Synthesis and Characterization of Poly(Arylene Ethers) and Functionalized Oligomers

by

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(ABSTRACT)

Molecular weight control and endgroup functionalization in poly(arylene ether sulfones) has been achieved by two synthetic routes. The first utilizes DMSO/sodium hydroxide and aminophenol to introduce the amine functionality. This route, though synthetically useful, suffers from serious limitations, such as hydrolytic side reactions and oxidation of the end capping reagent. An alternative route utilized K_2CO_3/NMP as base and solvent respectively. This approach has been used with great success in the preparation of both high molecular weight polymers and functionalized oligomers. We have extended this method to include amine terminated oligomers through the use of a novel aminophenolic compound 2-p-aminophenyl-2-p-hydroxyphenylpropane or MBA. The use of MBA to introduce terminal amine functionality allowed a simpler, 1-step synthesis of controlled molecular weight oligomers to be realized. Our investigations focused on bisphenol-A based systems, but this technique may be also utilized with other bisphenols.

The synthesis and characterization of a wide variety of derivatives of these functionally terminated oligomers was demonstrated. A number of potential post reactions involving these oligomeric diamines were investigated and synthetic techniques to prepare novel block and segmented copolymers were defined. As the molecular weight of the sulfone oligomer was varied, the percent sulfone character in a given polymeric material could be systematically changed. The effect was studied in block copolymers with poly(amide sulfones) and in novel modified epoxy and bismaleimide thermosetting systems.

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DEDICATION

To my mother, Joan, my brother David, and Nana, who have all been sources of inspiration and strength throughout my college career.

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GLOSSARY OF ACRONYMS

ATI	Acetylene Terminated Polyimides
ATPQ	Acetylene Terminated Phenyl Quinoxalines
ATS	Acetylene Terminated Sulfone
BIS A	Bisphenol A
BMI	Bismaleimide
BP	Biphenol
BTDA	Benzophenone Tetracarboxylic Acid Dianhydride
DBA	Diamino Derivative of Bisphenol A
DGEBA	Diglycidyl Ether of Bisphenol A
DMF	N,N'-Dimethyl Formamide
DMSO	Dimethyl Sulfoxide
DSC	Differential Scanning Calorimetry
ETS	Ethynyl Terminated Sulfone Oligomers
GPC	Gel Permeation Chromatography
HQ	Hydroquinone
IPA	Isopropanol
MBA	Monoamino Derivative of Bisphenol A
MDA	Methylene Dianiline
NH_2PSF	Diamine Terminated Poly(Arylene Ether Sulfone)
NMP	N-methylpyrrolidone
ODA	Oxydianiline
PBD	Poly(Butadiene)
PEO	Poly(Ethylene Oxide)
PMMA	Poly(Methyl Methacrylate)
PPE	Poly(Phenylene Ether)

PS	Poly(Styrene)
PTHF	Poly(Tetrahydrofuran) or Poly(Tetramethylene Oxide) PTMO
PVC	Poly(Vinyl Chloride)
SED	Sulfone Ether Diamine
TBA	Torsional Braid Analysis
TEA	Triethylamine
THF	Tetrahydrofuran
TMA	Thermal Mechanical Analysis

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Chapter 1

INTRODUCTION

The major trend in polymer chemistry today is no longer necessarily focused on the preparation of new homopolymers, but rather, significant effort is oriented towards modified polymer systems. The number of block and graft copolymers, polymers modified by post reactions and polymeric blends has greatly increased, as our knowledge of the important polymer parameters has widened. A major objective of this investigation was to synthesize a wide variety of difunctionally terminated oligomers by improved procedures and to characterize their structure, reactivity and physical behavior. Another aim was to incorporate these reactive intermediates into novel block copolymers or networks via post reactions and to establish some basic structure-property relationships for these new materials.

Thermoplastic poly(arylene ether sulfones) prepared through step-growth polymerization techniques have many desirable properties and were employed throughout this study as oligomeric backbone structures. The detailed synthetic schemes for this work will be discussed in a later section. This section will begin with a general treatment of step-growth polymerization, followed by a literature review of pertinent functionally terminated oligomeric systems.

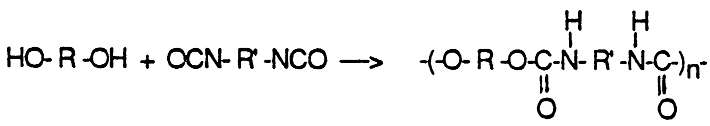
1.1 *Step-Growth Polymerization*

The classical division of macromolecules into addition or condensation polymers as proposed by Carothers may no longer be sufficiently precise, but it is useful and deeply entrenched in current thinking [1]. A review of this original classification and reasons for its limitations will be discussed in this section, as well as the accepted meaning of the term condensation or step-growth polymerization.

A condensation or step-growth polymer was originally defined as one in which the repeating unit lacks certain atoms initially present in its constitutent monomer(s). These polymers were formed from bi- or polyfunctional monomers by reactions involving elimination or ″condensation″ of some smaller molecule. Thermoplastic and thermosetting step-growth or condensation polymers were defined with polyesters and phenol-formaldehyde resins as examples of each respectively.

