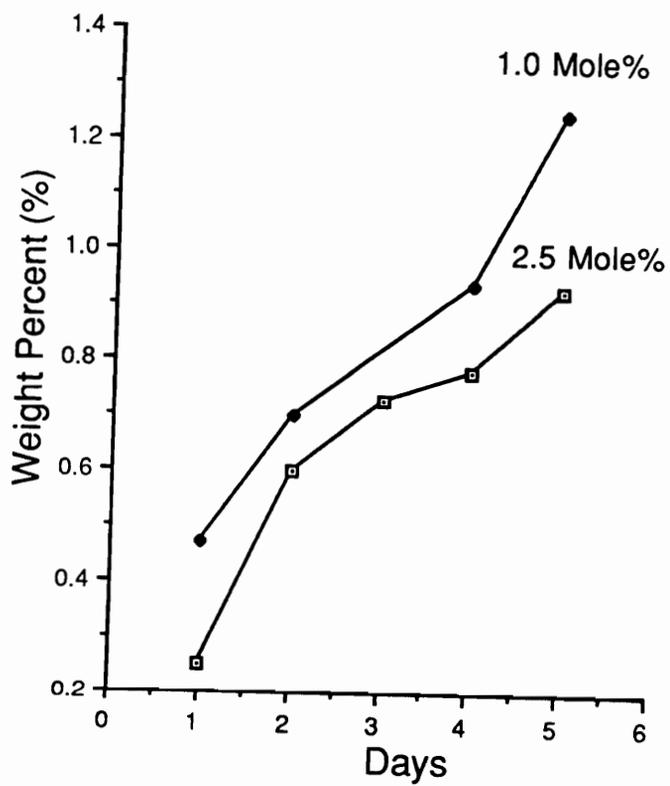


Figure 28 Comparison of chloroform uptake for 15 wt% of 2.5 and 1.0 mole% aminated PSF/PEPO copolymer into epoxy networks

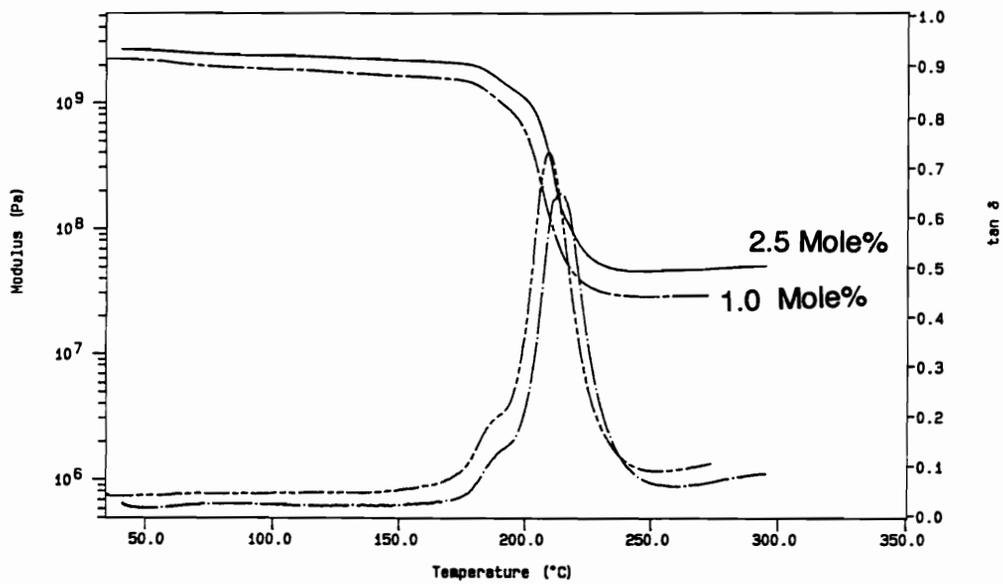
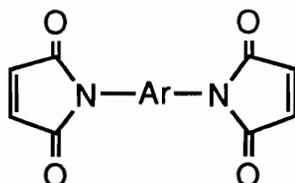


Figure 29 DMA of 15 wt% of 2.5 and 1.0 mole% aminated PSF/PEPO copolymers into epoxy networks

4.7 Modification of Pendant Amines to Maleimides

Another modification of the pendant amines was to convert the amines to maleimides, the generic structure of a bismaleimides is shown below



The Ar may be an aromatic moiety of a monomer or it can also be a repeat unit of a polymer backbone. Maleimides are one of the functional groups that can be thermally or microwave induced to undergo crosslinking reactions to afford insoluble three dimensional networks. In this investigation, copolymers with low concentrations of the pendant amines along the polymer backbone were utilized. The concentrations of the pendant amines which were investigated were 5, 10, and 15 mole percents of amino DFTPPO polymerized with DCDPS and bisphenol-A. A one to one stoichiometry of the activated dihalides to bisphenol-A was used. Characterizations of the aminated copolymers which were used are shown in Table 16. The control was a polysulfone from the polymerization of DCDPS and bisphenol-A. As shown by the intrinsic viscosities in chloroform which ranged from 0.49 to 0.59 dl/g for the aminated copolymers, high molecular weight copolymers were indeed synthesized. The number average molecular weights in NMP obtained by gel permeation chromatography performed with lithium bromide (GPC) supported the results from intrinsic viscosities. The molecular weight distributions (MWD) as judged by $\langle M_w \rangle / \langle M_n \rangle$ were close to two which are typical for polymers obtained by a polycondensation process. The GPC chromatograms of the control and copolymer with the highest amine concentration (15 mole%) is shown in Figure 30. The pendant amines

were converted to the maleimides by reacting with maleic anhydride in chloroform using sodium acetate and acetic anhydride. This mild reaction condition was used to minimize the possible crosslinking of the maleimides in solution.

Table 16 Characterizations of aminated PSF/PEPO copolymers used for the conversion to maleimides

Amino DFTPPO Charged (mole%)	$[\eta]_{\text{CHCl}_3}^{25^\circ\text{C}}$ (dl/g)	$\langle\text{Mn}\rangle^*$ (g/mole)	MWD	Titration $\langle\text{Mn}/\text{Amine}\rangle$ (g/mole)
Control	0.89	97,060	1.96	-----
5	0.59	55,220	1.87	8794
10	0.51	51,420	1.73	4578
15	0.49	46,510	2.20	3160

* GPC, universal calibration

A proton NMR of the 15% aminated PSF/PEPO copolymer and 15% maleimide copolymer in deuterated chloroform is provided in Figure 31. The presence of four aromatic protons ortho to the phosphine oxide was observed at 7.6 ppm along with the two protons ortho to the amine at 6.8 ppm. Also a broad singlet at 3.9 ppm was observed from the two amine protons. Upon conversion to the maleimide, the amine peak disappeared and a new peak from the olefin protons on the maleimide emerged at 6.9 ppm. The carbon NMR of the 15% aminated

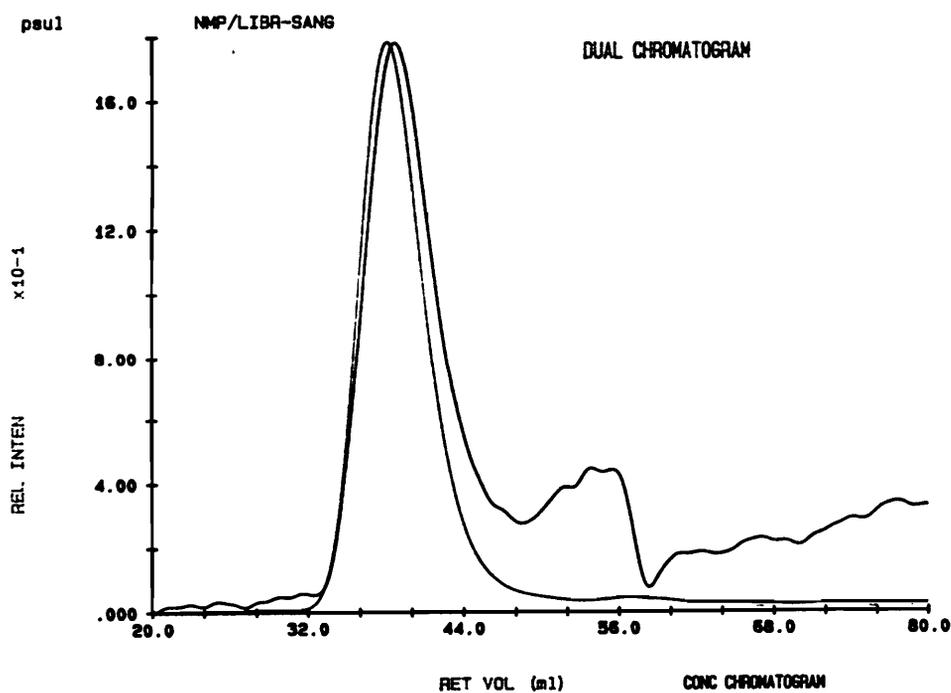
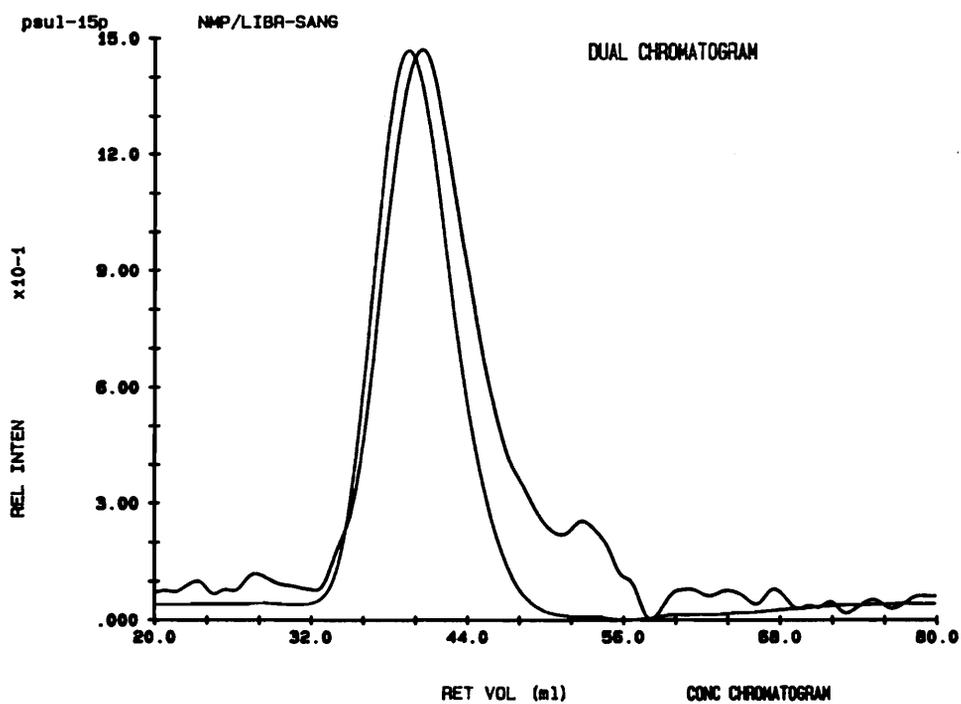


Figure 30 GPC of bisphenol-A based polysulfone control (bottom) and 15 mole% aminated PSF/PEPO copolymer (top)

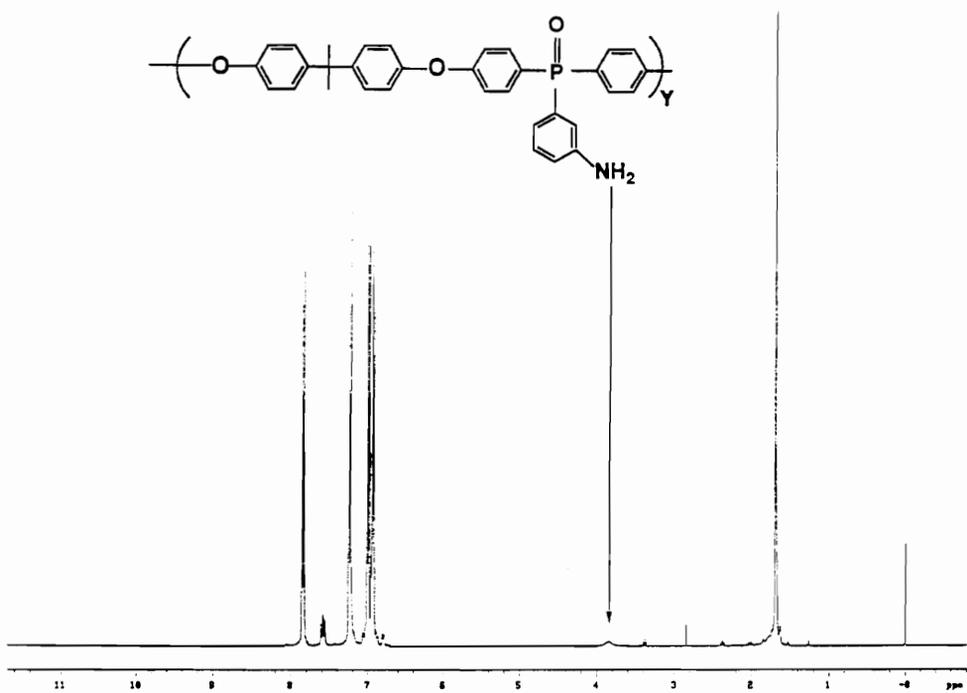
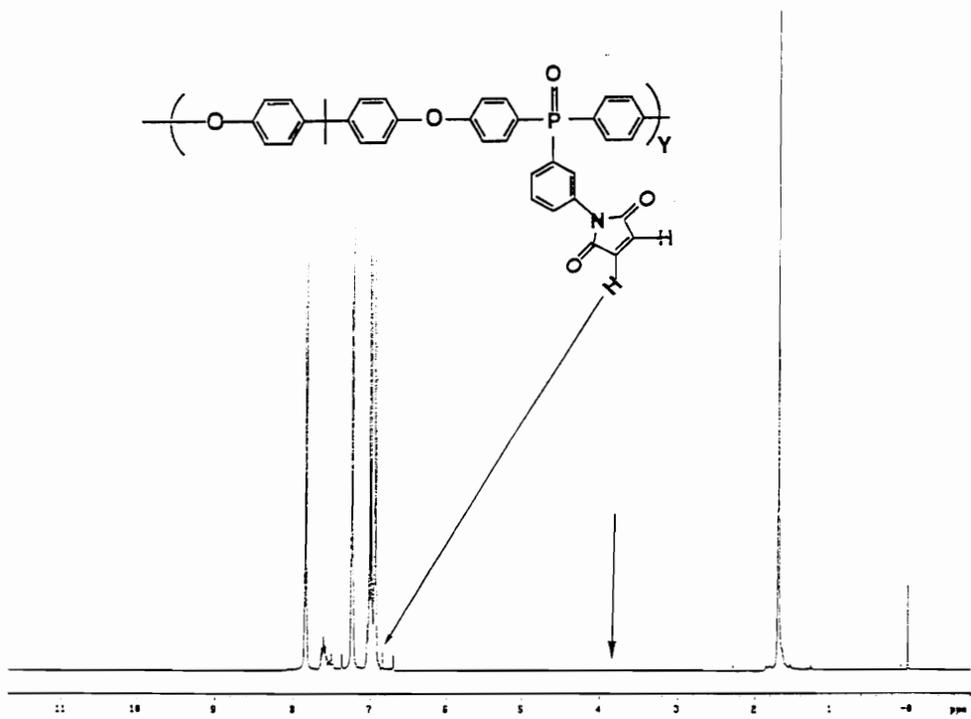


Figure 31 Proton NMR of 15% aminated PSF/PEPO copolymer (bottom) and 15% maleimide PSF/PEPO copolymer (top)

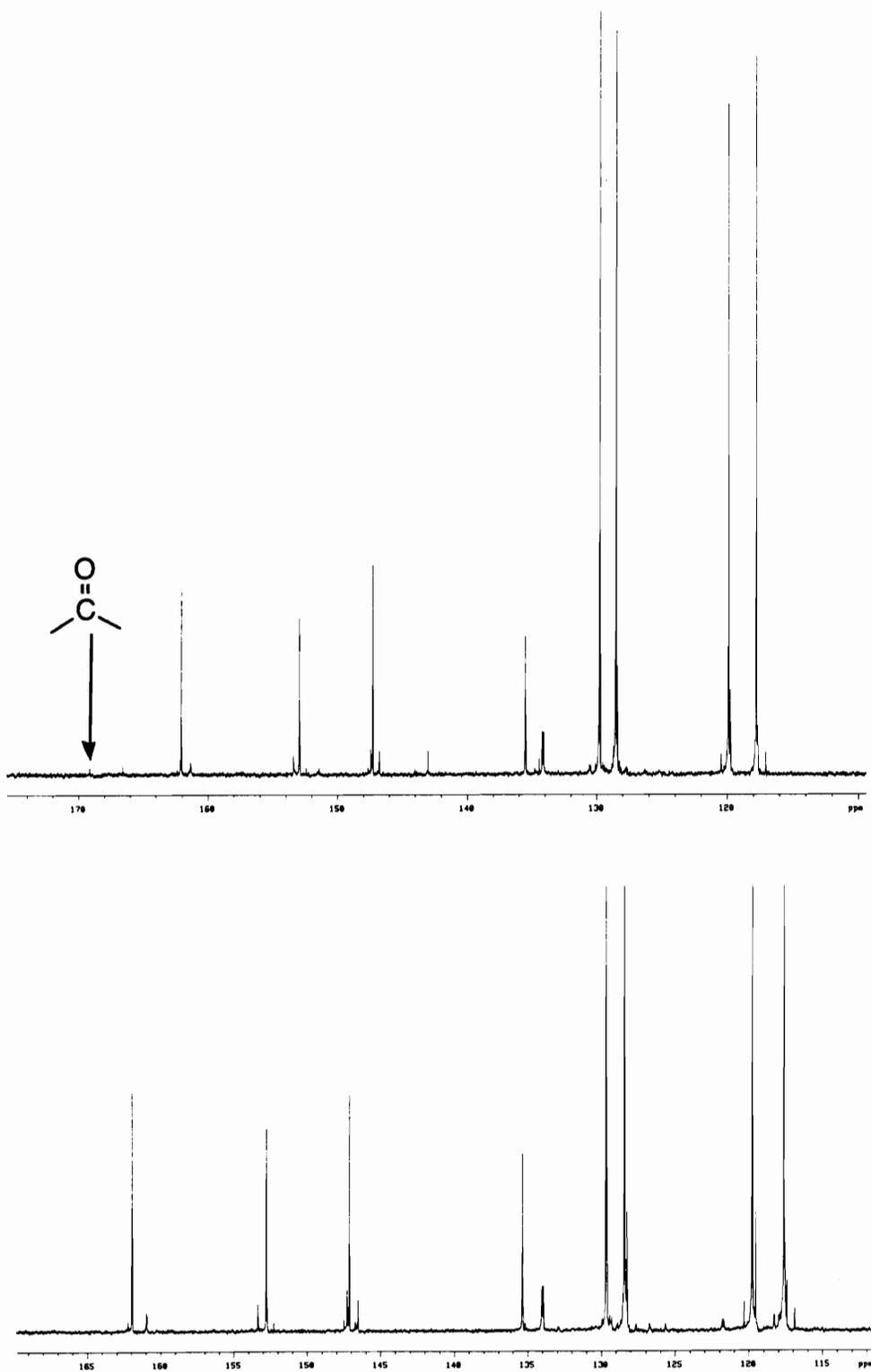


Figure 32 Carbon NMR of 15% aminated PSF/PEPO copolymer (bottom) and 15% maleimide PSF/PEPO copolymer (top)

copolymer and the 15% maleimide copolymer are shown in Figure 32. Upon conversion to the maleimide, the carbon of the maleimide carbonyl was observed as a small peak at 169 ppm.

4.8 Thermal Analysis of Cured Pendant Maleimides on PSF/PEPO Copolymers

The pendant maleimides were then thermally cured using a Pasadena Press at 250°C for 3 hours and then post cured at 280°C for an additional hour to afford three dimensional networks with increased T_g and solvent resistance. A differential scanning calorimetry (DSC) of a uncured 15% maleimide PSF/PEPO copolymer is shown in Figure 33. During the first scan, an exotherm from the curing of the maleimides was observed shortly after the T_g, the maximum exotherm was observed at ~230°C. During the second scan, a stable baseline was observed in the region where the exotherm was observed during the first scan. The T_g detected on the first scan was 182°C which increased to 209°C on the second heat. Characterization of the pendant maleimides system after they were thermally cured are shown in Table 17. The T_g values of the cured maleimides were higher than the T_gs of the aminated copolymers, this was due to the crosslinking of the maleimides. The T_gs of the cured maleimides were higher as the concentration of the maleimides along the backbone increased owing to the increase in the average crosslink density. The percent gelation from soxhlet extractions in chloroform was higher for the 15% maleimide copolymer than was for the 5% maleimide copolymer. As the concentration of the maleimides increased, more of the maleimides could undergo crosslinking reactions with other maleimides in the vicinity. For the 5% cured pendant

maleimide copolymer, the percent gelation of 89% was obtained as compared to 98% for the 15% maleimide copolymer, the lower value for the 5% may be due to the lower concentration of the maleimides, or perhaps to the possibility that not all of the maleimides actually reacted.

Additional data to support the crosslinking of the pendant maleimides were obtained from dynamic mechanical analysis (DMA). Shown in Figure 34 is a DMA of thin films analyzed on the extension mode of the control polysulfone and the cured 5% maleimide copolymer. For the control, as the material was subjected to temperatures near the T_g, the modulus began to decrease and continued to drop even more rapidly as the temperature increased until the sample broke shortly after the T_g. This was due to the lack of chemical bonds or crosslinked sites between the polymer chains. However, the DMA of the 5% pendant maleimide copolymer that was crosslinked showed a relatively constant modulus above the T_g, this was due to the covalent chemical bonds between the polymer chains.

Table 17 Characterization of cured pendant maleimides containing PSF/PEPO copolymers

Amino DFTPPO Charged (mole%)	DSC		DMA T _g (°C)	Gelation (%)
	T _g (Amino) (°C)	T _g (maleimide) (°C)		
0	-----	-----	192	-----
5	194	199	197	89
10	195	203	202	96
15	198	211	213	98

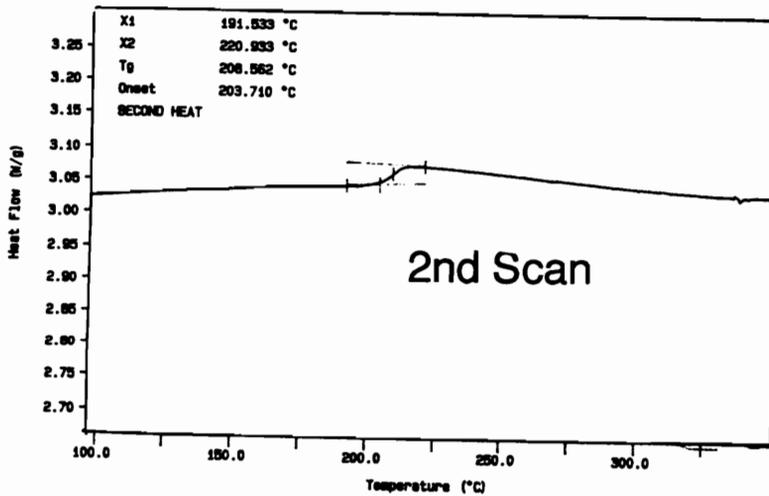
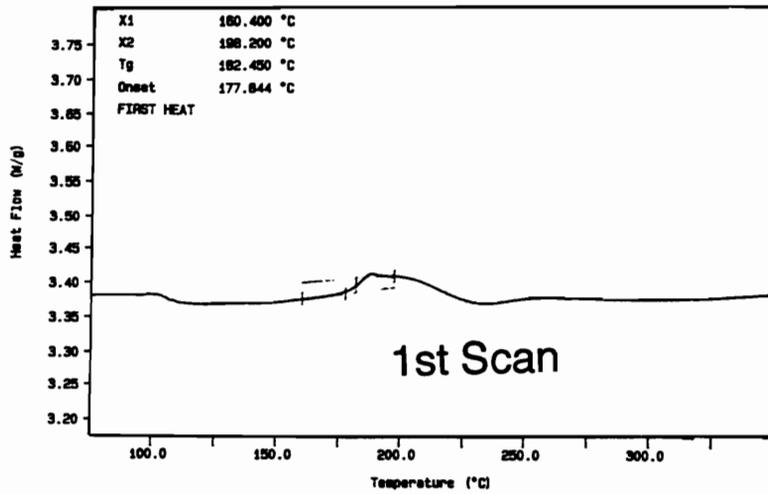


Figure 33 DSC first scan (top) and the second scan (bottom) of uncured 15% maleimide PSF/PEPO copolymer

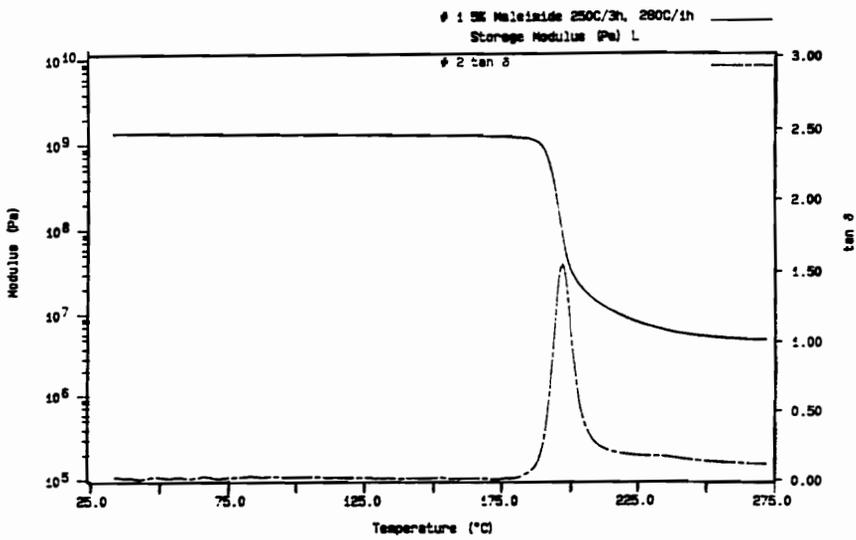
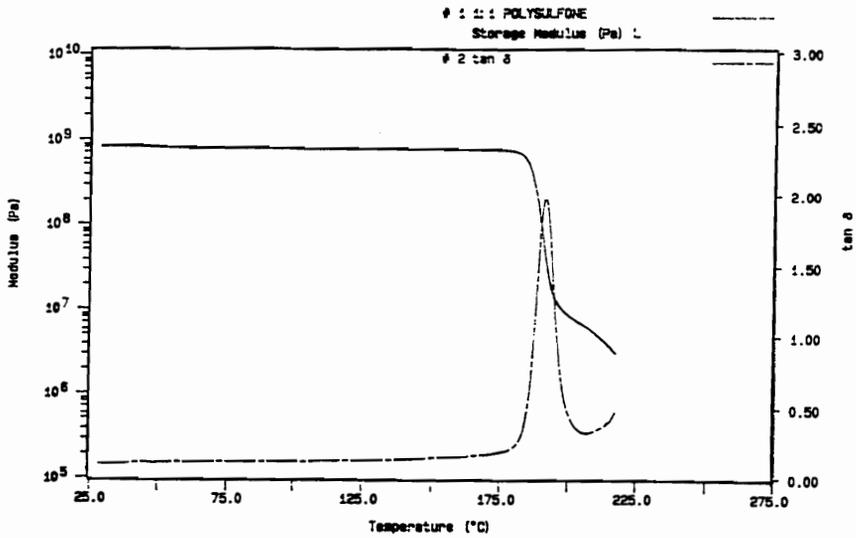


Figure 34 DMA of polysulfone control (top) and 5% cured maleimide PSF/PEPO copolymer

4.9 Conversion of Aminated Copolymers to Pendant Phenylethynylphenyl Imides (PEPI)

With maleimides, the curing of the maleimides occurs shortly after the T_g, so there is a relatively narrow processing window for the maleimides. Ethynyls or acetylenes represent another functional group which can undergo crosslinking reactions to afford networks. With phenylethynyls, the maximum exotherm for the curing occurs approximately 370°C (183). Due to a high cure temperature of phenylethynyls, incorporation of pendant phenylethynyls by the modification of aminated amorphous poly(arylene ethers) should result in a wide latitude of a processing window for these materials. Since the T_g of the common amorphous poly(arylene ethers) are between ~150-250°C, there should be approximately a 100°C processing window. The advantage with phenylethynyls on poly(arylene ethers) is the ability to mold and remold parts during the fabrication stage to obtain void free parts, then a subsequent thermal treatment for a brief period of time at a much higher temperature should afford materials with a higher T_g and a increased solvent resistance.

For this investigation, various mole percentages of amino DFTPPO were reacted with bis(4-fluorophenyl)phenylphosphine oxide (DFTPPO) and bisphenol-A. These were 5, 10, and 20 mole% of amino DFTPPO relative to the other monomers. A one to one stoichiometry of the activated dihalide monomers to the bisphenol-A was used. Shown in Table 18 are the characterizations of the aminated poly(arylene ether phosphine oxides) (PEPO) which were utilized in this investigation. The control was the homopolymer from the polymerization of bisphenol-A and DFTPPO. As verified by the high intrinsic viscosities which ranged from 0.81 dl/g for the 20% aminated PEPO to 1.01 dl/g for the 5% aminated PEPO, high molecular weight polymers were indeed synthesized.

Table 18 Characterization of aminated PEPOs for conversion to PEPI PEPOs

Amino DFTPPO Charged (mole%)	T _g (°C)	$[\eta]_{\text{CHCl}_3}^{25^\circ\text{C}}$ (dl/g)	<Mn>/ Amine (g/mole)
Control	201	1.09	-----
5	203	1.01	9,649
10	205	0.99	4,732
20	208	0.81	2,469

As discussed previously, the general trend of higher T_gs for the higher concentrations of the pendant amines were observed as well as the decrease in the average molecular weight per amine as the concentration of the amine increased.

The conversion of the aminated PEPOs to the phenylethynylphenyl imides (PEPI) was conducted by the reaction of the amines with 4-phenylethynylphthalic anhydride to form the amic acid. Cyclodehydrations of the amic acids to the phenylimides were conducted at 185°C in NMP using o-dichlorobenzene as the azeotrope. In contrast to the conversion of pendant amines to maleimides, the conversion of aminated PEPOs to PEPIs was conducted at a much higher temperature due to a high curing temperature of phenylethynyls. All of the PEPI PEPOs were readily soluble in chloroform after the conversion from the amine, this was indicative that no crosslinking occurred during the chemical modification.

The IR of the aminated PEPO and the PEPI for the highest amine content (20%) is shown in Figure 35. Due to the low concentration of the amine, the two peaks for the primary aromatic amine was not observed. The two spectra were nearly identical, except for the presence of two peaks corresponding to the imide carbonyls at 1729 and 1782 cm^{-1} for the PEPI PEPO. The proton NMR of 4-ethynylphthalic anhydride, 20% aminated PEPO and 20% PEPI PEPO is given in Figure 36. The amine protons were observed only as a very small peak at 3.9 ppm which was difficult to detect due to a low concentration of the amine. Upon conversion of the amine to the PEPI, the presence of new peaks between 7.8 and 8.1 ppm were observed, these peaks were due to the three aromatic protons on the phthalimide. Additional data to verify the incorporation of PEPI onto the polymer backbone was observed from the carbon NMR. The carbon NMR of 4-ethynylphthalic anhydride, 20% aminated PEPO and 20% PEPI PEPO is shown in Figure 37. The main peaks of interest was the two ethynyl carbons at 87.8 and 94.9 ppm, and the carbon of the carbonyl of the anhydride at 163 ppm. For the 20% aminated PEPO, the two ethynyl carbon peaks were not observed, however, for the 20% PEPI PEPO, the ethynyl carbon peaks were observed at 88 and 95 ppm as well as the carbonyl of the imide at 162 ppm.

4.10 Thermal Analysis of Cured Pendant Phenylethynylphenyl Imides on PEPOs

The PEPI PEPO copolymers were then thermally cured at 350°C for 30 minutes to afford networks with higher T_gs and increased solvent resistance. The results for the cured PEPI PEPO polymers is shown in Table 19.

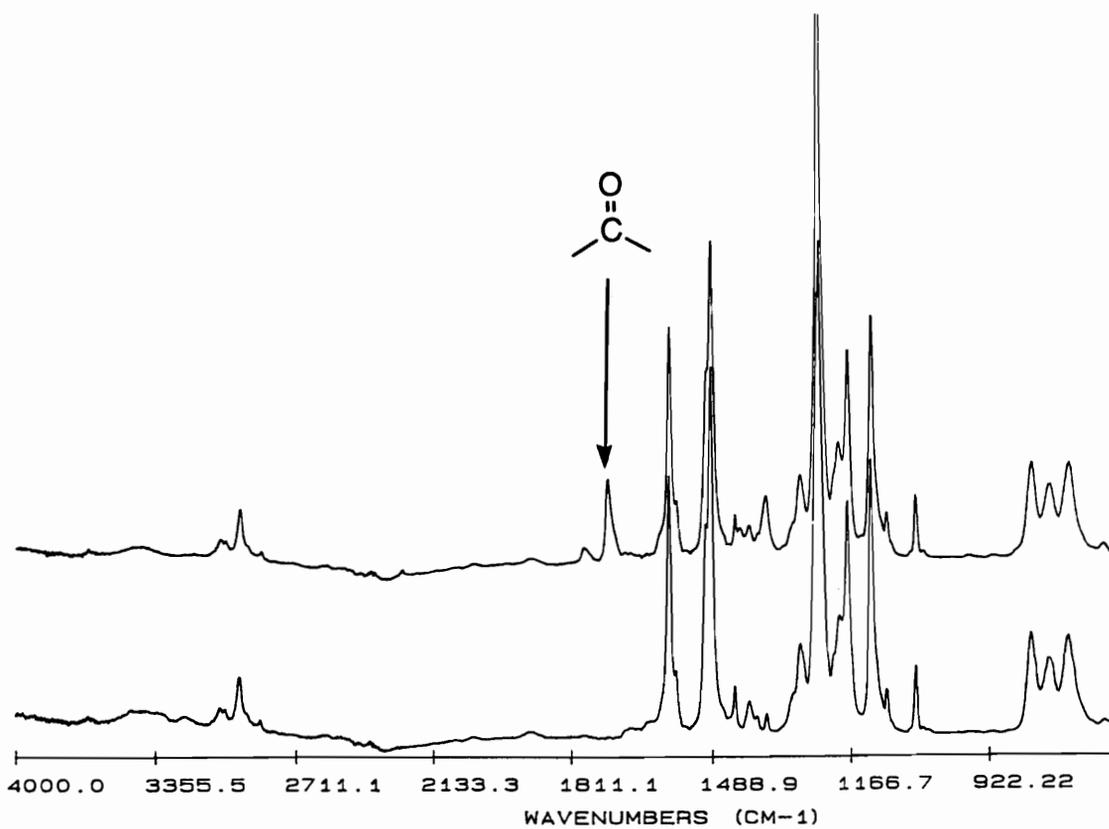


Figure 35 FT-IR of 20% aminated PEPO (bottom) and 20% PEPI PEPO (top)

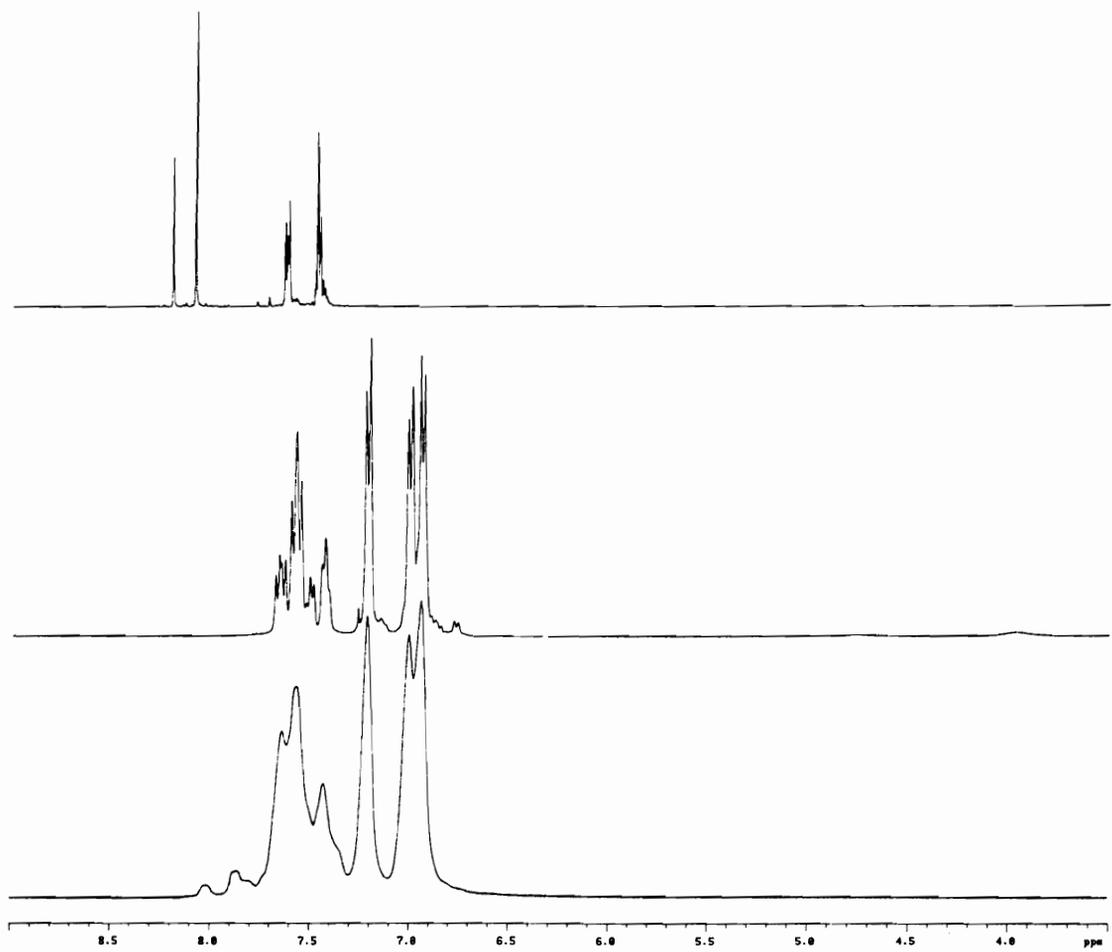


Figure 36 Proton NMR of 20% aminated PEPO (bottom), 20% PEPI PEPO (middle) and 4-phenylethynylphthalic anhydride (top)

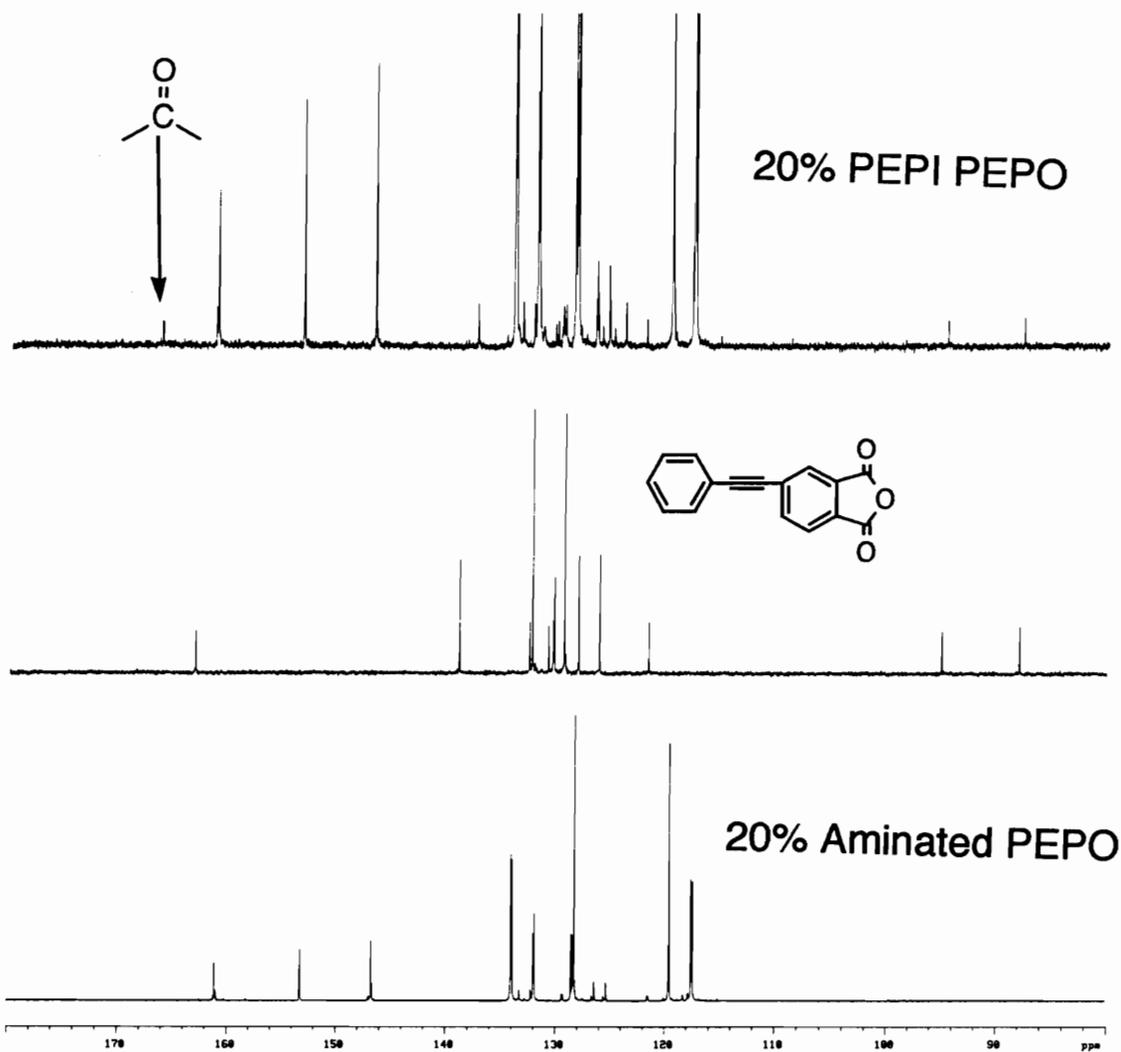


Figure 37 Carbon NMR of 20% aminated PEPO (bottom), 20% PEPI PEPO (top) and 4-phenylethynylphthalic anhydride (middle)

Table 19 Comparison of Tg values for pendant amine and cured phenylethynylphenyl imides on poly(arylene ether phosphine oxides)

Amino DFTPPO Charged (mole%)	Tg (°C)	PEPI PEPO (mole %)	Tg Uncured (°C)	Tg Cured (°C)	Gel Fraction (%)
Control	201	0	-----	-----	0
5	203	5	201	201	93
10	205	10	201	207	98
20	208	20	201	218	99

The Tg decreased in all instances upon conversion of the amines to the phenylethynyls. The decrease in the Tg may have been attributed to the loss of hydrogen bonding as the amines were converted to the phenylethynyls. Comparison of the Tg of the uncured and cured phenylethynyls showed higher Tgs for the cured phenylethynyls, an exception was the 5% PEPI PEPO in which no change in the Tg was observed. This was probably due to the low concentration of the amine which resulted in only a small extent of hydrogen bonding for the aminated PEPO prior to the conversion to the phenylethynyls. The gel fraction that remained after 3 days of soxhlet extraction with chloroform yielded values which ranged from 93 percent for the lowest phenylethynyl concentration to 99 percent for the highest concentration. The lower number for the lowest concentration of phenylethynyl was possibly due the incomplete

reaction of all the phenylethynyls or the sequence distribution of comonomer.

The control which did not have any crosslinked sites did not have a gel fraction, as expected

A DMA of a thin film analyzed using the extension mode of the control PEPO and the cured 20% PEPI PEPO is shown in Figure 38. There was a greater stability for the crosslinked material in the region after the T_g (maximum in $\tan\delta$) which was probably due to the presence of crosslinked sites between the polymer chains. For the thermoplastic control, there was a rapid decrease in the modulus until the sample broke. The TGAs in air of the control, 5% aminated PEPO, and cured 5% PEPI PEPO are provided in Figure 39. Due to the presence of amines, the initial decomposition of 5% aminated PEPO occurred slightly at a lower temperature than the control and the cured 5% PEPI PEPO. Of the three samples, the cured sample displayed a better thermo-oxidative stability, which may be due to the presence of aromatic structures possibly generated from the cure of phenylethynyls. The char yield at 880°C was highest for the crosslinked sample followed by the control and the aminated PEPO.