A more useful definition focuses on the kinetics and mechanism of the polymerization process rather than on the polymeric structure formed [2]. Some of the main features of a step-growth polymerization are as follows [3].

1. The growth of a polymer molecule proceeds via step-wise intermolecular reaction and involves only one reaction type.
2. Monomer units can link with one another or with oligomeric species of any size. Polymer molecules form over the course of the entire reaction, and growth occurs as reactive ends meet to form a link.
3. All functional groups are assumed to be of equal reactivity, whether they are monomers or polymeric chains of any length.
4. Many step-growth polymers involve an equilibrium between reactants on one hand and macromolecular plus small molecule products on the other. Some high molecular weight polymers cannot coexist with such monomers in equilibrium systems. All molecular species are present in calculable distributions and the course of the polymerization is statistically controlled.
5. Condensation polymers by the above definition are produced in a step-growth polymerization technique. Conversely, all step-growth polymerizations cannot be thought of as producing condensation polymers. An example of this is a polyurethane synthesis, as illustrated in equation (1), in which no small molecule is eliminated.



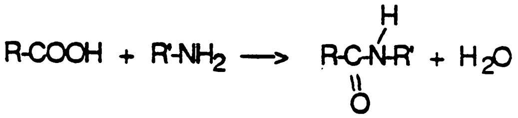
$$HO\text{-}R\text{-}OH + OCN\text{-}R'\text{-}NCO \longrightarrow \text{-}(O\text{-}R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}\overset{\overset{H}{|}}{N}\text{-}R'\text{-}\overset{\overset{H}{|}}{N}\text{-}\underset{\underset{O}{\|}}{C}\text{-})_n\text{-} \qquad (1)$$

Yet this reaction exhibits the kinetics and most other characteristics associated with step-growth polymerizations.

These features illustrate, in part, the requirements for obtaining high molecular weight polymers. One must also work with highly pure monomers (typically > 99.9% pure). Secondly, if two reactants are utilized, a perfect stoichiometric balance of the two difunctional monomers must be maintained. Thirdly, there must be an absence of side reactions (feature 1) and finally, conditions must exist that allow the reaction to be pushed to very high conversions (features 4 and 5).

Thus, for step-growth reactions, molecular weight increases only slowly until one reaches very high conversions as illustrated in Figure 1. In fact, the overall process is governed by the fractional extent of conversion, usually designated as "P". For example, if one started with 1.0 mole of phenolic hydroxyl groups, it would be necessary to consume approximately 99% of that one mole, or reduce the concentration to 0.01 moles, before one could anticipate reaching high molecular weight. Thus if monomers were less than 99% pure, it would be impossible to obtain chain lengths great enough to obtain adequate mechanical properties. The molecular weight is proportional to $1/(1-P)$.

As an illustration of a linear step-growth process, one may refer to equation (2), which illustrates a model amidation reaction



$$R\text{-}COOH + R'\text{-}NH_2 \longrightarrow R\text{-}\underset{\underset{O}{\|}}{C}\text{-}\overset{H}{N}\text{-}R' + H_2O \qquad (2)$$

Here, an amine is shown reacting with a carboxylic acid to form an amide with the elimination of water. If one envisions utilizing two perfectly difunctional monomers, a linear species results. Also, R and R′ may be monomeric units, as well an oligomeric species. The implication of this (features 2 and 3) is that all oligomers are capable of reacting with other suitably terminated species, whether they are trimers reacting with monomers, dimers, trimers, etc. In the general case, one considers an n-mer reacting with an m-mer to produce the next higher (m + n) oligomer. Therefore, as the molecular weight slowly builds through the major portion of the reaction, a variety of oligomeric species exist. These must in turn react with each other to ultimately generate high molecular weight. This entire process must, of course, continue until P begins to approach 0.99 or higher.

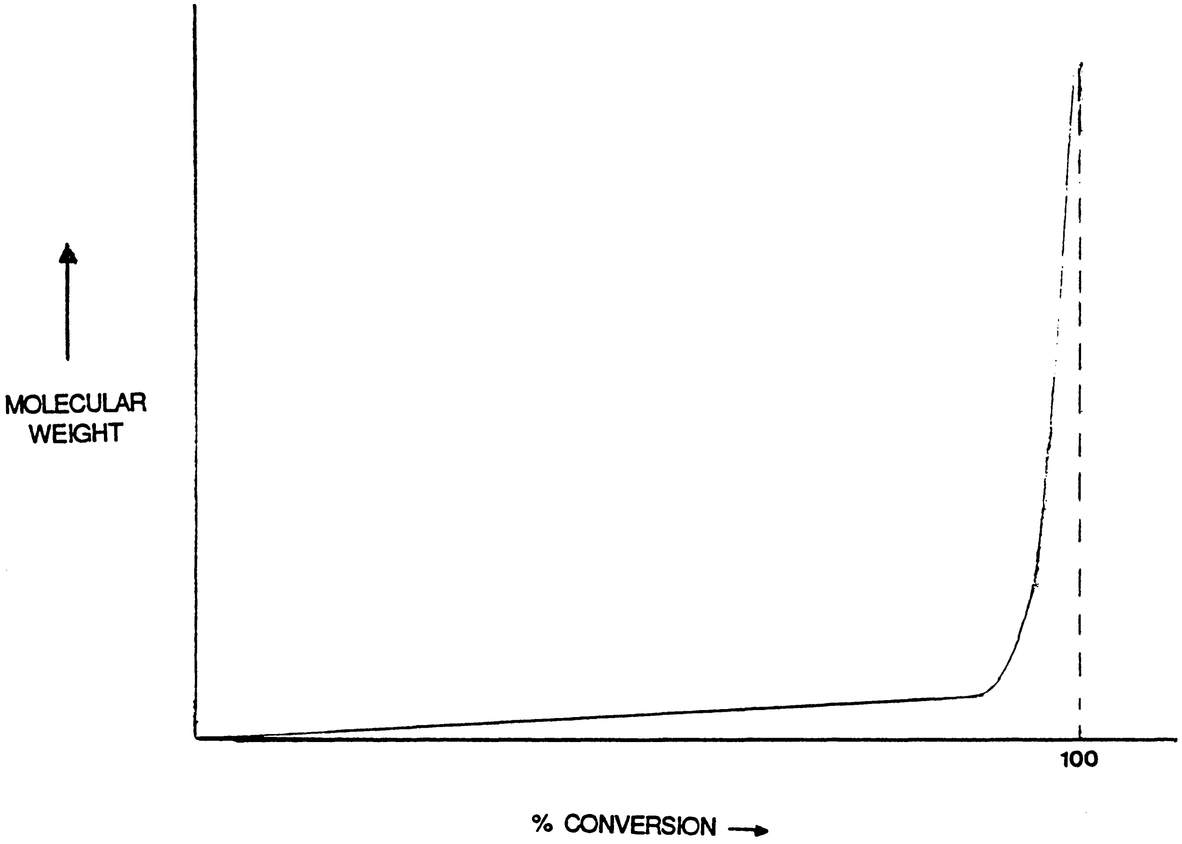


Figure 1: Dependence of molecular weight on percent conversion in a step-growth polymerization

Since the amidation reaction is an equilibrium process, the water (or HCl if the acid chloride derivative is used) often must be removed in order to drive the reaction to the right, towards higher conversions (greater P) and hence high molecular weight.

The rate of polymerization in a step-growth reaction is proportional to the group collision frequency and is not dependent on the diffusion rate of the entire chain. It has been demonstrated that the second functional group on a growing chain is not influenced by the first if it is separated by several carbon atoms. This, in essence, leads to the principle of equal reactivity. This means that the reactivity of growing molecules will not change significantly during the course of the polymerization, since a statistical chain segment effectively determines reaction kinetics and this statistical segment is more mobile than the entire molecule. Although sterically hindered reactants and heterogeneous processes are exceptions, the principle of equal reactivity has allowed these reactions to be treated statistically. Proof that this principle is essentially correct may be illustrated by the correct predictions of molecular weights and molecular weight distributions.

A most important principle in step-growth polymerizations is the understanding of the Carothers equation. This is a basic equation governing the theoretical predictions of molecular weight and it can be used to design very high molecular weight polymers or functionally terminated oligomers of controlled molecular weight. There are three basic assumptions which must hold for the derivation of the Carothers equation.

1. The reactivity of all functional groups of the same kind are equivalent and independant of the size of the molecule to which it is attached. As the polymerization nears completion, the rate of polymerization is low, not because of low reactivity of the functional groups, but due to their low concentration.
2. All functional groups in an n-functional monomer are of equal reactivity. (This assumption breaks down in a few cases, notably the 2,4- vesus the 2,6-isomer of toluene diisocyanate, TDI. The group in the 2- or 6-position will be less reactive due to steric crowding as compared to the group in the 4-position.)

3. Finally, the proper derivation of the Carothers equation assumes a single phase, homogeneous reaction mixture.

Using these basic assumptions, the Carothers equation may now be derived [4].

Functionality may be defined as the number of reactive positions in a monomer unit. If F_i denotes the functionality for species i, and there are N_i moles of such species, then one can define F_{av}, the average functionality or the number of functional groups per monomer molecule as;

$$F_{av} = \frac{\Sigma N_i F_i}{\Sigma N_i} \tag{3}$$

Next we will need to define P, the extent of reaction, as the number of functional groups used to the number of functional groups initially present.