4.11 Modification of Aminated PSF/PEPO Copolymers to Pendant Phthalimides

Modifications of the aminated PSF/PEPO copolymers to phthalimides were also conducted in an attempt to obtain materials with higher T_g values and a better thermo-oxidative behavior. The purpose of this investigation was based on the assumption that the presence of bulky pendant phthalimides should result in an increase in the T_g . Since the concentration of the amine along the polymer backbone can be controlled, the extent of the increase in the T_g of pendant

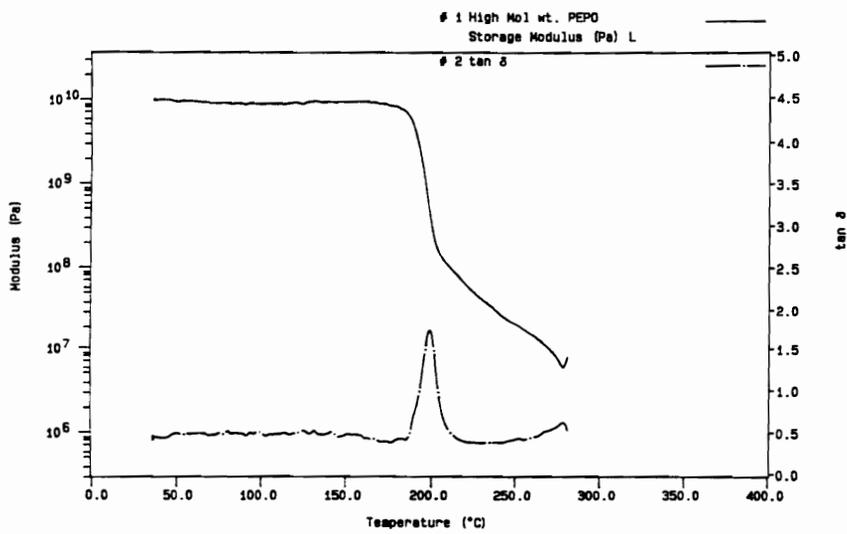
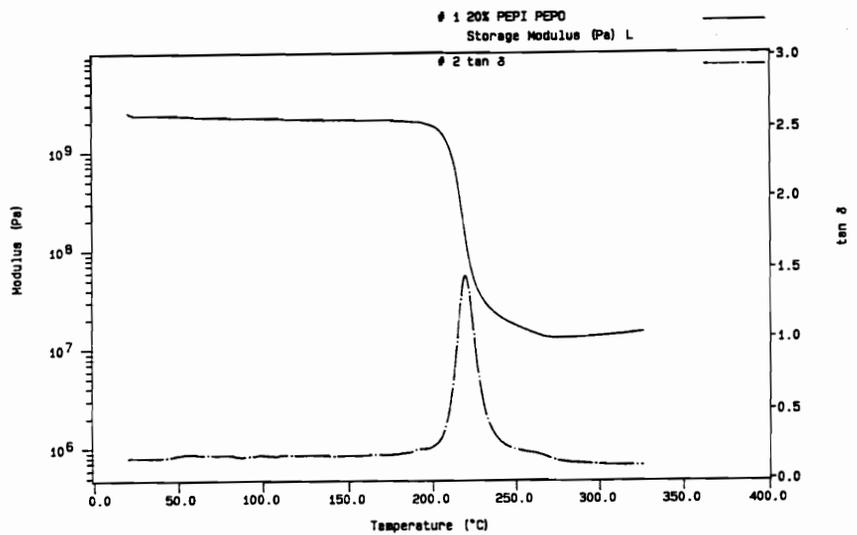


Figure 38 DMA of PEPO control (bottom) and cured 20% PEPI PEPO (top)

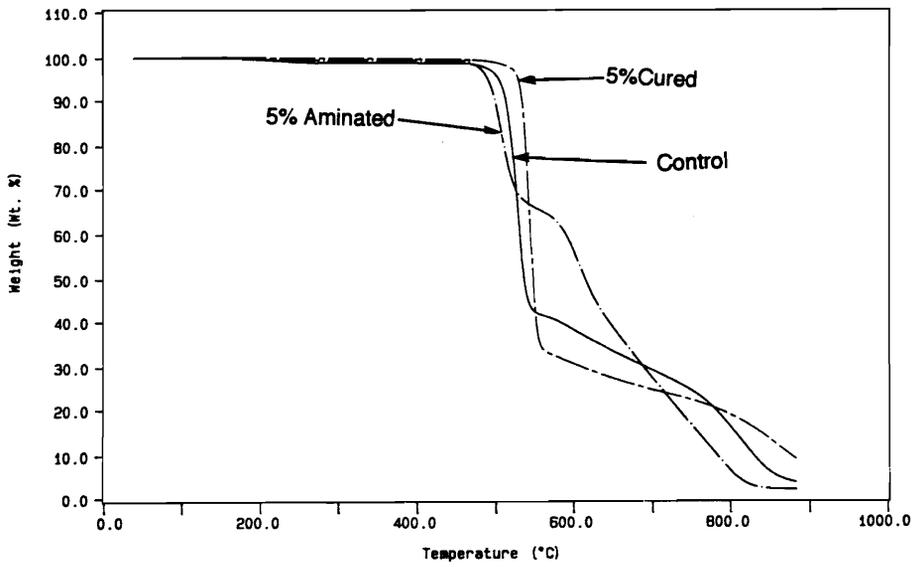


Figure 39 TGA weight loss behavior of PEPO control, 5% aminated PEPO and 5% cured PEPI PEPO

phthalimides can be varied precisely. For this investigation, various mole percentages of amino DFTPPO was polymerized with DCDPS and bisphenol-A. In all of the polymerizations, a one to one stoichiometry of the activated dihalide monomers to the bisphenol-A was used. The characterization of the aminated copolymers which were used for this investigation is shown in Table 20.

Table 20 Characterization of aminated PSF/PEPO copolymers utilized for modification to pendant phthalimides

Amount of Amino DFTPPO Charged (mole%)	$[\eta]_{\text{CHCl}_3}^{25^\circ\text{C}}$ (dl/g)	Titration (g/mole)
Control	0.89	-----
5	1.00	9,324
10	0.61	4,965
20	0.45	2,525
30	0.41	1,566

For the reasons discussed previously, there is an apparent decrease in the molecular weight as more amino DFTPPO was incorporated. The conversion of the amines to phthalimides was conducted by the reaction of the amines with

phthalic anhydride to form the amic acid. Cyclodehydration of the amic acid to the corresponding phthalimide was conducted at 185°C in NMP using o-dichlorobenzene as the azeotrope.

An FT-IR of the 30% aminated PSF/PEPO copolymer and the 30% phthalimide copolymer is shown in Figure 40. The two spectra were very similar except for the appearance of the amine absorbance at 3380 and 3466 cm^{-1} for the aminated copolymer and the absorbance of the imide carbonyl at 1725 cm^{-1} for the corresponding phthalimide. A proton NMR of 30% aminated copolymer and the 30% phthalimide copolymer is provided in Figure 41. Upon conversion to the phthalimide, a small broad peak at 3.9 ppm from the amine disappeared and the appearance of new peaks from the aromatic protons of the phthalimide was observed at 7.8 and 7.98 ppm. Better evidence for the conversion to pendant phthalimides was observed from the carbon NMR. A carbon NMR of phthalic anhydride and the 30% phthalimide copolymer is shown in Figure 41, note that the imide carbonyl was observed at 167 ppm for the phthalimide derivative which was not present in the original aminated copolymer.

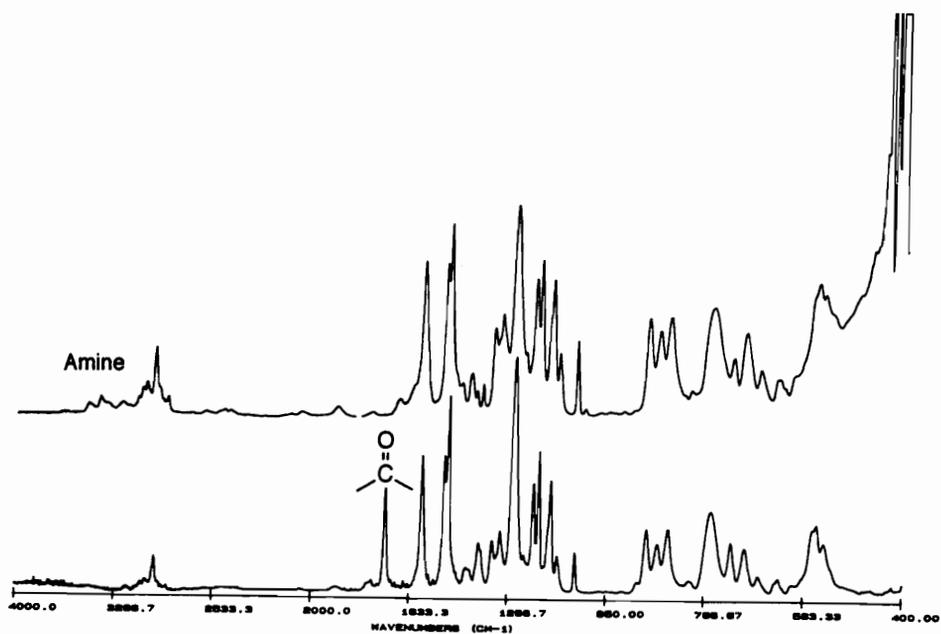


Figure 40 FT-IR of 30% aminated PSF/PEPO copolymer (top) and 30% phthalimide derivative PSF/PEPO copolymer (bottom)

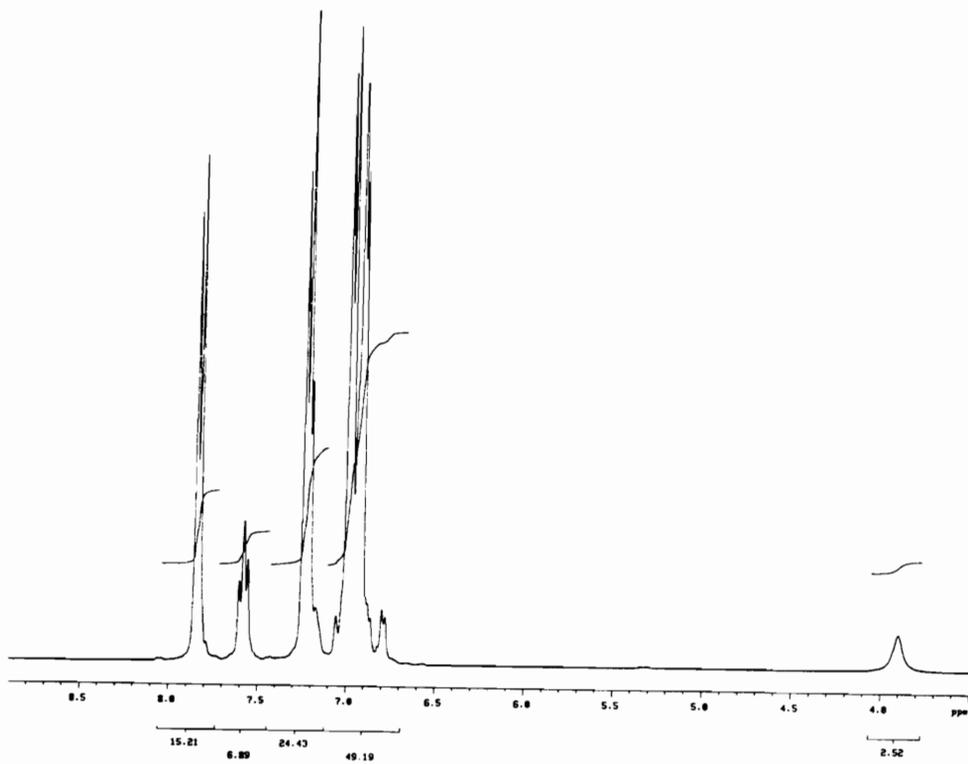
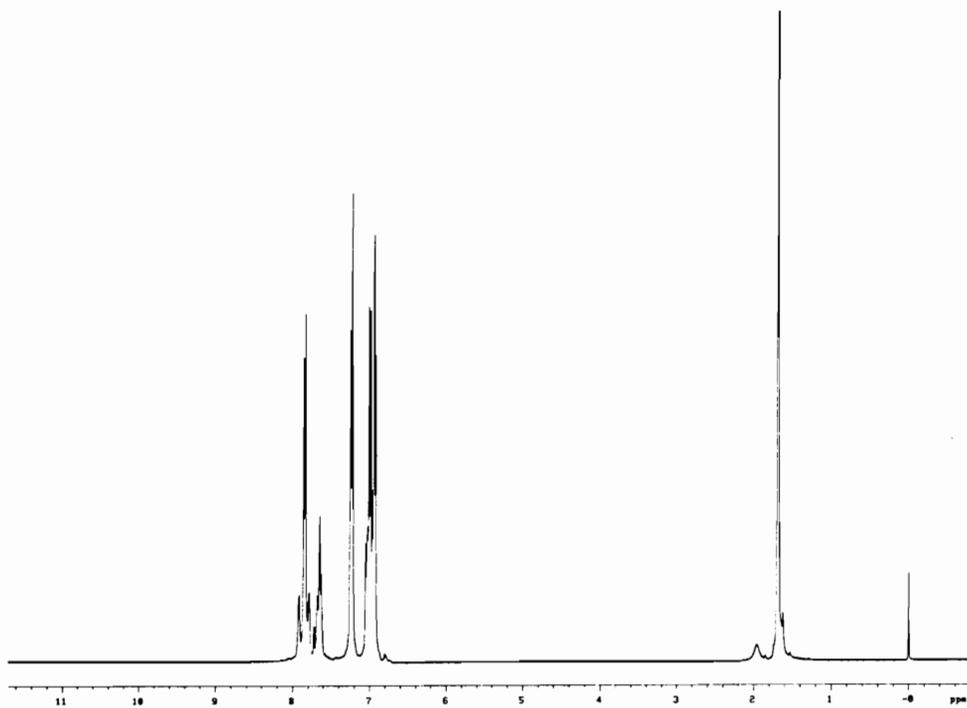


Figure 41 Proton NMR of 30% aminated PSF/PEPO copolymer (bottom) and 30% phthalimide copolymer (top)

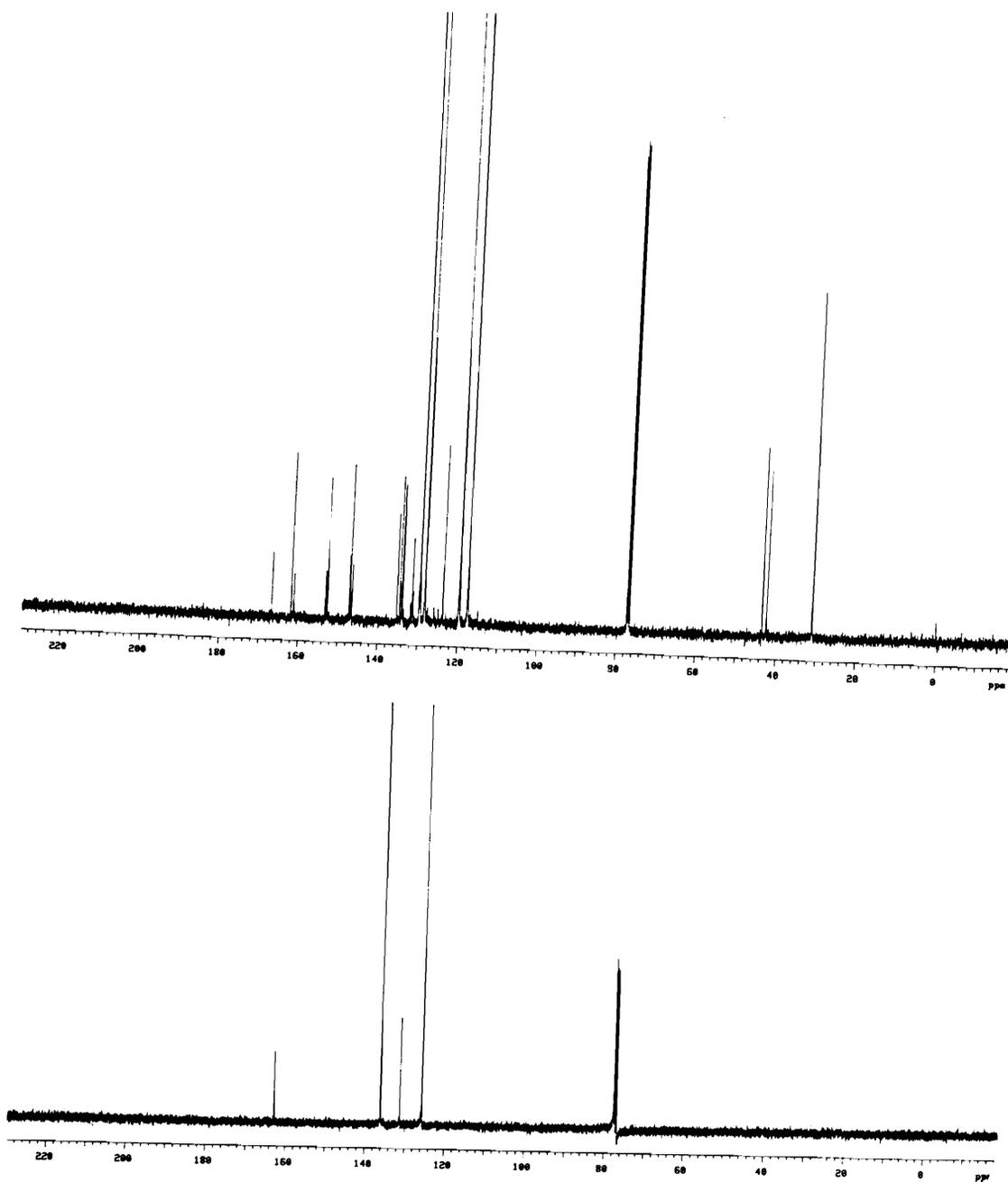


Figure 42 Carbon NMR of model phthalic anhydride (bottom) and 30% phthalimide PSF/PEPO copolymer (top)

4.12 Thermal Analysis of Pendant Phthalimide Copolymers

The comparison of the Tgs of the aminated and phthalimide PSF/PEPO copolymers is shown in Table 21.

Table 21 Comparison of Tg values for aminated and phthalimide derivatized PSF/PEPO copolymers

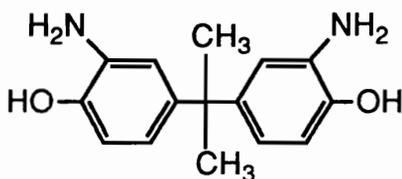
Amino DFTPPO Charged. (mole%)	Amine Tg (°C)	Phthalimide Tg (°C)
5	190	190
10	193	190
20	200	194
30	202	196

A general trend of the increase in the Tg as the concentration of the amine increased was observed, however, upon conversion to phthalimides, the phthalimides showed a lower Tg than the corresponding amines. The decrease in the Tg of pendant phthalimides is suggested to be due to the loss of intermolecular hydrogen bonding.

4.13 Investigation of Bis(ortho aminophenol) Monomers for the Synthesis of Pendant Amines on Poly(Arylene Ethers)

4.13.1 Synthesis and Characterization of 2,2'-Bis(3-Amino-4-Hydroxy Phenyl)Propane (o-Aminobisphenol-A)

An alternative way to obtain pendant amines on the back bone of poly(arylene ethers) was also investigated using the following ortho amino monomer as a possible candidate.



2,2'-Bis(3-amino-4-hydroxyphenyl)propane (o-Aminobisphenol-A)

Analogous to meta aminophenol, the assumption was that the derived phenolate would be much more nucleophilic than the aromatic amine and would, thereby, selectively react with activated dihalide monomers. The monomer bis 2,2'-(3-amino-4-hydroxy-phenyl) propane (o-aminobisphenol-A) was synthesized by nitration and reduction of bisphenol-A. The nitration of bisphenol-A to the o-nitrobisphenol-A was conducted using acetic acid as the solvent and the nitrating mixture was nitric acid in acetic acid. Acetic acid was chosen as the solvent due the competing reactions of nitration and sulfonation with sulfuric acid. In addition to the dinitro substituted product, a small amount of tri and tetra nitro substituted products were also obtained. This was due to the presence of the phenol group which activated the aromatic ring for further nitration. Despite the mixture of various nitro substituted products, crystallizations using acetic acid afforded exclusively the dinitro substituted

bisphenol-A. The IR of o-nitrobisphenol-A from KBr pellet is shown in Figure 43 and assignments of major functional groups are shown in Table 22.

Table 22 Identification of the major functional groups of 2,2'-bis(4-hydroxy-3-nitrophenyl) propane from infrared spectrum

Functional Group	Wave Number (cm ⁻¹)
Aromatic OH	3263
Isopropylidene	2973 1419 1377
Aromatic NO ₂	1539
Aromatic Double Bonds	1630 1483

Although IR qualitatively indicated which functional groups were present, the proton NMR provided a better measure of the purity of the product. Figure 43 shows the proton NMR of o-nitrobisphenol-A in deuterated chloroform. The phenolic protons were observed at 10.58 ppm as a small singlet as well as the isopropylidene protons at 1.8 ppm. In the aromatic region, the proton ortho to the nitro was deshielded the most and appeared as a singlet at 8.04 ppm; the proton ortho to the phenol was a doublet at 7.33 ppm, and the proton meta to the phenol was a doublet at 7.07 ppm. The result from the proton NMR was further supported by the carbon NMR which is shown in Figure 44.

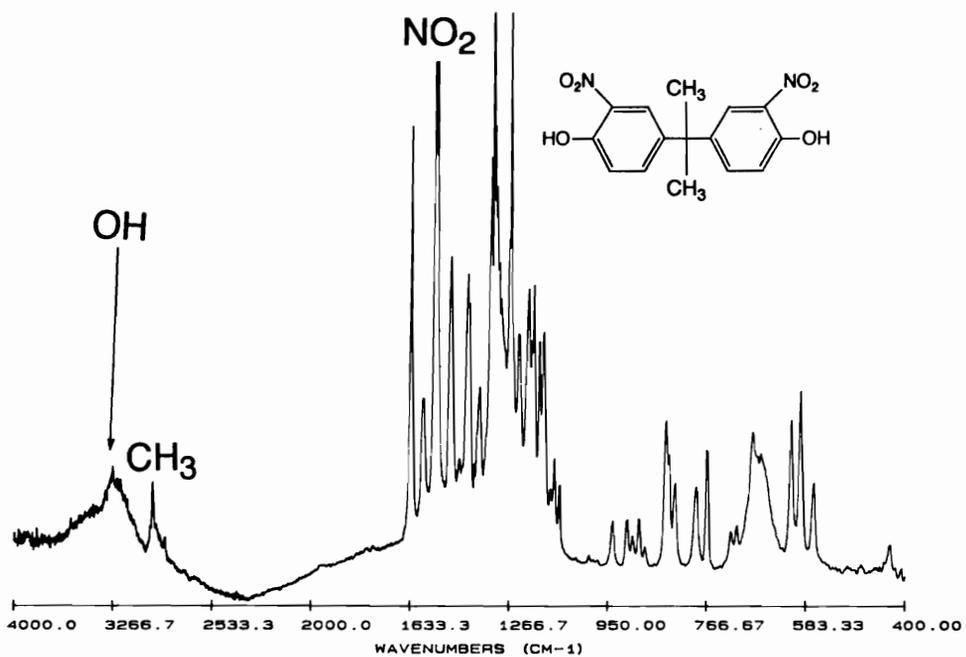


Figure 43 FT-IR of 2,2'-bis(4-hydroxy-3-nitrophenyl)propane from KBr pellet

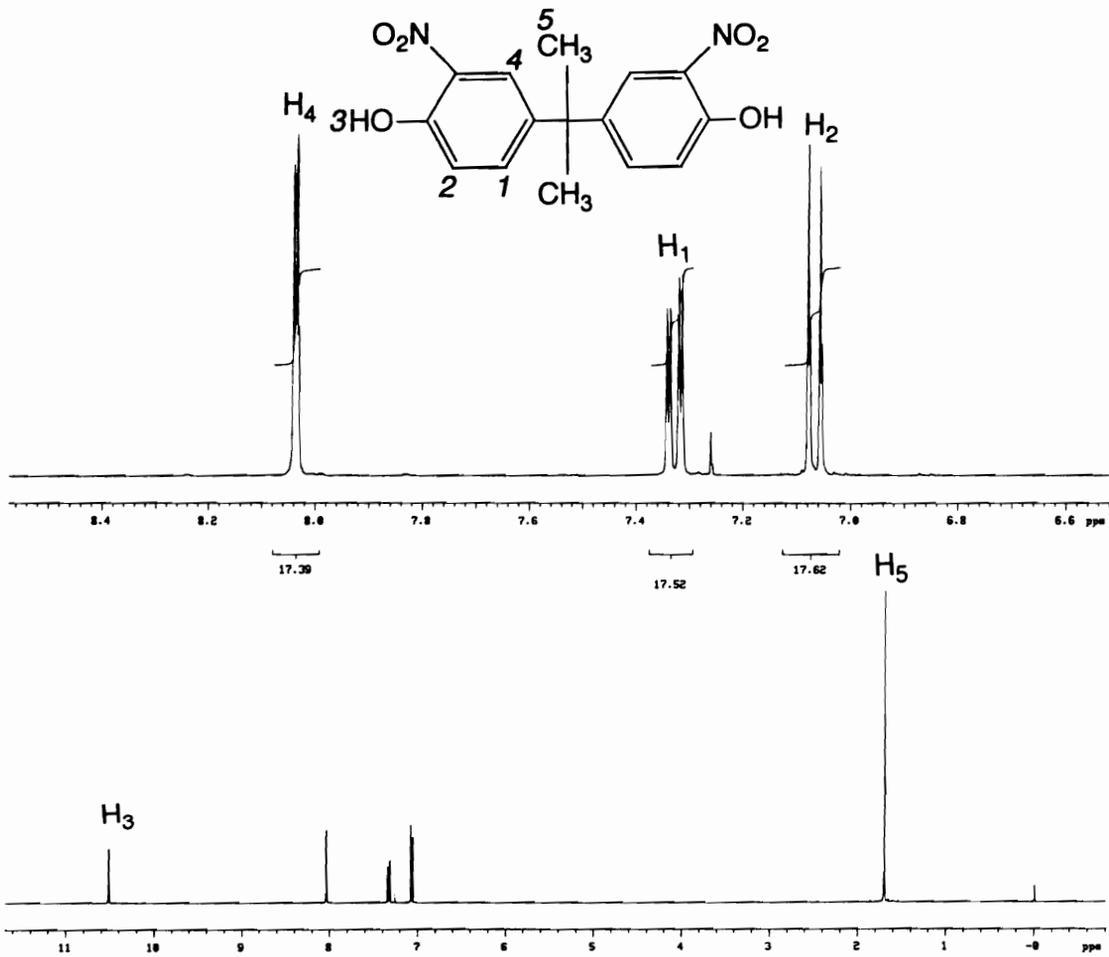


Figure 44 Proton NMR of 2,2'-bis(4-hydroxy-3-nitrophenyl)propane in deuterated chloroform