Let $\Sigma N_i = N_o$, the total number of monomer units initially present and let N represent the total number of unreacted monomer and various polymeric species when the extent of reaction is P. Hence, at this stage, (N_o-N) number of linkages have been formed. Two functional groups are necessary to form one linkage, thus 2(N_o-N) number of functional groups have been used when the extent of reaction is P. Therefore, P can now take the form

$$P = \frac{2(N_o - N)}{N_o F_{av}} \tag{4}$$

Now N ≡ the number of remaining molecules and is equal to $1/2(2N_o - PN_oF_{av})$. The number average degree of polymerization for the reaction mixture is $<X_n>$, defined as being equal to the total number of monomer units divided by the number of remaining molecules,

$$<X_n> = \frac{N_o}{1/2(2N_o - PN_oF_{av})} \tag{5}$$

or simplifying,

$$\langle X_n \rangle = \frac{1}{1/2(1-PF_{av})} \qquad (6)$$

Assuming F_{av} is 2.0 for preparation of linear species,

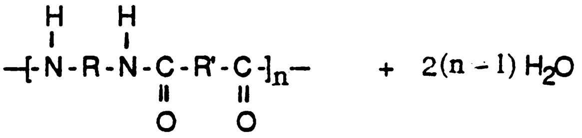
$$\langle X_n \rangle = \frac{1}{1-P} \qquad (7)$$

which illustrates that at very high extents of reaction, as P→1, $<X_n> \rightarrow \infty$. This theory predicts formation of a polymer of infinite molecular weight at the unrealistic value of P = 1.

Now let us consider the following A-A/B-B system for a polyamide.

$$n\,H_2N\text{-}R\text{-}NH_2 \;+ n\,HOOC\text{-}R'\text{-}COOH$$

F = 2.0	F = 2.0
A-A	B-B



$$-\!\!\left[\overset{H}{\overset{|}{N}}\text{-}R\text{-}\overset{H}{\overset{|}{N}}\text{-}\underset{O}{\underset{\|}{C}}\text{-}R'\text{-}\underset{O}{\underset{\|}{C}}\right]_n\!\!- \quad + \quad 2(n-1)\,H_2O \qquad (8)$$

Let N_A = the number of moles of amine functional groups and that of the acid functional groups to be N_B. Then:

$$\frac{N_A + N_B}{2} = N_o \qquad (9)$$

Now if we introduce r and define it as the stoichiometric imbalance or the ratio of N_A to N_B, then

$$N_o = \frac{N_B + rN_B}{2} = \frac{N_B(1+r)}{2} \tag{10}$$

Now since P is defined as the fraction of a functional group reacted at any instant of time, let the fraction of A groups, the amine, be P and that of the B groups be rP. Now, the fraction of unreacted A and B groups are (1-P) and (1-rP), respectively and the total number of unreacted A and B groups are N(1-P) and N(1-rP) respectively. Therefore, the total number of molecules that contain unreacted A and B groups are

$$\frac{N_A(1-P) + N_B(1-rP)}{2} \tag{11}$$

Recalling a previous definition of $<X_n>$ [substituting equation (4) and (9) into Equation (5)];

$$<X_n> = \frac{\frac{N_A + N_B}{2}}{\frac{N_A(1-P) + N_B(1-rP)}{2}} \tag{12}$$

continuing:

$$\frac{N_A + N_B}{N_A + N_B - PN_A - rPN_A} = \frac{N_B(1 + r)}{rN_B + N_B - PN_A - rPN_B} \tag{13}$$

and finally:

$$\langle X_n \rangle = \frac{N_B(1 + r)}{N_B(1 + r - 2rP)} \tag{14}$$

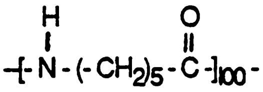
Again, one can see that in the limit of P→1,

$$\langle X_n \rangle = \frac{1 + r}{1 - r} \tag{15}$$

Equations (15) and (7) are intimately associated and of paramount importance. If $r = 1$, then in principle it should be possible to obtain a polymer chain of infinite molecular weight (as obtained earlier). Therefore by maintaining r very close to unity, high molecular weight polymers can be obtained.

Alternately, one can also systematically vary r in a desired fashion to control $< X_n >$. For example, if the amine is used in excess over that of the acid (Equation 8), r has a value less than one and it becomes possible to calculate a value, $< X_n >$, for the final product and furthermore to state that all oligomers would be amine terminated.

Another important aspect of the condensation polymerization process needs to be discussed and classified before proceeding any further. The term $< X_n >$ is defined here as the number average degree of polymerization of the polymerizing mixture and is not necessarily the same as the degree of polymerization, D.P. The D.P. is defined as the average number of repeating units per polymer molecule. We will now look at two examples to clarify this point. In an A-B system such as poly (ε-caprolactam) or nylon 6;



$$-[-\overset{H}{\overset{|}{N}}-(-CH_2)_5-\overset{O}{\overset{\|}{C}}-]_{100}-$$

Both D.P. and $<X_n>$ have the same value, 100. However in an A-B/B-B two component systems such as poly(hexamethylene adipamide) the D.P. and $<X_n>$ are quite different. $<X_n>$ is defined as 1.0 for each monomer. The D.P. in this case must be taken as the mean of the two, and, if it is, for example 100, $<X_n>$ is 200. Although there are the same average number of repeating units per molecule in each case (D.P. = 100), the A-A/B-B system contains twice as many molecules per repeat unit as does the A-B system. Hence one would acknowledge the average degree of polymerization, $<X_n>$, to be two times greater for the 2-component system than that found in the 1-component system.