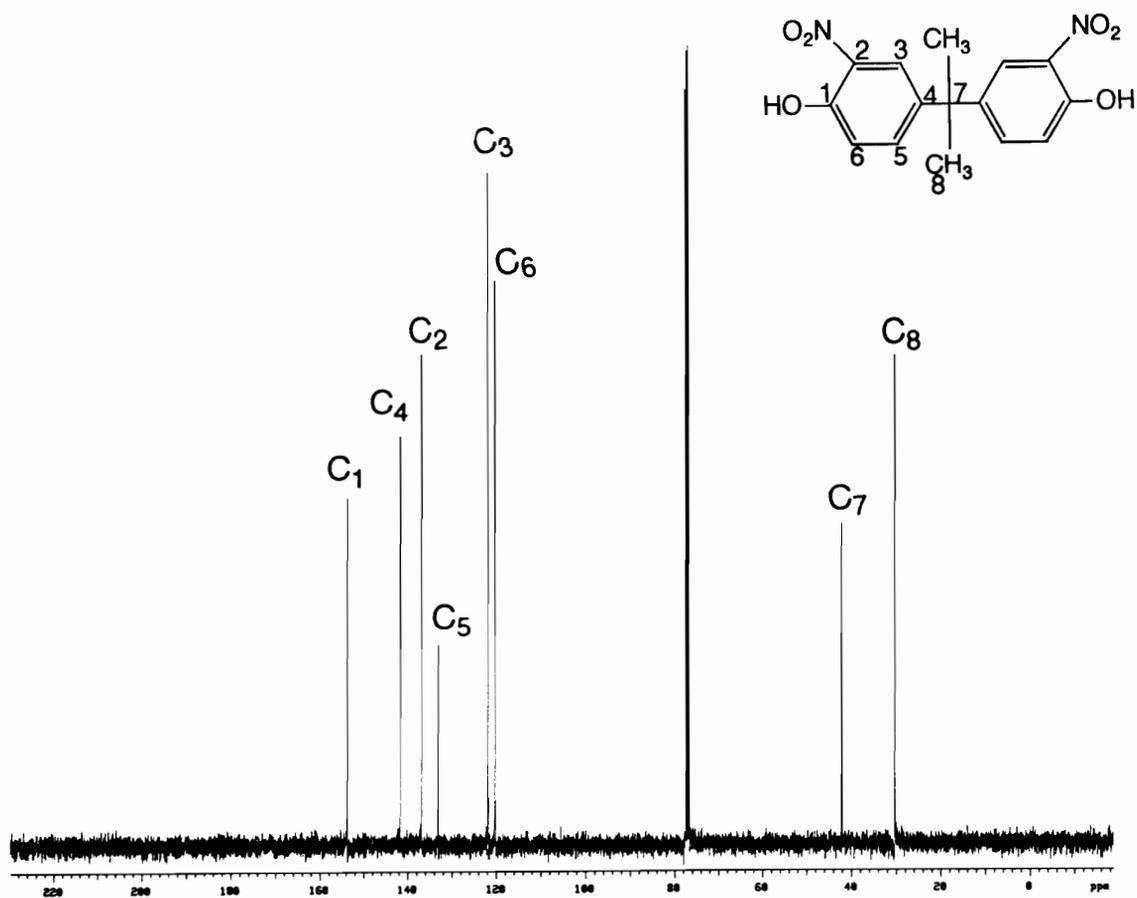


Figure 45 Carbon NMR of 2,2'-bis(4-hydroxy-3-nitrophenyl)propane in deuterated chloroform

The nitro groups were then reduced to the amine with palladium and hydrazine in ethanol. The resulting o-aminobisphenol-A was very difficult to purify and the best method to obtain a pure compound was to ensure a degree of high purity for the o-nitrobisphenol-A prior to the reduction. The conversion of the nitro to the amine was a quantitative process, but the obtained yield after work up was ~ 55%. The loss was due to the precipitation of the product during filtration of the palladium catalyst. Even though celite was washed with more hot ethanol, once o-aminobisphenol-A precipitated from solution it was very difficult to solubilize again. Even though reduction could also be conducted with hydrogen gas, the appearance of the reduced product using hydrazine was much better. The o-aminobisphenol-A was only very sparingly soluble in alcohols and it was insoluble in chloroform; Only dipolar aprotic solvents and acetone were good solvents, solubility in strong acids and bases were not determined. The IR of o-aminobisphenol-A from a KBr pellet is shown in Figure 46. Upon conversion of the nitro to the amine, two prominent peaks appeared at 3409 and 3325 cm^{-1} which were due to the presence of the primary aromatic amine. Even though there still appeared to be a strong absorbance near the region of the nitro group, the proton NMR conclusively confirmed the quantitative conversion of the nitro to the amine. The proton NMR of o-aminobisphenol-A in deuterated dimethylsulfoxide is shown in Figure 47. In contrast to the aromatic protons of o-nitrobisphenol-A which appeared between 7 and 8 ppm due to the influence of the nitro electron withdrawing groups, the aromatic protons of o-amino bisphenol-A shifted slightly upfield and appeared between 6.0 and 6.6 ppm. Also, the appearance of a broad singlet at 4.38 ppm

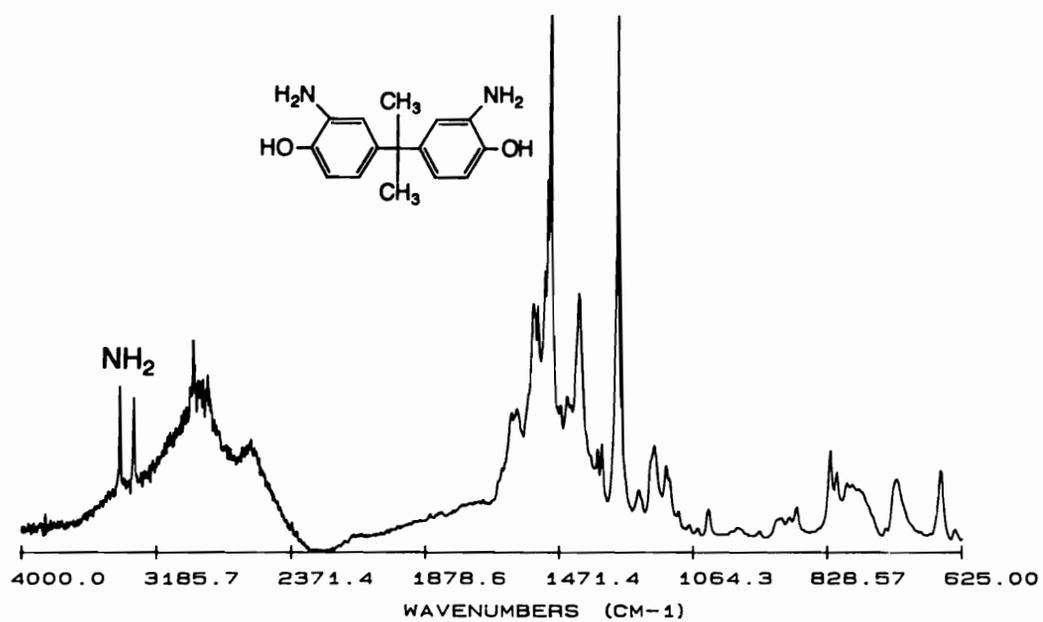


Figure 46 FT-IR of 2,2'-bis(3-amino-4-hydroxyphenyl)propane from KBr pellet

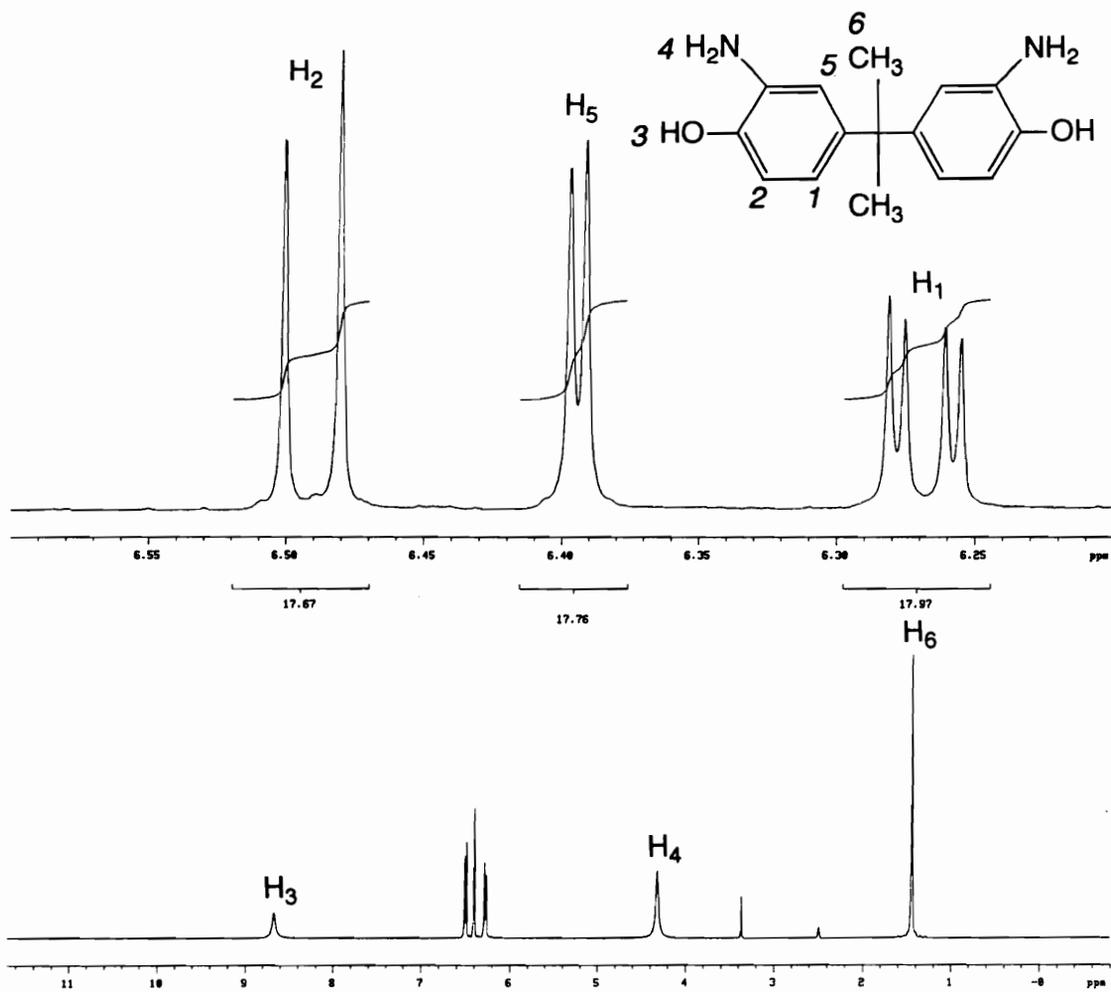


Figure 47 Proton NMR of 2,2'-bis(3-amino-4-hydroxyphenyl)propane in deuterated dimethylsulfoxide

was observed from the amine protons. The integration of the peaks confirmed the structure to be indeed the o-aminobisphenol-A.

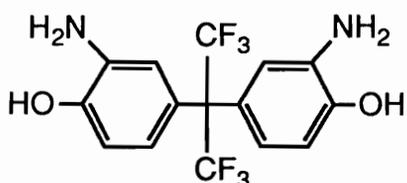
4.13.2 Copolymerizations of o-Aminophenol Monomers with DCDPS and Bisphenol-A

The copolymerizations were conducted using NMP and toluene in a 2 to 1 ratio and a 15% molar excess of potassium carbonate relative to the bisphenol was employed. An initial reaction temperature of 145°C was used for approximately 5 hours to azeotrope off the water and then polymerization was performed at 165°C for an additional sixteen hours. The concentration of o-aminobisphenol-A was varied from 5 to 15 mole percent and in all of the polymerizations, the overall stoichiometry of the activated dihalide monomer to the aromatic bisphenols was one to one. The results from the copolymerizations are shown in Table 23.

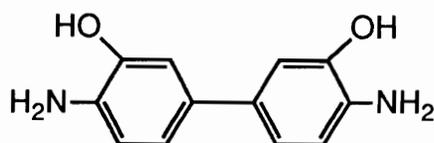
Table 23 Various charged mole percentage of o-aminobisphenol-A reacted with DCDPS and bisphenol-A

Charged Amount of Bis o-Aminobisphenol-A (mole%)	$[\eta]_{\text{CHCl}_3}^{25^\circ\text{C}}$ (dl/g)
Control	0.90
5	Gel
10	Gel
15	Gel

The control was the reaction of bisphenol-A and DCDPS. As can be seen from the table, attempted copolymerizations of o-Aminobisphenol-A with DCDPS and bisphenol-A resulted in the formation of gels, even for as low as 5 mole percent of o-aminobisphenol-A. With this comonomer, a slightly electron donating isopropylidene group is the linking group between two aromatic rings. To determine the effect of other linking groups, two other comonomers were also investigated. These aromatic bis(o-aminobisphenols) are shown below



2,2'-Bis(3-amino-4-dihydroxyphenyl)
hexafluoropropane

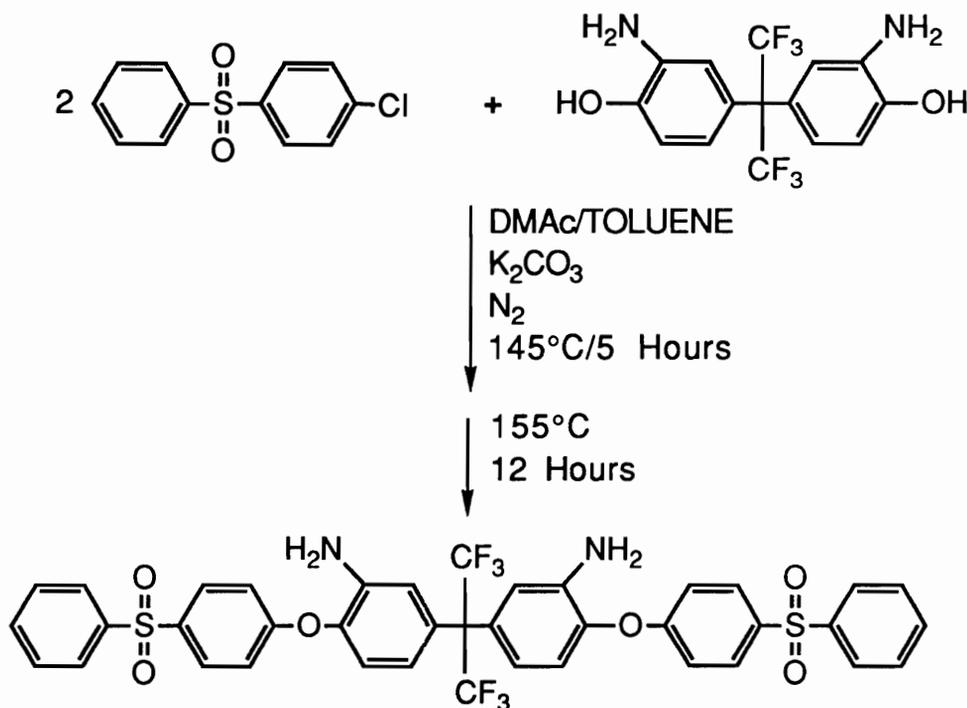


Dihydroxybenzidine

The 2,2'-bis(3-amino-4-dihydroxyphenyl)propane contained a hexafluoro isopropylidene as the linking group which is slightly electron withdrawing and dihydroxybenzidine which is directly bonded. Copolymerization of these monomers with DCDPS and bisphenol-A in the same proportions as o-aminobisphenol-A also resulted in the formation of gels. Based on these experimental results, one may conclude that the amine as well as the phenolate reacted with the activated dihalide!

4.13.3 Model Reaction of 4-Chlorophenyl Phenylsulfone and 2,2'-Bis(3-Amino-4-Hydroxyphenyl)Hexafluoropropane

To further confirm the reaction of the ortho amine, a following model study was conducted as shown in Scheme 29.



Scheme 29 A model reaction of 4-chlorophenyl phenylsulfone and 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane showing the anticipated structure formed if only the phenolate reacted

Two moles of 2-chlorophenyl phenylsulfone were reacted with one mole of bis 2,2'-bis(3-amino-4-hydroxy phenyl)hexafluoropropane. The reaction conditions were similar to the synthesis of high molecular weight copolymers as discussed earlier except that DMAc was used as the dipolar aprotic solvent instead of NMP and the reaction temperature was 155°C instead of 165°C. If only the phenolate reacted with the activated halide, then the only isolated product

would be the disubstituted product. However, if the amine also reacted, then other products would be obtained in addition to the disubstituted product. The reaction mixture was worked up by filtering off the inorganic salts, followed by neutralization with acetic acid and removal of DMAc at a reduced pressure. The product was then dried and analyzed by mass spectrometry (MS). The result from MS indicated that there were a distribution of products which resulted from the reaction of both the phenolate and the amine. The mass spectrum of the product from the model reaction is shown in Figure 48 and the identification of some of the major peaks along with their corresponding chemical structures are shown in Table 24. In the mass spectrum, the highest molecular mass peak was 1271, however, the mass of the tetra substituted product was 1232. The difference between these two molecular masses was 39 and this corresponded to the atomic weight of potassium. Therefore, the molecular mass of 1271 was interpreted as being due to a complex between the tetra substituted product and potassium. Even though the reaction mixture was filtered to remove excess potassium carbonate and the solution was acidified, apparently a small amount of it still remained in the DMAc solution. **From the relative intensities of the peaks, it appeared that the major component of the mixture was the disubstituted product from the reaction of both phenolates.** The tetra substituted product from the reaction of both amines and phenolates appeared to be only a small fraction of the total product but of course only some f=4 character might produce a gel, in a macromolecule. The proton NMR of the product from the model reaction along with the spectrum of each of the two reactants in deuterated dimethylsulfoxide are shown in Figure 49. The peaks for the aromatic protons and the amines were shifted which indicated

reaction(s) by the two reactants. Also, the amine peak in the product was a triplet and not a singlet as in 6F o-aminobisphenol-A. When the proton NMR was taken at higher temperatures, the amine peaks as well as the peaks between 8 and 10 ppm broadened. This may be due to a slow rate of proton exchange which consequently increased as the temperature increased. The broadening of these peaks as a function of temperature are shown in Figure 50. The presence of new peaks between 8 and 10 ppm for the crude product may be the protons from the phenol and the secondary amine. The carbon NMR of the product from the model reaction was very complex due to the presence of more than one product, and this is shown in Figure 51. Attempts to separate the mixture into their individual components by chromatography were very difficult. Only one of the components could be separated, the separation of the remaining components could not be accomplished due to their similar elution behavior, even in different mixtures of solvents. The proton NMR of the isolated component in deuterated dimethylsulfoxide is shown in Figure 52. Integration of the peaks indicated that it was the product corresponding to reaction of both the phenolates. This was further confirmed by carbon NMR and the IR which are shown in Figure 52 and Figure 53. In the IR, the presence of two sharp peaks at 3300 and 3400 cm^{-1} was observed which was due to the primary aromatic amine. The proton NMR of the fraction which contained the rest of the products remained complex, however, infrared spectrum of that fraction is also shown in Figure 53. The presence of a singlet near 3400 cm^{-1} indicative of a secondary aromatic amine was observed.

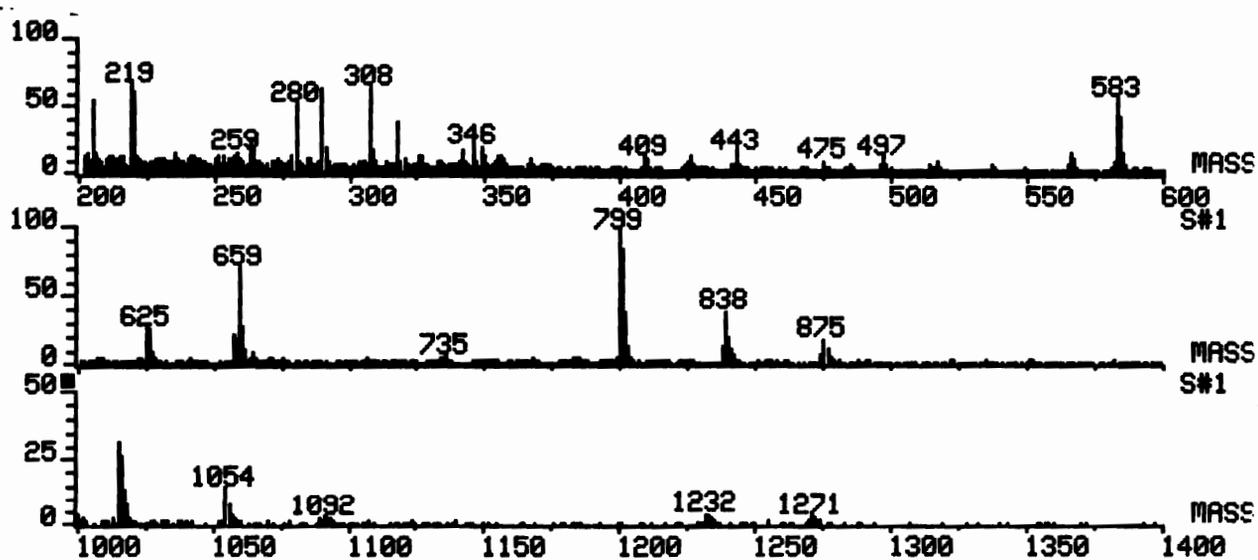
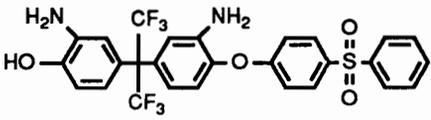
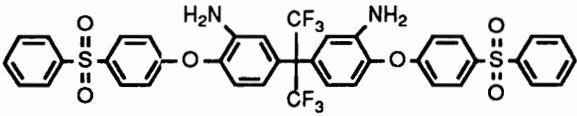
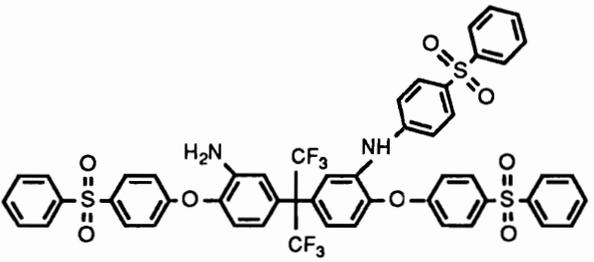
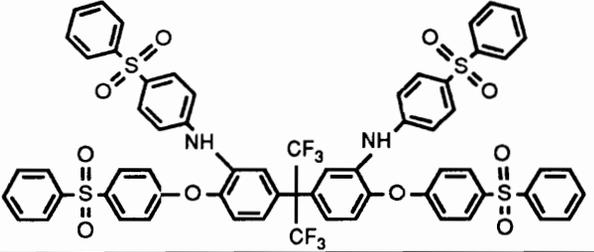


Figure 48 MS from a model reaction of 2,2'-bis(3-amino-4-hydroxyphenyl) hexafluoropropane and 4-chlorophenyl phenylsulfone

Table 23 Identification of chemical structures for a model reaction of 4-chlorophenyl phenylsulfone and bis 2,2'-(3-amino-4-hydroxyphenyl)hexafluoro propane

Chemical Species	Calculated Mol Wt. (g/mole)	Mass Spec Mol. Wt. (g/mole)
 <p>The structure shows a central hexafluoroisopropane core (two CF₃ groups on a central carbon) bonded to two 3-amino-4-hydroxyphenyl rings. Each of these rings is further substituted with a 4-phenylphenylsulfone group (-O-C₆H₄-SO₂-C₆H₅).</p>	582	583
 <p>The structure is identical to the one above, showing a central hexafluoroisopropane core bonded to two 3-amino-4-hydroxyphenyl rings, each substituted with a 4-phenylphenylsulfone group.</p>	799	799
 <p>The structure is identical to the one above, showing a central hexafluoroisopropane core bonded to two 3-amino-4-hydroxyphenyl rings, each substituted with a 4-phenylphenylsulfone group.</p>	1015	1015
 <p>The structure is identical to the one above, showing a central hexafluoroisopropane core bonded to two 3-amino-4-hydroxyphenyl rings, each substituted with a 4-phenylphenylsulfone group.</p>	1231	1232

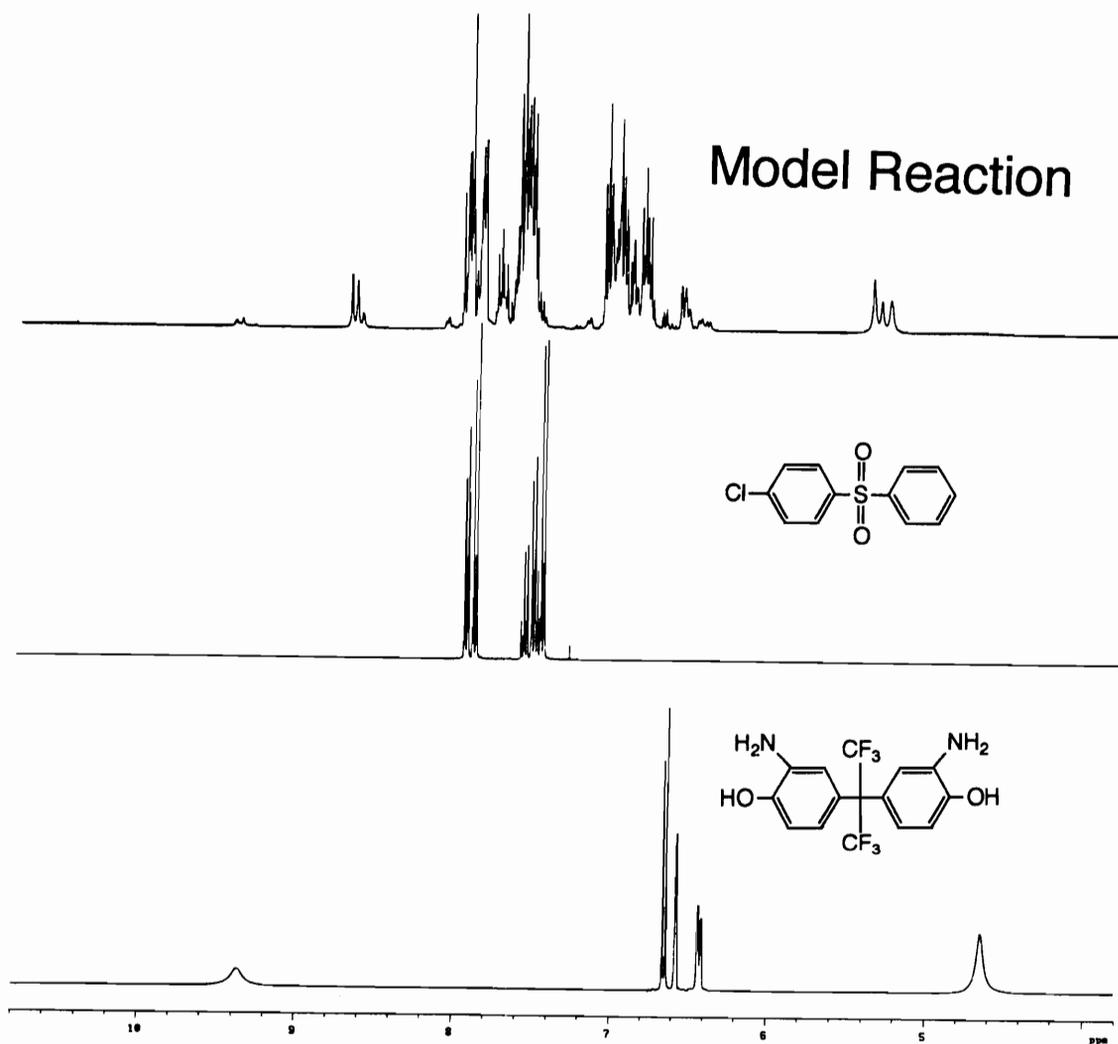


Figure 49 Proton NMR of bis 2,2'-(3-amino-4-hydroxyphenyl)hexafluoro propane (bottom), 4-chlorophenyl phenylsulfone (middle) and product from the model reaction in deuterated dimethylsulfoxide

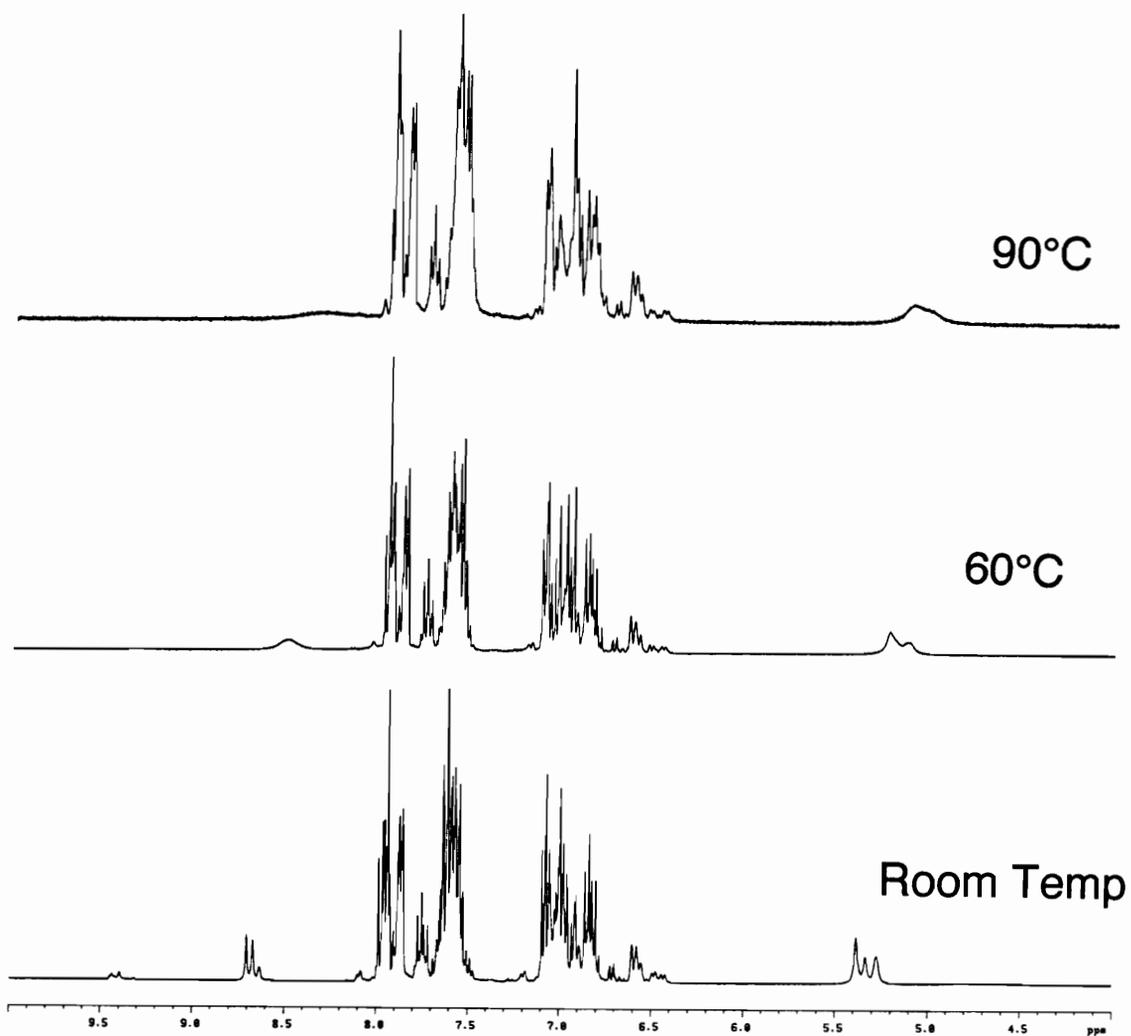


Figure 50 Proton NMR of the product from model reaction of bis 2,2'-(3-amino-4-hydroxyphenyl)hexafluoro propane and 4-chlorophenyl phenylsulfone in deuterated dimethylsulfoxide as a function of temperature

Model Reaction

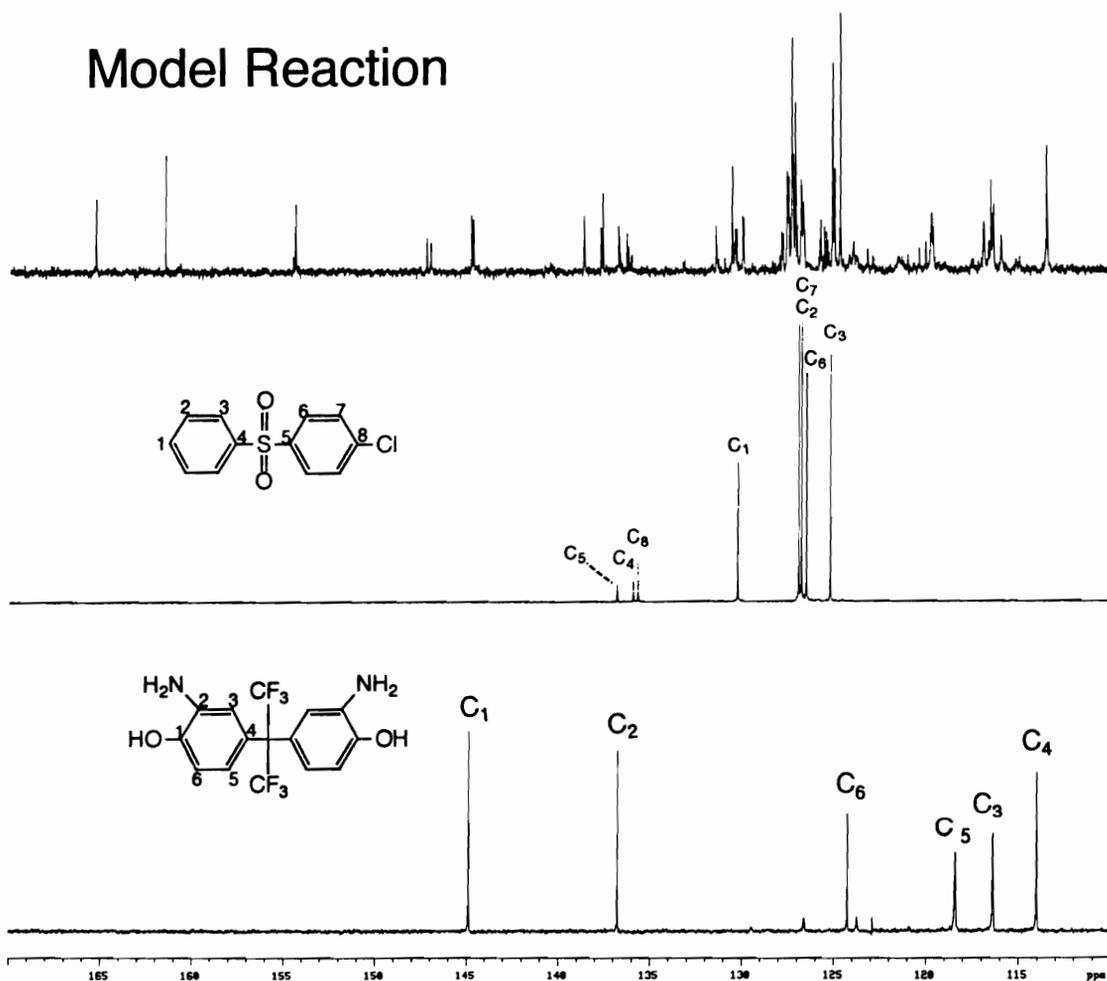


Figure 51 Carbon NMR of bis 2,2'-(3-amino-4-hydroxyphenyl)hexafluoro propane (bottom), 4-chlorophenyl phenylsulfone (middle) and product from the model reaction (top) in deuterated dimethylsulfoxide

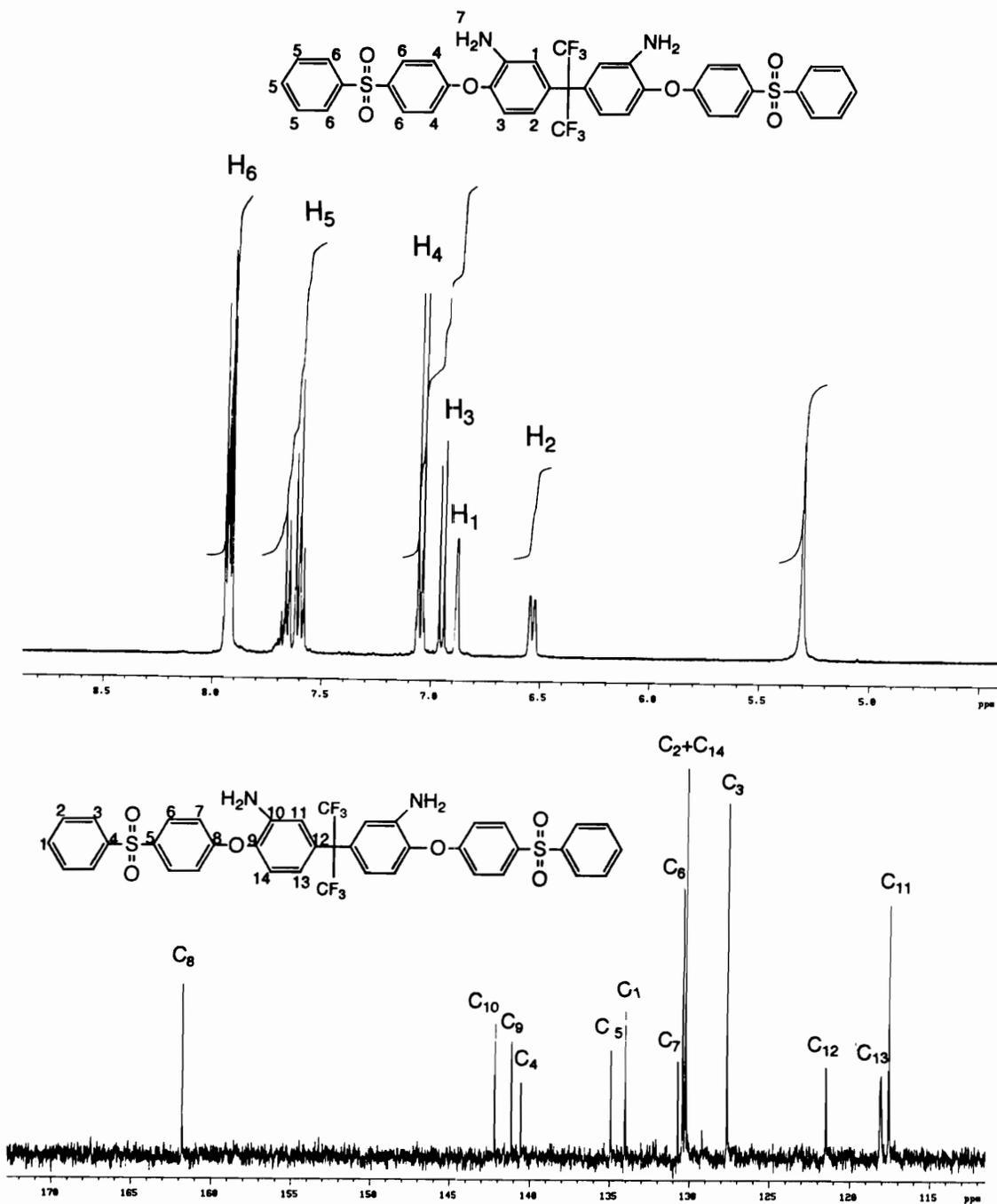


Figure 52 Proton and Carbon NMR of isolated component from the model reaction of bis 2,2'-(3-amino-4-hydroxyphenyl)hexafluoro propane and 4-chlorophenyl phenylsulfone in deuterated dimethylsulfoxide

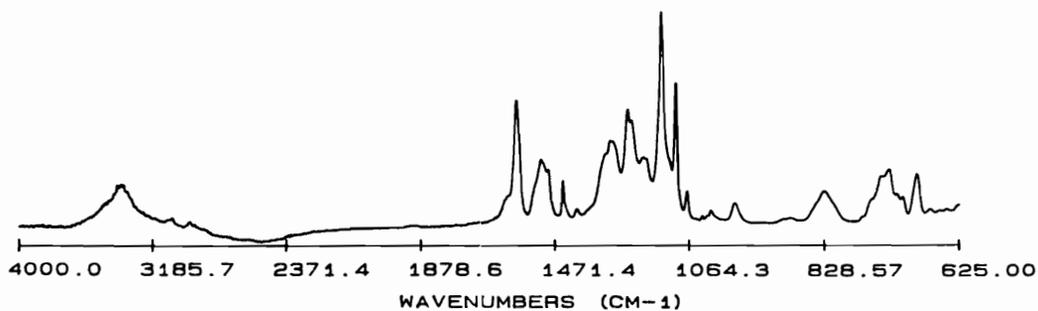
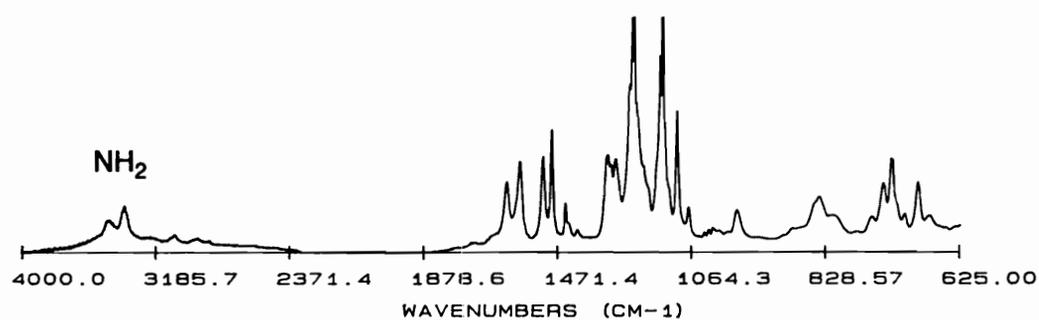


Figure 53 FT-IR of isolated component (top) from the model reaction of bis 2,2'-(3-amino-4-hydroxyphenyl)hexafluoro propane and 4-chlorophenyl phenylsulfone and rest of the components (bottom) from KBr pellet

4.13.4 Stoichiometric Polymerizations of o-Aminophenol (OAP) and Activated Dihalide Monomers

Having demonstrated that amine ortho to the phenol reacted as well as the phenolate, one to one polymerizations of o-aminophenol (OAP) and dichloro diphenylsulfone (DCDPS) were investigated as shown in scheme 28. Reaction conditions were varied to optimize the molecular weight and obtain the highest molecular weight possible. Various reaction parameters were changed and these were: the total reaction time, the amount of excess potassium carbonate, and even in one experiment, DCDPS was replaced with a more reactive difluorodiphenylsulfone (DFDPS). The amount of total reaction time was varied from 24 to 48 hours to determine if higher molecular weight materials could be obtained with longer reaction times. However, two decisions had to be made with respect to the functionality of OAP. Since one molecule of OAP contains only one phenol group it could be treated as a monofunctional monomer, this assumed that the reaction of the amine with DCDPS did not require potassium carbonate. The other case was the treatment in which OAP was treated as a difunctional monomer. Based on either a mono or a difunctional treatment of OAP, a twenty five percent excess potassium carbonate relative to OAP was added. Figure 53 shows a mass spectrum of one to one OAP and DCDPS in which OAP was treated as a monofunctional monomer. The total reaction time was 24 hours, 4 hours at 145°C and then twenty hours at 165°C. The highest mass peak was 1006, dividing this number by the molecular weight of the polymer repeat unit (359 g/mole), a value of about three was obtained for the number of repeat units. Again, this must imply that the phenolate and the amine reacted with DCDPS, otherwise, if only the phenolate reacted with DCDPS, then the molecular weight could only be

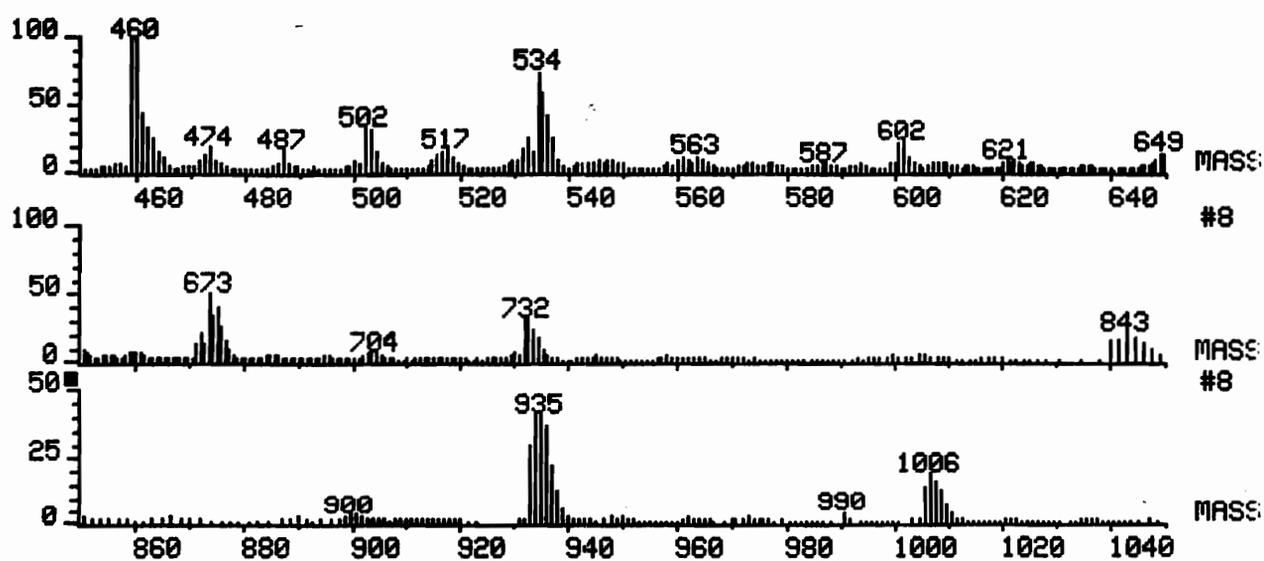


Figure 54 MS from stoichiometric reaction of OAP and DCDPS with monofunctional treatment of OAP for total reaction time of 24 hours

466 g/mole. Treatment of OAP as a difunctional monomer and adding a 25 percent excess potassium carbonate for the same total reaction time (24 hours) resulted in a higher intrinsic viscosity. This seemed to indicate that the extent of the amine reaction with DCDPS increased as more potassium carbonate was added. A proton NMR in deuterated dimethylsulfoxide of OAP and DCDPS in which the total reaction time for both was 24 hours, the only difference was the amount of potassium carbonate that was added is shown in Figure 55. Notice that the bottom spectrum in which OAP was treated as a monofunctional monomer showed a large peak ~4 ppm from the aromatic amine. In contrast, the upper spectrum showed a much smaller residual area for the aromatic amine, also, the intensity of peaks between 9 and 10 ppm was greater for the case where OAP was treated as a difunctional monomer. The intrinsic viscosities are shown in Table 25. The notation of 1X or 2X K_2CO_3 referred to whether OAP was treated as a monofunctional or a difunctional monomer. It can be seen that increasing the total reaction time from 24 to 48 hours in which OAP was treated as a difunctional monomer resulted in an increase in viscosity from 0.16 to 0.26 dl/g. The T_g was 260°C which increased to 276°C as the intrinsic viscosity increased from 0.16 to 0.26 dl/g. This value is much greater than expected for a simple arylene ether sulfone. Also, using difluorodiphenylsulfone (DFDPS) instead of DCDPS resulted in a similar intrinsic viscosity in a less reaction time than using DCDPS.