Let us suppose one wishes to prepare a diamine terminated nylon 6,6 oligomer of 5000 g/mole. Then, since the molecular weight of the repeat unit is 226.4,

$$\text{D.P.} = \frac{5000}{\text{Molecular weight of repeat unit}} \tag{16}$$

$$= 22.08$$

Therefore

$$<X_n> = 2(\text{D.P.}) = 44.16$$

and substituting into Equation 15;

$$44.16 = \frac{1+r}{1-r}$$

yields

$$r = 0.956$$

Since amine terminated oligomers are desired, excess diamine must be employed in the reaction. The proper amounts of hexamethylene diamine and adipic acid necessary to achieve this objective are 1.0 and 0.956 moles respectively. Molecular weight control may also be achieved by the addition of a small amount of a monofunctional reagent. In the aforementioned case with nylon

6,6, a small amount of benzoic acid yields a polyamide with unreactive phenyl endgroups. The polymer now possesses chain ends devoid of reactive functional groups, imparting enhanced stability with respect to certain polymer properties. The required calculation for this process is

$$r = \frac{N_A}{N_B + 2N_B'} \qquad (17)$$

where N_A and N_B are the moles of diamine and diacid as before and $2N_B'$ is the number of moles of benzoic acid. The coefficient 2 is used because 2 moles of the monofunctional reagent are necessary to maintain the same stoichiometric imbalance, r, as would 1 mole of the difunctional adipic acid. The same approach can be utilized in an A-B system where monofunctional reagents can be used as well as an A-A or B-B monomer.

The primary objective of molecular weight control in polymers has historically been associated with processability and cost. An infinite molecular weight polymer would possess a high viscosity and would be costly and/or impossible to process. A second objective is to preserve the shelf life of a polymer. Polymer properties are dependent on molecular weight and reach a 'plateau' where it takes a great increase in molecular weight to provide further noticable improvements in properties. A generalized look at this behavior may be seen in Figure 2. A point referred to here as $<MW_{(\min)}>$, is the minimum molecular weight necessary for attainment of reasonable polymeric properties. For commercial step-growth thermoplastic polymers, these values are often in the area of $<M_N>$ = 20-30,000 g/mole. In addition, non-functional polymeric endgroups should enhance polymer melt and lifetime stability. Reactive endgroups, such as amines, may under certain conditions continue to react in the final product or in subsequent processing steps.

A logical extension of molecular weight control/end group functionalization was the preparation of functionally terminated oligomers possessing reactive end groups. A system can be defined with monomers A-A, B-B, and B-C where 'C' is unreactive in the polymerization reaction toward 'A' or 'B'. Hence the B-C monomer can be mathematically treated as a monofunctional

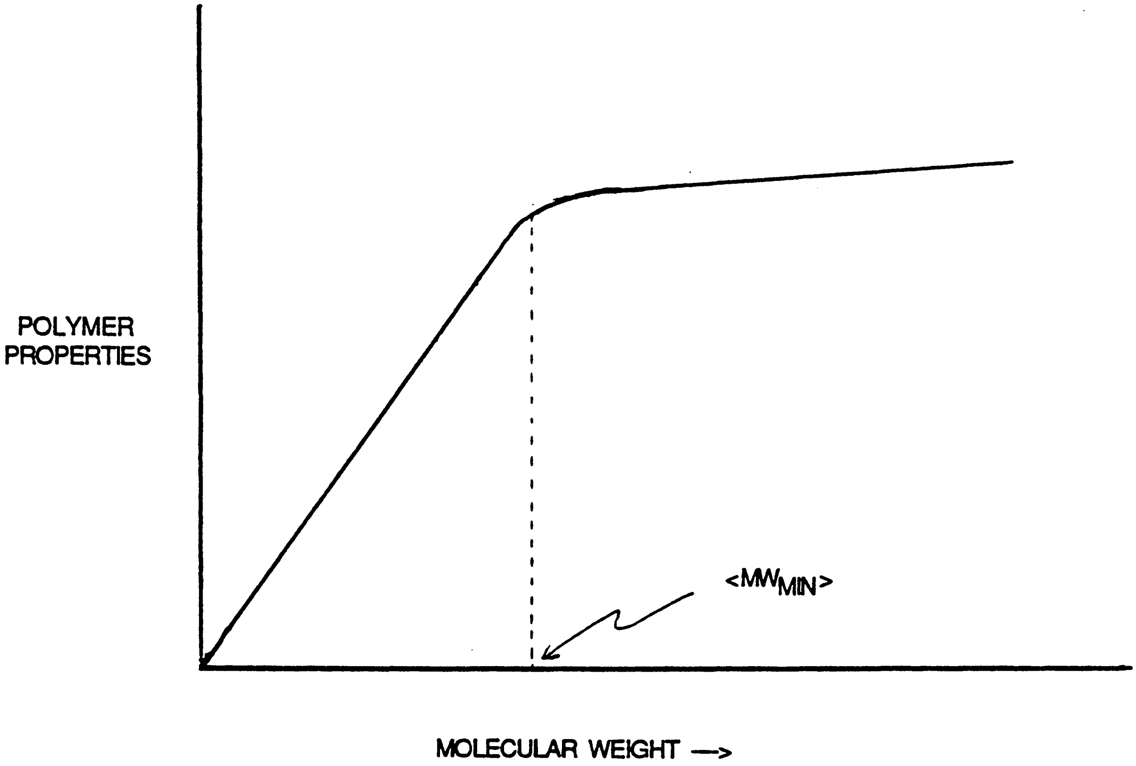
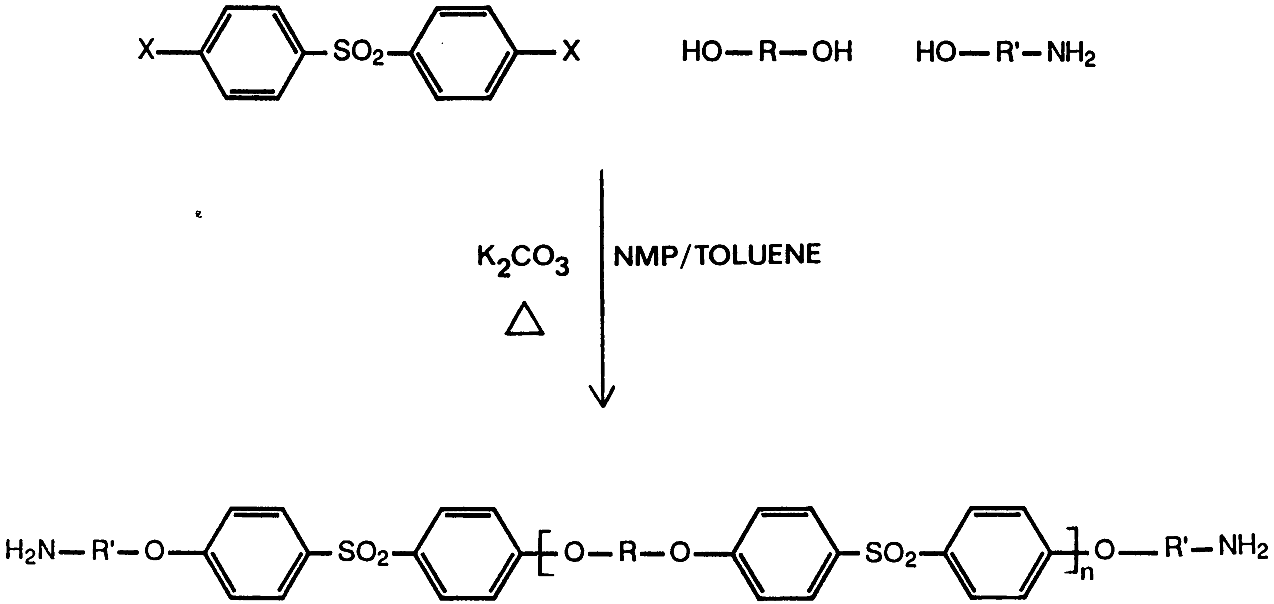