The oligomers from OAP and DCDPS/DFDPS were not soluble in chloroform, however, they were readily soluble in dipolar aprotic solvents and tetrahydrofuran (THF). The molecular weights of these oligomers were not high

enough to obtain films and attempted efforts produced only brittle and weak samples.

Table 25 Intrinsic viscosity and glass transition temperatures from stoichiometric polymerization of OAP and DCDPS/DFDPS

Sample	Oligomer	$[\eta]_{\text{NMP}}^{25^\circ\text{C}}$ (dl/g)	DSC (°C)
1	1:1 OAP + DCDPS 24 Hours 1 x K ₂ CO ₃	0.04	-----
2	1:1 OAP + DCDPS 24 Hours 2 x K ₂ CO ₃	0.16	260
3	1:1 OAP + DCDPS 48 Hours 2 x K ₂ CO ₃	0.26	276
4	1:1 OAP + DCDPS 21 Hours 2 x K ₂ CO ₃	0.15	258

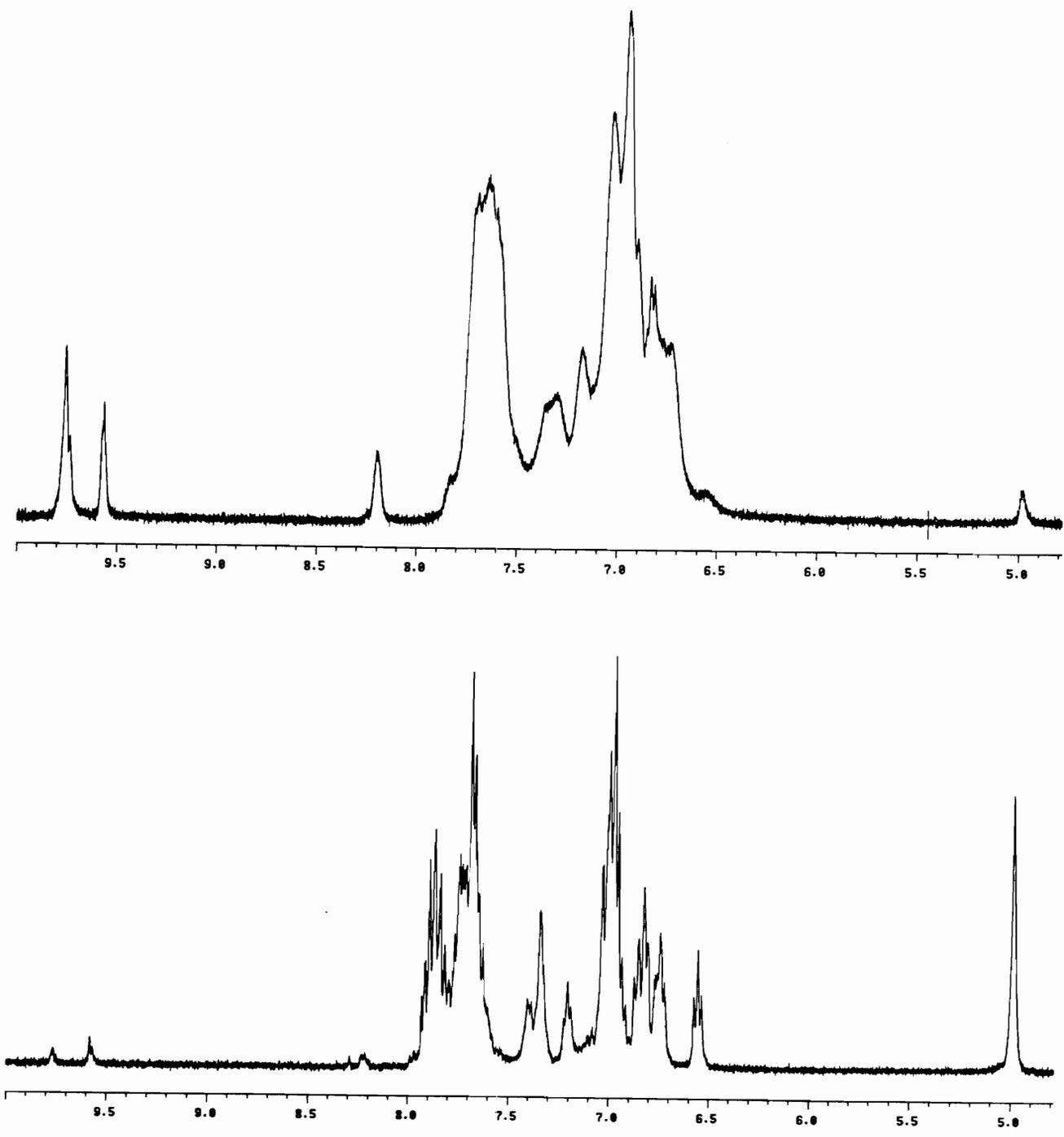


Figure 55 Proton NMR in deuterated dimethylsulfoxide for stoichiometric reaction of OAP and DCDPS with monofunctional treatment of OAP (bottom) and difunctional treatment of OAP (top) for a total reaction time of 24 hours

4.13.5 Polymerization of o-Aminophenol and Chlorine Terminated Polysulfone Oligomer

One to one polymerization of OAP and 5K chlorine terminated polysulfone was also conducted in which OAP was treated as a difunctional monomer as shown in Scheme 30. The reason for conducting this polymerization was that because the molecular weight of one of the reactants was high, it would not require a high extent of conversion in order to observe a dramatic increase in the intrinsic viscosity. The results from this investigation are shown in Table 26.

Table 26 Intrinsic viscosity and Tgs for the stoichiometric (f=2) reaction of OAP and 5K chlorine terminated polysulfone oligomer

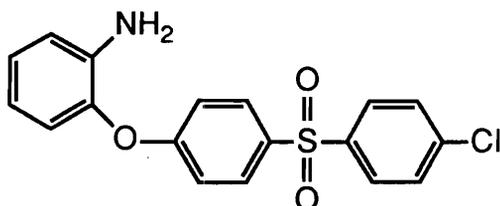
Oligomer	$[\eta]_{\text{CHCl}_3}^{25^\circ\text{C}}$ (dl/g)	DSC (°C)
5K Chlorine Terminated PSF <Mn>=5300 g/mole by NMR	0.16	165
1:1 OAP and 5K Chlorine Terminated PSF	0.35	185

The number average molecular weight for the chlorine terminated polysulfone was determined by the proton NMR from a ratio of the integration of the aromatic protons ortho to the chlorine to the isopropylidene protons. The intrinsic viscosity and the Tg of the 5K chlorine terminated polysulfone was 0.16

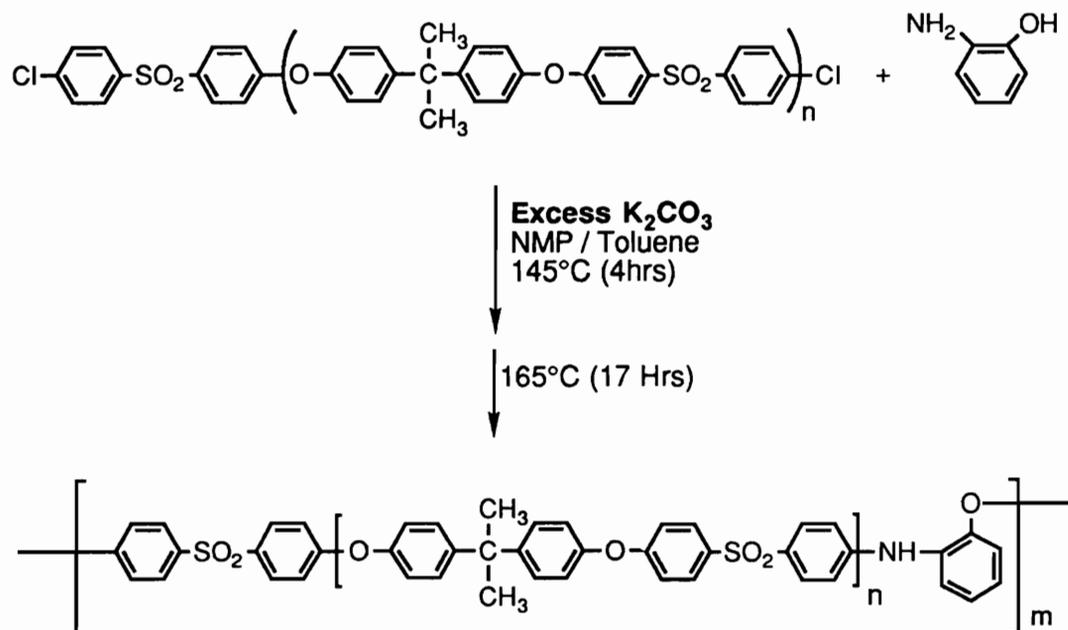
dl/g and 165°C respectively, after the reaction with OAP, the intrinsic viscosity nearly doubled to 0.35 dl/g and the T_g increased by another 20°C.

The IR of the 5k chlorine terminated polysulfone and the polymer from the one to one reaction with OAP is shown in Figure 56. Notice that the two spectra are identical to each other and the absorbance for the secondary amine was not observed. This was likely because only a very small concentration of the secondary amine relative to the polymer repeat unit was present. The same result was also obtained with proton NMR, however, the presence of new peaks in the aromatic region was observed and this is shown in Figure 57.

It is possible to consider at least three limiting factors which prevent the achievement of high molecular weight polymers from OAP and DCDPS. The first limitation is that aromatic amines are not very good nucleophiles. In order to obtain high molecular weight polymers from a polycondensation process, a high extent of conversion is required, with a poor nucleophile only a low extent of conversion is possible. A second limitation is steric hindrance problem of by having two potential reactive functional groups ortho to each other. The other limiting factor which may prevent high molecular polymers from OAP and DCDPS may be due to a reduced reactivity once either the phenolate or the amine react with DCDPS. The structure which would result if the phenolate reacted with DCDPS is shown below.



The presence of the sulfone could reduce the reactivity of the amine because of its electron withdrawing effect.



Scheme 30 Chain extension polymerization of OAP and 5K chlorine terminated polysulfone oligomer

4.13.6 Reaction of o-Aminophenol and Activated Dihalide Monomer Using Diphenylsulfone as the Solvent

Since a slightly higher intrinsic viscosity was obtained with a longer reaction time using NMP at 165°C, reactions at higher temperatures using diphenylsulfone as the solvent were also investigated. Initially, the monomers and potassium carbonate were transferred to the reaction flask along with diphenylsulfone, since diphenylsulfone was a solid at room temperature, the contents were washed into the reaction flask with a small amount of toluene. The temperature was then increased to 155°C for an hour to remove toluene

with a constant purge of nitrogen. When toluene was removed, the temperature was increased to 185°C for 1.5 hour and then increased to 235°C for another 1.5 hour. Many temperature regimes were investigated by varying the reaction times at 185°C and 235°C. However, in all cases, the resulting materials were insoluble. **This seemed to suggest that at high temperatures, the secondary amines reacted even further which resulted in the formation of networks.**

4.13.7 Thermal Analysis of Stoichiometric Polymerizations of o-Aminophenol and Activated Dihalide Monomers and Chlorine Terminated Polysulfone Oligomer

Even though only oligomers were obtained using NMP as the solvent at 165°C, the Tgs were relatively high. A Tg of 276°C for the highest intrinsic viscosity (0.26 g/dl) was observed. As a comparison, the Tg of a high molecular weight polysulfone from bisphenol-A and DCDPS is 190°C. The higher Tgs of these oligomers may be due to the presence of hydrogen bonding between the secondary amines with the highly polar sulfones. The adverse effect of the presence of secondary amines in the repeat unit resulted in these materials to have a strong affinity for moisture. Shown in Figure 58 was a common behavior which was observed of these materials during the first scans of DCS analysis. This was the first scan one to one OAP and DCDPS in which the total reaction time was 48 hours with difunctional treatment of OAP. There was a broad peak which started from about 50°C to 170°C which was due to the presence of moisture .

Figure 59 shows a TGA from the reaction of OAP with two different activated halides, DCDPS and DFDPS . Even though these two oligomers had

comparable intrinsic viscosity and Tg values, a noticeable difference was observed from the TGA analysis. The oligomer from the more reactive DFDPS displayed a gradual weight loss, whereas, the oligomer from DCDPS showed a more rapid weight loss. This may be due chain extension reactions between phenol terminated oligomers and fluorine terminated oligomers at high temperatures when DFDPS was used as the activated dihalide monomer. With the oligomer from a less reactive DCDPS, the rate of chain extension was less than the rate of thermal degradation. Shown in Figure 60 are TGAs in air of 5k chlorine terminated polysulfone and the polymer from OAP and 5k chlorine terminated polysulfone. The polymer from the reaction of OAP and 5k chlorine terminated polysulfone showed a slightly better thermal stability perhaps due to a higher molecular weight.

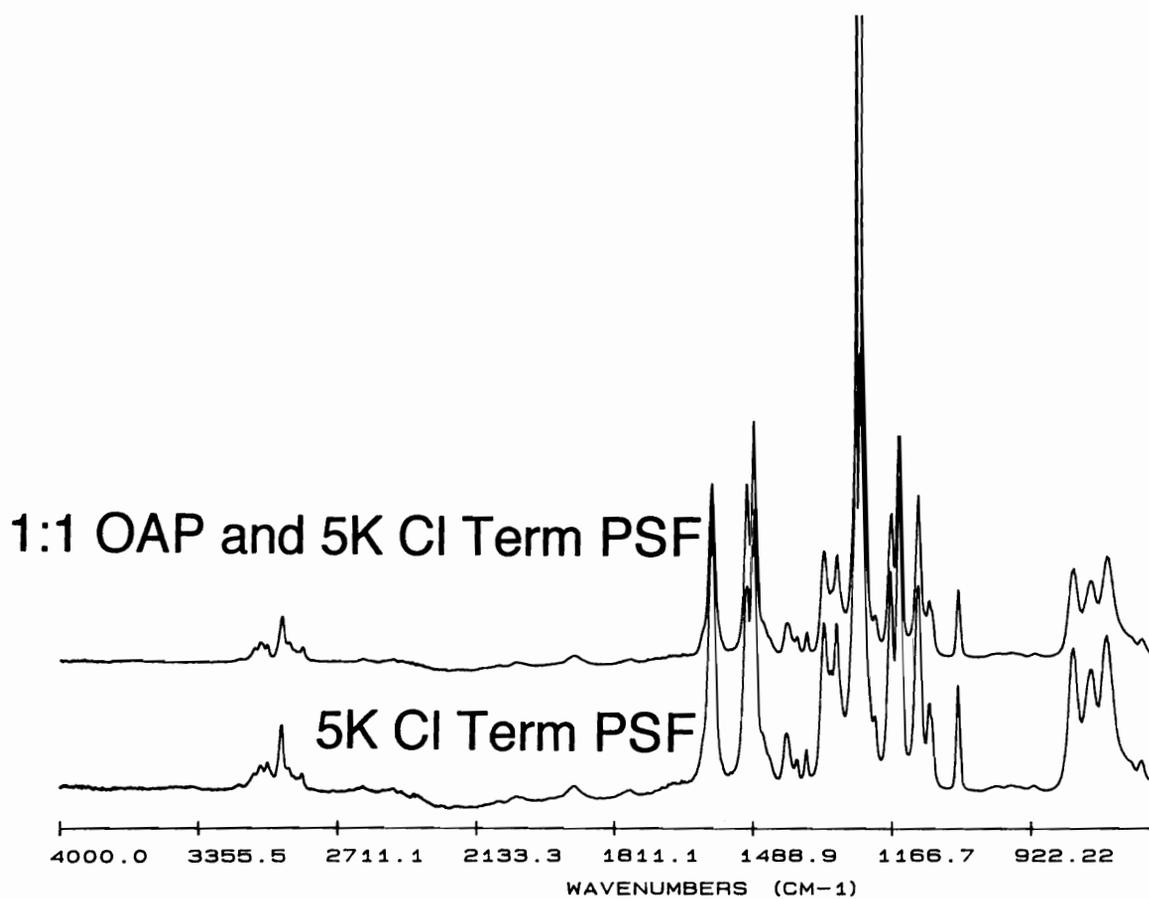


Figure 56 FT-IR of 5k chlorine terminated PSF (bottom) and from chain extension reaction with OAP (top)

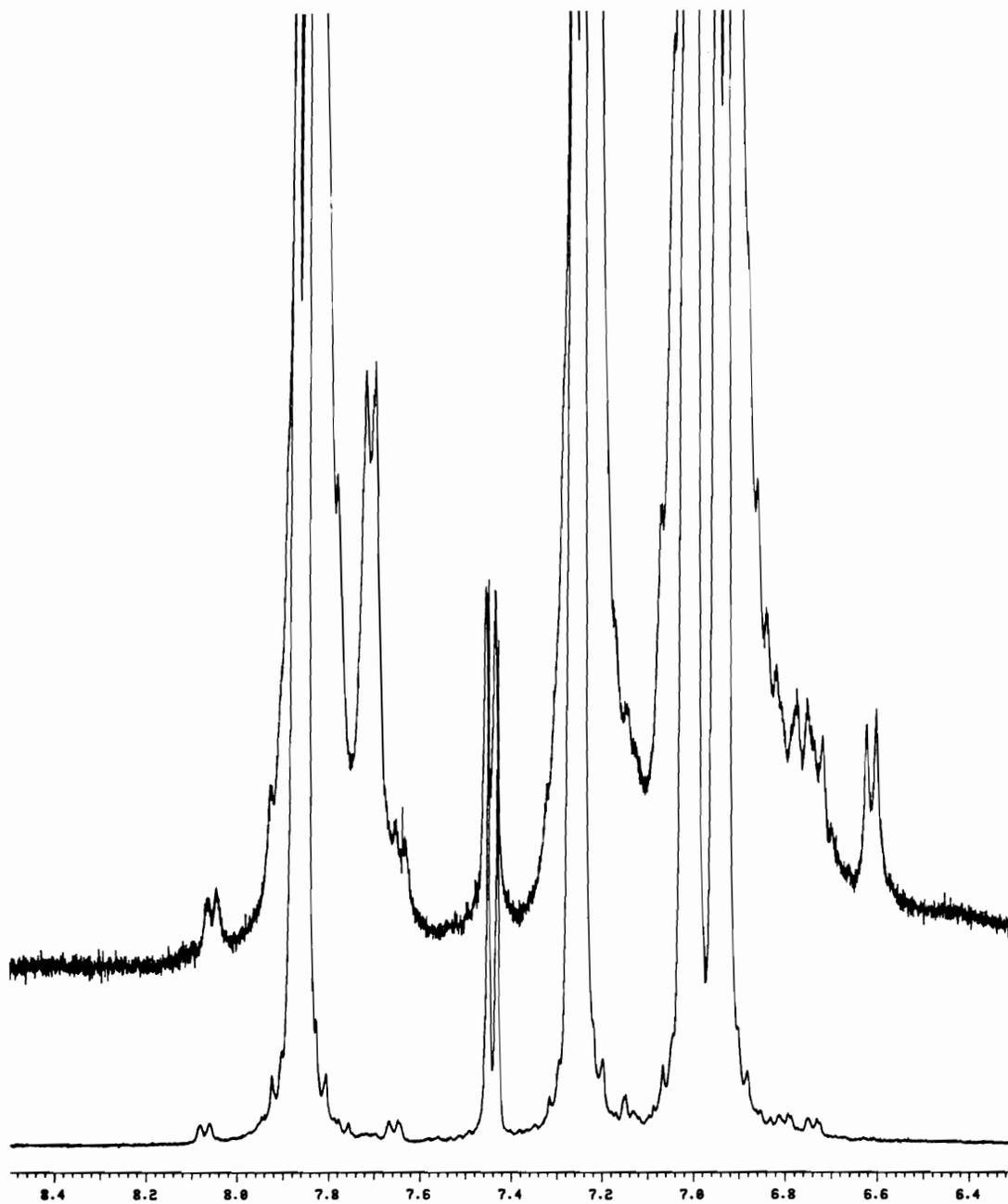


Figure 57 Proton NMR in deuterated dimethylsulfoxide of 5k chlorine terminated PSF (bottom) and from chain extension reaction with OAP (top)

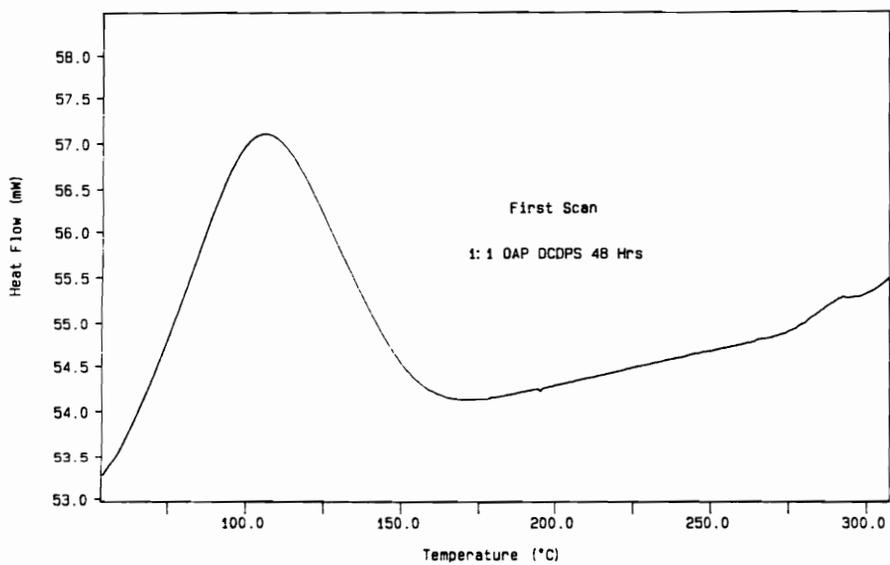


Figure 58 DSC of the stoichiometric reaction of OAP and DCDPS after 48 hours at 165°C

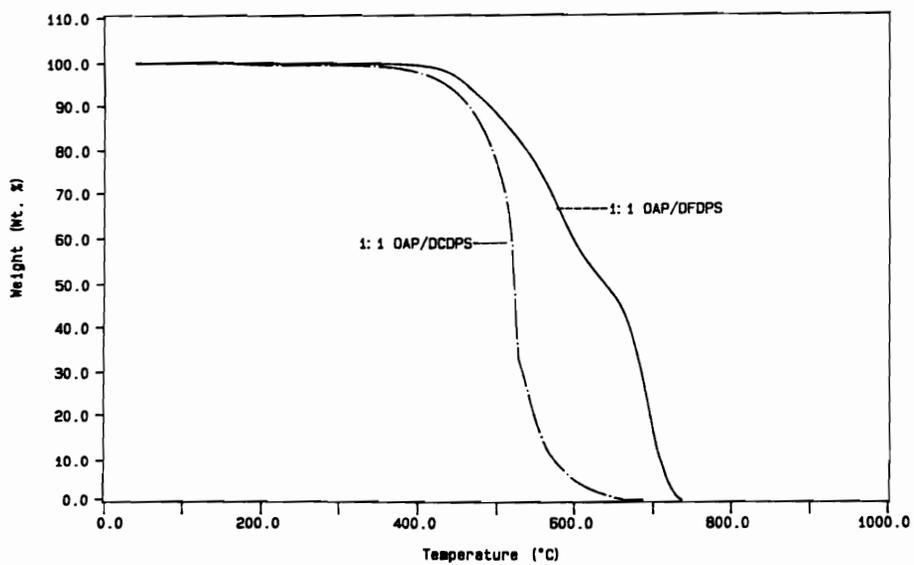


Figure 59 TGA in air of oligomers synthesized from OAP/DCDPS and OAP/DFDPS under stoichiometric condition

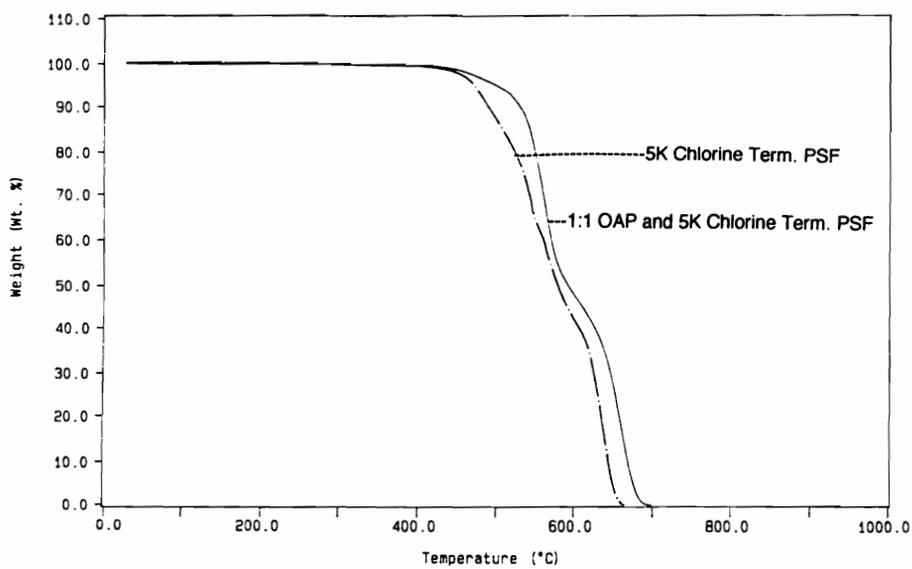


Figure 60 TGA behavior in air of 5k chlorine terminated PSF oligomer and OAP chain extension system

4.13.8 Why Does the Amine in o-Aminophenol React?

In an attempt to rationalize why the amines ortho to the phenol react, the first question that should be asked is whether aromatic amines can react with activated halides under the polymerization conditions. Table 27 shows a comparison of the nucleophilicities of various reagents toward 1-chloro-2,4-dinitrobenzene. Notice the relative orders of phenoxide ions, hydroxide ion, and aniline. Even though 1-chloro-2,4-dinitrobenzene is more reactive than DCDPS, still qualitative conclusions can be deduced from the table. The first point is that aniline comes immediately after hydroxide ion, from previous work by Johnson et al.(19), hydroxide ions at 160°C will definitely react with DCDPS. The second point is that water is less nucleophilic than aniline and since water should be excluded from the polymerization mixture because it can hydrolyze the activated halide, it may be logical that certain aromatic amines could react with DCDPS during the polymerization.

One of the earlier investigation of polymerization of amines with a activated dihalide monomer was reported by D. Brown (197) in 1968. He attempted polymerizations of difluorodiphenylsulfone (DFDPS) with various primary and secondary amines in a dipolar aprotic solvent in the presence of an acid acceptor. Polymerizations were conducted at or near the boiling point of the solvent for several hours (not specified). Of the amines he investigated, he was only able to obtain high molecular weight polymers from DFDPS and the cycloaliphatic diamine bis(4-piperidyl)-1,3-propane. When he used hexamethylene diamine or oxydianiline as the diamine, he obtained networks.

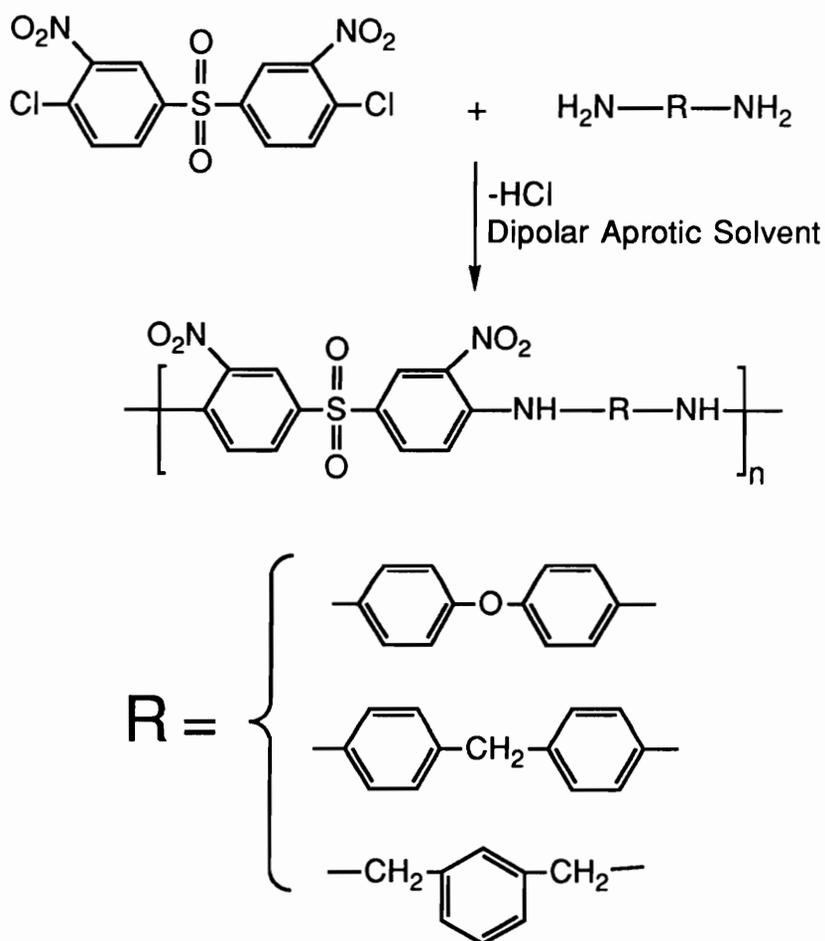
Table 27 Nucleophilicities of various reagents toward activated halides (194)

Amide ion Triphenylmethyl anion Phenylamide ion Sulphite ion Mercaptide ions	React with phenyl halides at low temperatures
Alkoxide ions Phenoxide ions Piperidine Hydroxide	React with 1-chloro-2,4-dinitrobenzene at room temperature
Aniline Ammonia Sulphinat ions	React with 1-chloro-2,4-dinitrobenzene at 100°C
Halide ions Water	React with 1-chloro-2,4-dinitrobenzene at 170°C or higher

Other polymerizations of aromatic amines with activated dihalide monomers was reported by Imai et al (198). The reaction scheme is shown in Scheme 31. They also used a dipolar aprotic solvent and an acid acceptor, but the activated dihalide monomer they used was bis(4-chloro-3-nitrophenyl) sulfone (BCNS) which is more reactive than DCDPS and DFDPS. The optimum condition was determined to be 24 hours at 100°C. They were able to obtain inherent viscosity as high as 0.52 g/dl by polymerizing BCNS with oxydianiline (ODA) using N-ethylmorpholine as the acid acceptor. Unlike Brown, they did not obtain networks when they used ODA as the aromatic diamine, this was probably due to a milder reaction condition used by Imai et al.

Others have also demonstrated that aromatic amines will react with activated halides under suitable conditions (199-203).

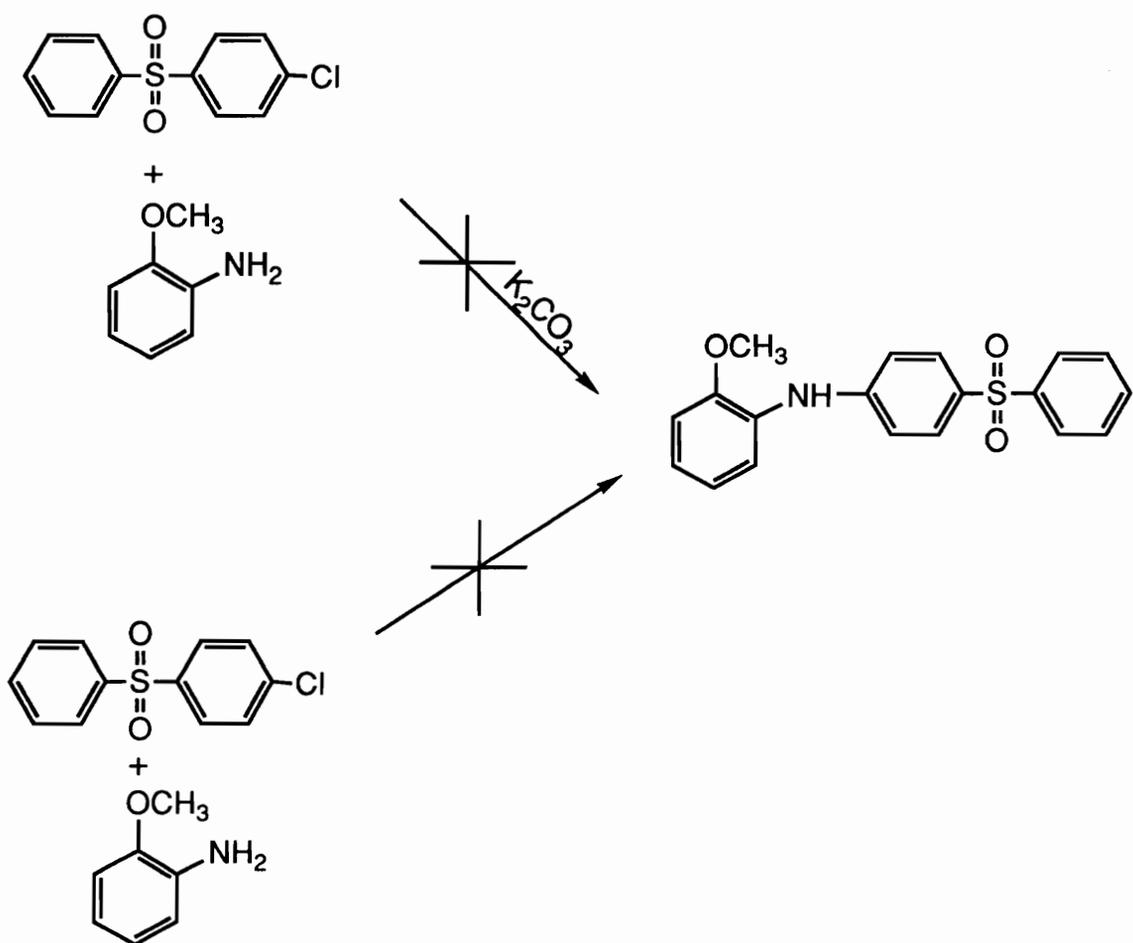
Based on some of the experimental evidence that have been reported and discussed so far, aromatic amines will react with activated halides. Even though Imai et al. obtained a relative high molecular weight polymer from ODA and BCNS, one must consider that BCNS is much more reactive than DCDPS and ODA is one of the more reactive diamine because of the ether linking group which can donate electrons.



Scheme 31 Reaction of bis(4-chloro-3-nitrophenyl)sulfone with various aromatic diamines

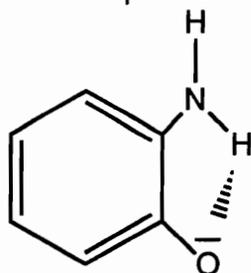
If aromatic amines react with DCDPS during polymerization, then why is it that meta or para aminophenol have been successfully used as endcappers for the molecular weight controlled synthesis of amine terminated poly(arylene ether ethers)? This may be due to a very small or negligible extent of the amine reaction when the amine is either meta or para to the phenol.

The next logical question that needs to be addressed is why do amines ortho to the phenol react with DCDPS to a greater extent than amines on either meta or para to the phenol? There seems to be no conclusive experimental evidence in the literature to rationalize why this seems to be the case. It clearly seems to indicate that by having an amine ortho to the phenol the reactivity of the amine is enhanced. A model reaction was conducted by reacting 4-chlorophenylphenyl sulfone with o-anisidine as shown in scheme 32. Ortho anisidine is similar to o-aminophenol except that hydroxyl is replaced by a methoxy group. The presence of electron releasing methoxy group should enhance the nucleophilicity of the amine. The reaction condition and the work up procedure was the same as the previously discussed model reaction of 4-chlorophenyl phenylsulfone and 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoro propane. Reaction with and without potassium carbonate was investigated, however, in both cases, no reaction occurred based on thin layer chromatography and proton NMR.



Scheme 32 Model reaction of 4-chlorophenyl phenylsulfone with o-anisidine

There seems to be a special requirement, namely, the presence of a phenol ortho to the amine. One possible explanation to account for this behavior may be that with o-aminophenol, there is a possibility of intramolecular hydrogen bonding, whereas for meta or para aminophenol this is not possible.



The effect of this intramolecular hydrogen bonding may result in an increased nucleophilicity of the aromatic amine. This is only a speculation and in order to fully understand the mystery of ortho aminophenols, more research is required to further elucidate these interesting preliminary results. Nevertheless, the novel oligomeric poly(aminophenoxy sulfones) are interesting new materials and could have applications as non-volatile antioxidants, polymer supports for organic synthesis etc..

5.0 CONCLUSIONS

A novel monomer, 3-aminophenyl-bis(4-fluorophenyl)phosphine oxide (amino DFTPPO) was synthesized by nitration and reduction of bis(4-fluorophenyl)phenylphosphine oxide. It was copolymerized with activated dihalide monomers and bisphenol-A to afford statistical incorporation of pendant amines along the polymer backbone. High intrinsic viscosities of the resulting copolymers as well as proton NMR and titration results confirmed the high purity of amino DFTPPO. The concentration of amines along the polymer backbone was controlled by varying the ratio of amino DFTPPO relative to the other comonomers. The pendant amine copolymers were characterized using proton and carbon NMR, IR, and potentiometric titration. A unique feature of the copolymers is that molecular weight can be controlled independently with respect to concentration of amine.

The copolymers having pendant amine groups were investigated as toughening components of otherwise brittle epoxy networks prepared with epoxy resin (Epon 828) and 4,4'-diaminodiphenylsulfone. The concentration of amines along the polymer backbone and the weight fraction of the thermoplastic modifier were important variables for increasing fracture toughness and development of multiphase morphologies of modified epoxy networks. The optimum value was ~2.5 mole percent based on a range of 0-30 mole percent investigated. Very significant improvements were obtained at ~25-30 weight percent thermoplastic modifier, where phase inversion was observed.

The pendant amines were also converted to maleimides by reaction with maleic anhydride. The pendant maleimides were thermally cured to afford

networks with increased solvent resistance and higher glass transition temperatures (T_g). The pendant amines were also converted to pendant phenylethynylphenyl imides which afforded a much wider processing window than the maleimides. The networks generated from thermal cure of phenyl ethynylphenyl imides also displayed higher T_g s and good solvent resistance.

The pendant amines were converted to phenylimides by reaction with phthalic anhydride. The T_g s of the pendant phenylimide copolymers were slightly lower than the corresponding copolymers with pendant amines. The decrease in T_g was attributed to loss of intermolecular hydrogen bonding.

In an effort to investigate other methods for generating polymers with pendant amines on poly(arylene ethers), bis(o-aminophenol) monomers were copolymerized with 4,4'-dichlorodiphenylsulfone and bisphenol-A. This resulted in gels, which indicated that the aromatic amine as well as the phenolate had reacted with the activated dihalides. This was further confirmed by the successful oligomerization of o-aminophenol itself with 4,4'-dichlorodiphenyl sulfone, which afforded NMP soluble novel poly(sec-amino phenoxy diphenylsulfones) with high glass transition temperatures ($T_g \sim 276^\circ\text{C}$).

REFERENCES

1. J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, 49, 273, 1951.
2. *MTP Int. Rev. Sci.: Org. Chem., Ser. One, Volume 3, 33-63.* Edited by Zollinger, Heinrich, Butterworth, London, Eng., 33, 1973.
3. L. M. Stock, *Aromatic Substitution Reactions*, Edited by K.L. Rinehart Jr. Prentice-Hall Inc., Englewood Cliffs, N.J., 1968.
4. *Chemistry of Carbon Compounds*, Edited by E. H. Rodd, Volume 3 Part A: Aromatic Compounds, Elsevier Publishing Company, New York, p 49, 1954.
5. *Organic Chemistry, Second Edition*, R.T. Morrison and R. N. Boyd, Allyn and Bacon, Inc., p828, 1967.
6. E. J. Fendler, J. H. Fendler, N. I. Arthur and C. E. Griffin, *J. Org Chem.*, 31, 2319, 1966.
7. J. Hayami, S. Otani, F. Yamaguchi and Y. Nishikawa, *Chemistry Letters*, 739, 1987.
8. J. Meisenheimer, *Liebigs Ann. Chem.*, 323, 205, 1902.
9. M. J. Strauss, *Chem. Rev.*, 70, 667, 1970.
10. C. A. Fyfe, S. W. H. Damji and A. Koll, *J. Amer. Chem. Soc.*, 101, 951, 1979.
11. G. G. Messmer and G. J. Palenik, *Aust. J. Chem.*, 11, 302, 1958.
12. J. A. Miller, *Aromatic Nucleophilic Substitution*, Elsevier London, 1968.
13. J. F. Bunnet, E. W. Garbisch and K. M. Pruitt, *J. Amer. Chem. Soc.*, 101, 951, 1979.
14. E. Berliner and L. C. Monack, *J. Amer. Chem. Soc.*, 74, 1574, 1952.
15. N. Kornblum, L. Cheng, R. C. Kerber, M. M. Kestner, B. N. Newton, H. W. Pinnick, R. G. Smith and P. A. Wade, *J. Org. Chem.*, 41, 1560, 1976.
16. J. F. Bunnet, E. W. Garbisch and K. M. Pruitt, *J. Amer. Chem. Soc.*, 79, 385, 1957.

17. J. D. Reinheimer, C. Taylor and P. E. Rohrbaugh, *J. Amer. Chem. Soc.*, 83, 835, 1961.
18. S. M. Mayanna and J. R. Raju, *J. Indian Chem. Soc.* 48(10), 943, 1971.
19. R. N. Johnson, A. G. Farnham, R. A. Clendinning, W. F. Hale and C. N. Merriam, *J. Polymer Sci.: Part A-1*, 5,2375, 1967.
20. A. B. Newton and J. B. Rose, *Polymer*, 13, 465, 1972.
21. S. Maiti and B. K. Mandal, *Prog. Polym. Sci.*, 12, 111, 1986.
22. R. S. Mani, B. Zimmerman, A. Bhatnager and D. K. Mohanty, *Polymer*, 34(1), 171, 1993.
23. V. Percec, R. S. Clough, P. L. Rinaldi and B. E. Litman, *Macromolecules*, 24(21), 5889, 1991.
24. I. P. Storozhuk, V. I. Bakhmotov, A. K. Mikitaev, P. M. Valetskii, Yu. I. Musaev, V. V. Korshak and E. I. Fedin, *Vysokomol. Soed.*, A19(8), 800, 1977.
25. D. K. Mohanty, J. L. Hedrick, K. Gobetz, B. C. Johnson, I. Yilgor, E. Yilgor, R. Yang and J. E. McGrath, *Polym. Prepr.*, 23(1), 284, 1982;
R. Viswanathan, Ph. D. Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, VA, 24061, 1981.
26. R. Viswanathan, B. C. Johnson and J. E. McGrath, *Polymer*, 25, 1827, 1984.
27. J. L. Hedrick, D. K. Mohanty, B. C. Johnson, R. Viswanathan, J. A. Hinkley and J. E. McGrath, *J. Polm. Sci.: Chem. Ed.*, 23, 287, 1986.
28. J. L. Hedrick, J. J. Dumais, L. W. Jelinski, R. A. Patsiga and J. E. McGrath, *J. Polym. Sci.: Part A: Polym. Chem.*, 25, 2289, 1987.
29. S. R. Schulze and A. L. Baron, *Adv. Chem. Ser.*, 91,689,1969.
30. T. E. Attwood, A. B. Newton and J. B. Rose, *Br. Polym. J.*, 4, 391, 1972.
31. V. Carlier, B. Jambe, J. Devaux, R. Legras and P. T. McGrail, *Polymer*, 34(1),167, 1993.
32. H. R. Kricheldorf and G. Bier, *Polymer*, 25, 1151, 1984.
33. H. R. Kricheldorf, U. Delius and K. U. Tonnes, *New Polymeric Mater.*, 1(2), 127, 1988.