Figure 2 : General effect of polymer molecular weight on final properties

reagent, as in the case presented previously, using Equation (17). Oligomeric species can now be prepared with predictable molecular weights containing reactive endgroup functionalities.

An example that successfully illustrates this point is a central theme of this dissertation. Equation (18) shows the reaction of an activated aromatic halide with a bisphenol and an end-capping reagent. This nucleophilic aromatic substitution reaction yields a molecular weight controlled arylene ether sulfone oligomer which is also diamine terminated. The aromatic amine endgroups are unreactive during the course of the nucleophilic aromatic substitution reaction. However, these oligomeric diamines can be further reacted as expected in typical reactions employing diamines, i.e., with diepoxides, diacid chlorides, etc.

Essentially, step-growth polymerizations can be viewed as a quantitative form of organic chemistry. There are embarassingly few organic reactions (to the non-polymer chemist) that are suitable for obtaining the >99%+ yields necessary for high molecular weight polymer synthesis. There are however, a large number of laboratory prepared systems known [3]. Once again the only necessities for a successful step-growth polymerization are the previously described four basic requirements: monomer purity, stoichiometric balance, absence of side reactions and very high conversions.


X—SO$_2$—X
HO—R—OH
HO—R'—NH$_2$
K_2CO_3
△
NMP/TOLUENE
H$_2$N—R'—O—SO$_2$—[O—R—O—SO$_2$]$_n$O—R'—NH$_2$

(18)

Chapter 2

LITERATURE REVIEW OF FUNCTIONALLY TERMINATED OLIGOMERS

2.1 *INTRODUCTION*

During the last 25 years, much research has been directed towards improving the processability of high temperature polymers. Most approaches have involved the incorporation of flexible moieties within the polymer backbone to permit processing as thermoplastics, or the placement of reactive groups on oligomeric chain ends which could be further reacted to chain extend the molecular weight. The applications of reactive oligomers depend on their chemical structures, which, in turn, affect the rheology and other physical characteristics of the resulting material. Successful preparation of a particular reactive oligomer which meets with desired specifications requires an understanding of the structure-property relationships of the polymeric system as well as the control of the chemistry involved.

Functionally terminated oligomers may be broadly classified into two groups depending on their method of incorporation into polymer systems. The first group contains endgroup functionalities such as amines or hydroxyl groups that lend themselves to chemical post reactions which yield block or segmented copolymers. The second group contains thermally polymerizable endgroups such as acetylenes or maleimides. The following section will begin with a review of thermally polymerizable oligomers, followed by a section concerning block copolymer synthesis from functionalized oligomers.

2.1.1 *Acetylene Terminated Oligomers*

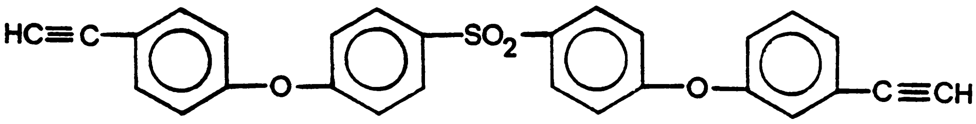
Thermosetting resins are generally composed of low molecular weight oligomers for fabrication convenience which upon curing convert to infusible, crosslinked network insoluble in all solvents. Because of this irreversible crosslinking reaction, some very useful physical properties such as heat and creep resistance, mechanical strength, etc., are obtainable through proper design of the polymer structure. Thermosetting resins have been used extensively in industry for applications such as structural adhesives, composites, reaction injection moldings, coatings and sealants which need to resist severe service conditions.

The acetylene (ethynyl) group has attracted attention in polymer and polymer precursor systems due to its synthetic versatility, long pot-life, relatively wide processing latitude, and low moisture sorption. The acetylenic groups can in principle react via free-radical, cationic or coordination initiation or by "thermal" treatment [5]. The work on thermally curable acetylene-containing materials over the last 10 years has produced several significant advances such as: (1) a new inexpensive synthetic route to acetylene-containing compounds, (2) fundamental information on chemical structure - cure - property relationships; (3) cured resins with attractive properties; and (4) a technology providing a broad scope of resin products for various applications [6].

Polymeric or "resin" chemistry research has focused primarily on the thermally induced reaction leading to chain extension, branching, crosslinking and rigidification. Oligomers and polymers containing acetylenic (end) groups have excellent shelf-lives, can be cured under moderate conditions without the evolution of volatiles and cured resin systems possess better solvent and moisture resistance in comparison to uncrosslinked materials, as well as a favorable combination of mechanical and physical properties [7].

Although many diacetylenic (diethynyl) compounds have been reported, relatively little work has been disclosed regarding the nature of the product obtained from the thermal reaction of simple diacetylenic compounds [6]. This is generally due to the insolubility of the products which makes identification and structural characterization difficult. The complexity of the system can be illustrated with some of the potential pathways: Straus coupling results in enynes, Glazer coupling gives rise to diacetylenes, Diels-Alder products are possible as well as trimers, naphthalenes and conjugated polyenes. Early work naively suggested that the chain extension occurred primarily via trimerization of the ethynyl groups [8], but later work [9,10] revealed the greater complexity of the reaction. Using solid state ^{13}C NMR with cross polarization techniques and magic angle spinning, the product obtained after curing for 4 hours each at 340 and 370°C was characterized [10]. All acetylene character was apparently lost, but not more than 30% of the acetylene groups underwent trimerization; a number of other reactions predominated.

Significant effort has been directed at the synthesis and polymerization of bis [4-(3′-ethynylphenoxy)phenyl] sulfone, 1



1

which is more commonly referred to as acetylene terminated sulfone or ATS [11]. An early attempt to synthesize this material utilized a nucleophilic displacement reaction of potassium 3-ethynylphenoxide with bis(4-chlorophenyl) sulfone in dry DMSO at 100°C. The resultant tacky yellow gum, T_g = 14°C, was an 85/15% mixture of ATS and two low molecular weight vinyl ether oligomers [12]. These oligomers resulted from the addition of a phenoxide salt across a terminal ethynyl group. To eliminate this side reaction, an alternate synthesis employing a palladium catalyzed reaction of bis[4-(3′-bromo phenoxy) phenyl] sulfone with 2-methyl-3-butyn-2-ol was developed [13]. This protecting group was subsequently cleaved with sodium hydroxide. This method provided purer material and less oligomer.

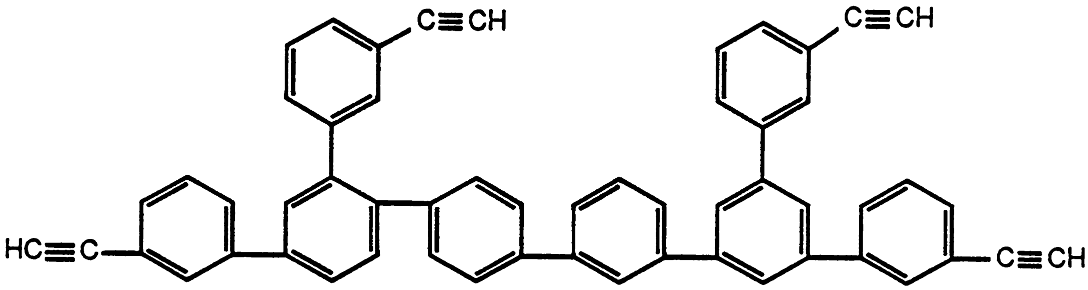
A lower cost methodology employs the Ullmann ether reaction, but still results in a mixture of ATS (79%) and oligomeric species (21%) [14]. Pure ATS is reported to be nearly a white crystalline solid, M.P.= 50°C, but no work has been disclosed on this material. This may be due chiefly to the advantages realized with oligomers present in the system. Oligomers can function to depress the melting or softening point, thus providing a desirably tacky material at room temperature. Thus a resultant melt-impregnated adhesive tape or prepreg would be tacky at room temperature. The average molecular weight between crosslinks, $<M_c>$, in this material after curing will be greater, leading towards more flexible behavior.