34. Y. Imai and Y. Oishi, *Prog. Polym. Sci.*, 14, 173, 1989.
35. H. R. Kricheldorf and P. Jahnke, *Makromol. Chem.*, 191, 2027, 1990.
36. H. R. Kricheldorf, *Polym. Prep.*, 32(1), 395, 1991.
37. H. R. Kricheldorf and P. Jahnke, *Makromol. Chem.*, 191, 2027, 1990.
38. J. L. Hedrick, *Polym. Bull.*, 27, 655, 1992.
39. K. J. Ivin and J. B. Rose, 'Advances in Macromolecular Chemistry', (Ed. W. M. Pasika), Academic Press, London and New York, Vol1, 336, 1968.
40. J. B Rose, *Polymer*, 15, 456, 1974.
41. P. A. Staniland , C. J. Wilde, F. A. Bottino, G. D. Pasquale, A. Pollicino and A. Recca, *Polymer*, 33(9), 1976, 1979.
42. J. E. McGrath, M Matzner, L. M. Robeson and R. Barclay Jr., *J. Polym. Sci.: Polym. Symp.*, 60, 29, 1977.
43. A. Noshay, M. Matzner and T. C. Williams, *Ind. Eng. Chem. Prod. Res. Develop.*, 12(4), 269, 1973.
44. M. J. Mullins, R. Galvan, M. T. Bishop, E. P. Woo, D. B. Gorman and T. A. Chamberlin, *Polym. Prepr.*, 33(1), 414, 1992.
45. S. Hashimoro, I. Furukawa and K. Ueyama, *J. Macromol. Sci.*, A11, 2167, 1977.
46. J. W. Rakshys, R. W. Taft and W. A. Sheppard, *J. Amer. Chem. Soc.*, 90, 5236, 1968.
47. E. Bay, US 4760191, to Akzo America Inc.,1988.
48. E. Weiss and H. J. Kleiner, *Phos. Sulf.*, 34, 39, 1987.
49. H. Schindlbauer, *Chem. Ber.*, 100, 3432, 1967.
50. S. Besecke, G. Schoeder, W. Ude and W. Wunderlich, DE 3203186, 1983.
51. S. Hirose, K. Nakamura, T. Hatakeyama and H. Hatakeyama, *Seni Gakkaishi*, 43(11), 595, 1987.
52. S. Hirose, K. Nakamura, T. Hatakeyama and H. Hatakeyama, *Seni Gakkaishi*, 44(11), 563, 1988

53. R. L. Holzberlein, D. K. Mohanty, C. D. Smith, S. D. Wu and J. E. McGrath, *Polym. Prepr.*, 30(1), 293, 1989.
54. C. D. Smith, D. K. Mohanty and J. E. McGrath, *Soc. Adv. Matl. Proc. Eng. Ser.*, 35, 108, 1990.
55. C. D. Smith, A. Gunger, K. M. Keister, H. A. Marand and J. E. McGrath, *Polym. Prepr.*, 32(1), 93, 1991.
56. W. Ude and J. Knebel, US 4745225, to Rohm Gmbh, 1988.
57. D. B. Priddy Jr., M. Franks, M. Konas, M. A. Vrana, T. H. Yoon and J. E. McGrath, *Polym. Prepr.*, 34(1), 370, 1993.
58. J. P. Quentin, US 3709841, to Rhone Poulanc 1973.
59. A. Noshay and L. M. Robeson, *J. Appl. Polym. Sci.*, 20, 1885, 1976.
60. B. C. Johnson, I. Yilgor, C. Tran, M. Iqbal, J.P. Wightman, D. R. Lloyd and J. E. McGrath, *J. Polym. Polym. Chem. Ed.*, 22, 721, 1984.
61. M. Ueda, H. Toyota, T. Ouchi, J.I. Sugiyama, K. Yonetake, T. Masuko and T. Teramoto, *J. Polym. Sci. Polym. Chem.*, 31, 853, 1993.
62. I. Esser and I. W. Parsons, *Polym. Comm.*, 32(17), 578, 1991.
63. I. C. H. M. Esser and I. W. Parsons, *Polymer*, 34(13), 2837, 1993.
64. Y. Imai, M. Ueda and M. li, *Makromol. Chem.*, 179, 2989, 1978.
65. Y. Imai, M. Ueda, M. li, *J. Polym. Sci. Polym. Letters Ed.*, 17, 85, 1979.
66. J. E. Mulvany and J. J. Wu, *J. Polym. Sci. Polym. Chem.*, 24, 2373, 1986.
67. W. H. Daly, S. Lee and C. Rungaroonthaikul, *ACS Symp. Ser.*, 364, 9, 1988.
68. H. A. Naik and I. W. Parsons, P. T. McGrail and P. D. MacKenzie, *Polymer*, 32(1), 140, 1991.
69. P. Cunningham, R. J. Roach, J. B. Rose and P. T. McGrail, *Polymer*, 33(18), 3951, 1992.
70. F. A. Bottino, A. Mamo, A. Recca, J. Brady, A. C. Street and P. T. McGrail, *Polymer*, 34(13), 2901, 1993.
71. S. Y. Kim and J. W. Labadie, *Polym. Prepr.*, 32(1), 164, 1991.

72. J. A. Mikroyannidis, *J. Polym. Sci. Polym. Chem.*, 28, 669, 1990.
73. E. D. Weil, *Encyclopedia of Polymer Science and Technology*, H. F. Mark, C. G. Overberger and N. M. Bikales, Eds., Vol. 11, Wiley Interscience, New York, 1986.
74. C. D. Smith, H. Grubbs, H. F. Webster, A. Gungor, J. P. Wightman and J. E. McGrath, *High Performance Polymers*, 3(4), 211, 1991.
75. C. D. Smith, Ph. D. Dissertation, Virginia Polytechnic Institute and State University Blacksburg, Virginia, 24061, 1991.
76. G. Allen, J. McAinsh and G. M. Jeffs, *Polymer*, 12, 85, 1971.
77. G. Spathis, E. Kontou and P. S. Theocaris, *J. Poly. Sci.: Part A: Polym. Chem.*, 25, 1285, 1987.
78. J. J. Dumais, A. L. Cholli, L. W. Jelinski, J. L. Hedrick and J. E. McGrath, *Macromolecules*, 19, 1884, 1986.
79. C. L. Aitken, J. S. McHattie and D. R. Paul, *Macromolecules*, 25, 2910, 1992.
80. L. M. Robeson, A. G. Farnham and J. E. McGrath, *Molecular Relaxations in Polymers*, D. J. Meier Ed., Gordon and Breach Sci. Pub. New York, Vol. 4, 405, 1978.
81. T. E. Attwood, M. B. Cinderey and J. B. Rose, *Polymer*, 34(6), 1321, 1993.
82. J. E. Harris and R. N. Johnson, *Encyclopedia of Polymer Science and Engineering*, Vol. 13, 2nd Edition, John Wiley and Sons Inc., p 196, 1988.
83. D. K. Mohanty, T. S. Lin, T. C. Ward and J. E. McGrath, *Sampe Symp.*, 31, 945, 1986.
84. W. Risse and D. Y. Sogah, *Macromolecules*, 23, 4029, 1990.
85. D. R. Kelsey, L. M. Robeson and R. A. Clendinning, *Macromolecules*, 20, 1204, 1987.
86. K. R. Lyon, D. K. Mohanty, G. D. Lyle, T. Glass, H. Marand, A. Prasad and J. E. McGrath, *SAMPE Symp.*, 36(1), 417, 1991.
87. K. R. Lyon, A. Texier, A. Gungor, R. M. Davis and J. E. McGrath, *SAMPE Symp.*, 37, 1301, 1992.
88. J. B. Rose, BP 1414421, to ICI 1975.

89. T. E. Attwood, P. C. Dawson, J. L. Freeman, L. R. J. Hoy, J. B. Rose and P. A. Staniland, *Polymer*, 22, 1096, 1981.
90. I. Fukawa, T. Tanabe and T. Dozono, *Macromolecules*, 24, 3838, 1991.
91. I. Fukawa, T. Tanabe and T. Dozono, *J. Chem. Soc. Perkin Trans 2*, 3, 377, 1992.
92. W. H. Bonner, U. S., 3,065,205, to Du Pont, 1962.
93. I. Goodman, J. E. McIntyre and W. Russell, BP 971227, to ICI, 1964.
94. Y. Iwakura, K. Uno and T. Takiguchi, *J. Polym. Sci.: Part A-1*, 6, 3345, 1968.
95. B. M. Marks, U. S., 3441538, to Raychem, 1969.
96. K. J. Dahl, U. S., 3956240 to Raychem, 1976.
97. H. M. Colquhoun and D. F. Lewis, *Polymer*, 29, 1902, 1988.
98. V. Jansons and K. Dahl, *Makromol. Chem., Macromol. Symp.*, 51, 87, 99.
99. R. A. Clendinning, D. R. Kelsey, J. H. Botkin, P. A. Winslow, M. Yousseffi, R. J. Cotter, M. Matzner and G. T. Kwiatkowski, *Macromolecules*, 26, 2361, 1993.
100. J. E. Harris, P. A. Winslow, J. H. botkin, L. M. Maresca, R. A. Clendinning, R. J. Cotter, M. Matzner and G. T. Kwiatkowski, *Macromolecules*, 26, 2366, 1993.
101. J. H. Botkin, R. J. Cotter, M. Matzner and G. T. Kwiatkowski, *Macromolecules*, 26, 2372, 1993.
102. M. T. Aronhime and J. K. Gillham, in 'Epoxy Resins and Composites IV', *Adv. Polym. Sci.*, 78, Springer-Verlag, New York, p 83, 1986.
103. J. K. Gillham, in 'Encyclopedia of Polymer Science and Engineering', J. I. Kroschwitz, Ed., John Wiley and Sons, New York, vol. 4, p 519, 1988.
104. R. B. Prime, in 'Thermal Characterization of Polymeric Materials', E. A. Turi, Ed., Academic Press, New York, p435, 1981.
105. J. K. Gillham, *Polymer Engineering Science*, 26(20), 1429, 1986.
106. B. S. Kim, T. Chiba and T. Inoue, *Polymer*, 34(13), 2809, 1993.

107. G. D. Lyle, J. S. Senger, D. H. Chen, S. Kilic, S. D. Wu, D. K. Mohanty and J. E. McGrath, *Polymer*, 30, 978, 1989.
108. I. M. Brown and T. C. Sandreczki, *Macromolecules*, 23, 94, 1990.
109. K. R. Carduner and M. S. Chattha, *Polym. Mater. Sci. Eng.*, 56, 660, 1987.
110. A. C. Lind and C. G. Fry, *Polym. Mater. Sci. Eng.*, 59, 466, 1988.
111. Z. S. Petrovic, J. B. Simendic, T. Malavasic and W. J. MacKnight, *Polymer*, 31, 1514, 1990.
112. M. J. Jurek and J. E. McGrath, *SAMPE J.*, 31, 913, 1986.
113. H. Stenzenberger, in 'Structural Adhesives', Ed. A. J. Kinloch, Elsevier, London, p77, 1986.
114. D. O. Hummel, K. U. Heinen, H. D. Stenzenberger and H. Siesler, *J. Appl. Polym. Sci.*, 18, 2015, 1974.
115. I. K. Varma, S. P. Gupta and D. S. Varma, *J. Appl. Polym. Sci.*, 33, 151, 1987.
116. G. T. Kwiatkowski, L. M. Robeson, G. L. Brode, A. W. Bedwin, *J. Polym. Sci., Polym. Chem. Edn.*, 13, 961, 1975.
117. J. S. Senger, G. York, S. Chen, K. Ung and J. E. McGrath, in the Proceedings of the American Society for Composites, 4th Technical Conference, Technomic, Lancaster, p 631-637, 1989.
118. J. S. Senger, Ph. D. Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 24061, 1990.
119. H. Stenzenberger, *British Polym. J.*, 20(5), 389, 1988.
120. M. Bergain, A. Combet and P. Grosjean, BP 119018, 1970.
121. J. V. Crivello, *J. Polym. Sci., Polym. Chem. Ed.*, 11, 1185, 1973.
122. C. M. Tung, C. L. Lung and T. T. Liar, *ACS Polym. Mat. Sci. Eng.*, 52, 139, 1985.
123. H. D. Stenzenberger, W. Romer, M. Herzog, S. Pierce, M. S. Canning and K. Fear, 31st Int. SAMPE Symp., 31, 920, 1986.

124. H. D. Stenzenberger, P. Koning, M. Herzog, W. Romer, W. Pierce and M. S. Canning, 19th Int. SAMPE Tech. Conf., 19, 372, 1987.
125. S. P. Wilkinson, S. C. Liptak, J. J. Lesko, D. A. Dillard, J. Morton, J. E. McGrath and T. C. Ward, Proceedings of the Sixth Japan-U. S. Conference on Composite Materials, June 22-24, 240, 1992.
126. International Encyclopedia of Composites, S. Lee Ed., vol. 2, VCH Publishers Inc., p80, 1990.
127. L. Schechter, J. Wynastra and R. P. Kurkky, Ind. Eng. Chem., 48(1), 94, 1956.
128. J. J. King and J. P. Bell, "Reactions in a Typical Epoxy Aliphatic Diamine System," R. S. Bauer, Ed., Epoxy Resin Chemistry, ACS Symp. Ser. 114, American Chemical Society, Washington D.C., 1979.
129. R. G. Pearson, H. Sobel and J. Songstad, J. Am. Chem. Soc., 90(2), 319, 1968.
130. C. K. Riew, E. H. Rowe and A. R. Siebert, Adv. Chem. Ser., 154, 326, 1976.
131. A. J. Kinloch, S. J. Shaw, D. A. Tod and D. L. Hunston, Polymer, 24, 1341, 1983.
132. A. F. Lee and R. A. Pearson, J. Mater. Sci., 21, 2462, 1986.
133. J. N. Sultan and F. J. McGarry, Polym. Eng. Sci., 13, 29, 1973.
134. S. Montarnal, J. P. Pascault and H. Sautereau, K. Riew Edit., Am. Chem. Soc., Symp. Series No. 222, 193, 1989.
135. W. D. Bascom, R. L. Cottingham and P. Peyer, J. Appl. Polym. Sci., 19, 2545, 1975.
136. L. T. Manzione, J. K. Gillham and C. A. McPherson, J. Appl. Polym. Sci., 26, 907, 1981.
137. S. Montarnal, J. P. Pascault, H. Sautereau, In Rubber-Toughened Plastics, C. K. Riew Ed., Advances in Chemistry, 222, American Chemical Society, Washington D. C., 193-223, 1989.
138. D. Verchere, J. P. Pascault, H. Sautereau, S. M. Moshier, C. C. Riccardi and R. J. J. Williams, J. Appl. Polym. Sci., 42, 701, 1991.

139. A. J. Kinloch and R. J. Young, "Fracture Behavior of Polymers", Applied Science, New York, 1983.
140. R. C. Laible and F. J. McGarry, *Polym. Plast. Technol. Eng.*, 27, 335, 1976.
141. C. Bucknall and T. Yoshii, *Br. Polym. J.*, 10, 53, 1978.
142. A. C. Meeks, *Polymer*, 15, 675, 1974.
143. A. C. Grillet, G. Jocelyne, J. F. Gerard and J. P. Pascault, *Polymer*, 32(10), 1885, 1991.
144. J. N. Sultan and F. J. McGarry, *Polym. Eng. Sci.*, 13(1), 29, 1973.
145. R. A. Pearson and A. F. Yee, *J. Mater. Sci.*, 24, 2571, 1989.
146. F. Haaf, H. Breuer, A. Echte, B. J. Schmitt and J. Stabenow, *J. Sci. Ind. Res.*, 40, 659, 1981.
147. S. K. Douglass, P. W. R. Beaumont and M. F. Ashby, *J. Mater. Sci.*, 15, 1109, 1980.
148. C. K. Riew, E. H. Rowe and A. R. Siebert, In *Toughness and Brittleness of Plastics*, Ed. R. D. Deanin and A. M. Crugnola, *Adv. Chem. Ser.* 154, American Chemical Society, Washington D. C., p326-343, 1976.
149. W. D. Bascom, R. Y. Ting, R. J. Moulton, C. K. Riew and A. R. Siebert, *J. Mater. Sci.*, 16, 2657, 1981.
150. A. G. Evans, Z. B. Ahmad, D. G. Gilbert and P. W. R. Beaumont, *Acta Metall.*, 34, 79, 1986.
151. A. F. Yee and R. A. Pearson, *J. Mater. Sci.*, 21, 2462, 1986.
152. C. B. Bucknall and T. Yoshii, *Br. Polym. J.*, 10, 53, 1978.
153. J. N. Sultan and F. J. McGarry, *J. Polym. Sci.*, 13, 29, 1973.
154. W. D. Bascom, R. Y. Ting, R. J. Moulton, C. K. Riew and A. R. Siebert, *J. Mater. Sci.*, 16, 2657, 1981.
155. V. T. Truong, Y. B. Truong and B. C. Ennis, *Polym. Comm.*, 32(9), 275, 1991.
156. C. B. Bucknall and I. K. Partridge, *Polymer*, 24, 639, 1983.

157. C. B. Bucknall and A. H. Gilbert, *Polymer*, 30, 213, 1984.
158. J. L. Hedrick, I. Yilgor, G. L. Wilkes and J. E. McGrath, *Polym. Bull.*, 13, 201, 1985.
159. J. L. Hedrick, I. Yilgor, M. Jurek, J. C. Hedrick, G. L. Wilkes and J. E. McGrath, *Polymer*, 32(11), 2021, 1991.
160. S. C. Kim and H. R. Brown, *J. Mater. Sci.*, 22, 2589, 1987.
161. F. Zengli and S. Yishi, *Chinese J. Polym. Sci.*, 7(4), 1988, 1989.
162. S. Amdur, A. T. Y. Cheng, C. J. Wong, P. E. Ehrlich and D. R. Allendoerfer, *J. Polym. Sci. Polym. Chem. Ed.*, 16, 407, 1978..
163. J. J. Ratto, P. J. Dynes and C. L. Hamermesh, *J. Polym. Sci. Polym. Chem. Ed.*, 18, 1035, 1980.
164. P. M. Hergenrother, *J. Macromol. Sci. Rev. Macromol. Chem.*, C19, 1, 1980.
165. P. M. Hergenrother, *Ency. Polym. Sci. Eng.*, Vol1, 2nd Ed., John Wiley and Sons, Inc., New York, 61, 1985.
166. W. T. K. Stevenson and I. J. Goldfarb, *J. Appl. Polym. Sci.*, 42, 665, 1991.
167. W. T. K. Stevenson, I. J. Goldfarb, E. J. Soloski and M. J. Houtz, *J. Appl. Polym. Sci.*, 42, 679, 1991.
168. R. Frentzel and C. S. Marvel, *J. Polym. Sci. Polym. Chem. Ed.*, 17, 1073, 1979.
169. W. Kantlehner, H. Bohme and H. G. Viehe, eds., "Iminium Salts in Organic Chemistry", John Wiley and Sons, Inc., New York, 6, 1979.
170. C. E. Castro and R. D. Stephens, *J. Org. Chem.*, 28, 2163, 1963.
171. E. T. Sabourin, *Am. Chem. Soc. Div. Petr. Chem. Prepr.*, 24, 233, 1979.
172. A. Onopchenko, E. T. Sabourin and C. M. Selwitz, *J. Org. Chem.*, 44, 1233, 1979.
173. G. Lucotte, L. Cormier and B. Delfort, *Polym. Bull.*, 24, 577, 1990.
174. W. B. Austin, N. Bilow, K. J. Kelleghan and K. S. Y. Lau, *J. Org. Chem.*, 46, 2280, 1981.

175. P. M. Hergenrother, *J. Polym. Sci. Polym. Chem. Ed.*, 20, 3131, 1982.
176. F. Martinez, J. Abajo, R. Mercier and B. Sillion, *Polymer*, 38(15), 3286, 1992.
177. B. Delfort, G. Lucotte and L. Cormier, *J. Poly. Sci. Polym. Chem.*, 28, 2451, 1990.
178. G. Lucotte, L. Cormier and B. Delfort, *J. Polym. Sci. Polym. Chem.*, 29, 879, 1991.
179. R. G. Bryant, B. J. Jensen and P. M. Hergenrother, *Polym. Prepr.*, 33(1), 916, 1992.
180. M. Strukels, M. Paventi and A. S. Hay, *Macromolecules*, 26, 1777, 1993.
181. C. Samyn and C. S. Marvel, *J. Polym. Sci. Polym. Chem. Ed.*, 13, 1095, 1975.
182. C. S. Marvel and C. Samyn, U.S. Pat. 3935167, 1976.
183. B. J. Jensen and P. M. Hergenrother, *J. M. S.-Pure Appl. Chem.*, A30(677), 449, 1993.
184. A. L. Landis, N. Bilow, R. H. Boschan, R. E. Lawrence and T. J. Aponyi, *Polym. Prepr.*, 15(2), 533, 1974.
185. P. M. Hergenrother, *Polym. Prepr.*, 21(1), 81, 1988.
186. M. D. Sefcick, E. O. Stejskal, R. A. McKay and J. Schaefer, *Macromolecules*, 12, 423, 1979.
187. J. J. Ratto, P. J. Dynes and C. L. Hamermesh, *J. Polym. Sci. Polym. Chem. Ed.*, 18, 1035, 1980.
188. S. A. Swanson, W. W. Fleming and D. C. Hofer, *Macromolecules*, 25, 582, 1992.
189. I. M. Pickard and I. M. Goldfarb, *Polym. Prepr.*, 20(2), 375, 1979.
190. R. F. Kovar, G. P. Ehlar and F. E. Arnold, *J. Polym. Sci. Polym. Chem. Ed.*, 15, 1081, 1977.
191. P. M. Hergenrother, G. F. Sykes and P. R. Young, *ACS Pet. Chem. Prepr.*, 24, 243, 1973.

192. G. I. Nosova, V. V. Kudvayavstev, Y. M. Boyarchuck, E. P. Gasilova, S. V. Lukasov, E. F. Galaktionova and T. I. Zhukova, *Polym. Sci. (Engl. Trans.)*, 34(6), 471, 1992.
193. G. W. Meyer, T. E. Glass, H. J. Grubbs and J. E. McGrath, *Polym. Prepr.* 35(1), Submitted for ACS meeting in San Diego, 1994.
194. *Chemistry of Carbon Compounds*, Edited by E. H. Rodd, Volume 3 Part A: Aromatic Compounds, Elsevier Publishing Company, New York, p 57, 1954.
195. T. Sulzberg and R. J. Cotter, *J. Polym. Sci. Polym. Lett.*, 7, 185, 1969.
196. N. I. Bekasova, V. V. Korshak, M. A. Surikova, L. I. Komarova and I. Y. Voloshina, *Polym. Sci. USSR*. A23(1), 138, 1981.
197. D. Brown, *J. Polym. Sci.*, Part B, 6, 415, 1968.
198. Y. Imai, M. Ueda and K. Otaira, *J. Polym. Sci. Polym. Chem.*, 15, 1457, 1977.
199. Z. Rapport and J. F. Bunnet, *Acta Chemica Scandinavica*, B28, 478, 1974.
200. A. Franc and V. Koudelkova, *J. Chromatography*, 170, 89, 1979.
201. W. T. Janaki and N. Rathinammal, *J. Indian Chem. Soc.*, LXIV, 250, 1987.
202. I. Onyido and J. Hirst, *J. Phy. Org. Chem.*, 4, 367, 1991.
203. T. A. Emokpae, J. Hirst and P. U. Uwakwe, *J. Chem. Soc. Perkin Trans.*, 2, 2191, 1990.
204. M. J. Jurek and J. E. McGrath, *Polymer*, 30, 1552, 1989.
205. S. Jayaraman, G. Meyer, T. M. Moy, R. Srinivasan and J. E. McGrath, *Polym. Prep.*, 34(1), 513, 1993.
206. T. Yoon and J. E. McGrath, *J. Adhesion*, accepted, 1993.

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