The properties of cured ATS are dependent on the time, temperature and atmosphere of the curing stage [15,16]. As one would expect, higher cure temperatures (up to ≅300°C) result in resins with higher T_g's since molecular segmental motion is essential for bulk reactions to occur. The $T_{g\infty}$ for a cured ATS is reported to be at 360°C.

ATS has also been evaluated as a reactive plasticizer in various linear poly(arylene ether sulfones) [17-19]. During the curing stage, its role was to lower the melt temperature, and accordingly, the processing conditions without severely altering the mechanical properties. Blends of various amounts of ATS (T_g = 0°C) with Radel® (T_g = 270°C) showed significantly improved processability and when cured, better solvent resistance under stress, together with a higher T_g (240°C). Similar results were obtained for blends of ATS with UDEL P-1700 poly(arylene ether sulfone) [18]. Other acetylene terminated resins based on bisphenol A, its hexafluoroisopropylidene substituted derivative and several other compounds have recently been reported [19,20].

These ATS systems are, in general, not well-defined systems since they contain both vinyl and ethynyl polymerizable groups. Attempts to study the chemical structure-curing-property relationships of purely ethynyl containing oligomers prompted the development of systems with better synthetic control over the position and amount of ethynyl groups.

Acetylene terminated phenylene oligomers were introduced semi-commercially in 1974 by Hercules under the name of H-Resin [22]. These materials were synthesized from the reaction of aromatic diacetylenes, i.e. diethynylbenzenes [23], with Ziegler-Natta catalysts ($TiCl_4/AlEt_2Cl$) to yield oligomers with a representative structure as shown in $\utilde{2}$. Upon curing between 200-300°C, a highly crosslinked resin is produced via addition reactions. A low strength, highly brittle very crack sensitive material results. This should have been expected since the $<M_c>$ is small and the large amount of rigid phenylene groups allow little molecular motion to develop energy dissipation pathways. Although this material circumvented the problem of containing more than one polymerizable moiety, e.g. extra vinyl ether groups, it still did not yield good structure-property correlations due to its largely unknown structure and obvious mixture of products.



2

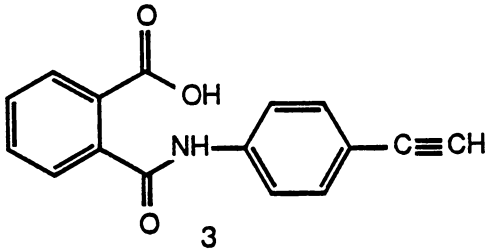
Due to its poor combination of properties, processability and price, H-Resin was not commercially successful.

A somewhat simpler approach to study the thermal crosslinking reaction employed the synthetic methodology of linear, oligomeric materials containing either pendant or terminal ethynyl groups [6]. To maintain the focus on functionally terminated oligomers, the very interesting area of pendant polymerizable groups will not be presented here.

Most synthetic pathways to these difunctionally terminated oligomers involve the controlled molecular weight procedures available in step-growth polymerizations, as outlined in the previous chapter. Assuming known molecular weights and functionalities of 2.0 for these prepolymers, the effect of backbone molecular weight on cured resin properties could then be studied with greater confidence. In essence, the $<M_n>$ of the starting oligomer becomes the $<M_c>$ for the network after curing. Hence these materials may be useful in modeling network systems. Thermoplastics such as polyether sulfones and polyimides have been extensively used since they possess many desirable properties; among them, good strength, high T_g, high modulus and flexibility. The insertion of crosslinks in thermoplastic materials would be expected to increase solvent resistance, impart greater strength and increase the structural rigidity of the resultant matrix resin.

The first synthesis of acetylene terminated polyimides or ATI's were reported in 1974 [8,23]. These began by reacting 2 moles of an aromatic tetracarboxylic acid dianhydride (benzophenone tetracarboxylic dianhydride, BTDA) with an aromatic diamine in a polar solvent, eg. N,N'-dimethyl formamide, yielding a dianhydride terminated amic acid precursor. Further reaction of the dianhydride oligomer with an ethynyl substituted aromatic amine, followed by chemical or thermal cyclodehydration of the amic acid, results in an ATI oligomer. Equation 18 shows the synthesis of Thermid 600, a typical ATI. Through proper modification of the Carothers equation, the $< M_n >$ between ethynyl groups can theoretically be predicted.

Many structurally different ATI's have been produced from the plethora of available starting materials [24-27]. Model compound studies have been performed [29] to determine the steric and/or electronic effect of the ethynyl substituted aniline on end-capping and curing efficiency. This was done, in part, to determine why ATI oligomers terminated with 3-ethynylaniline and 3-(3'-ethynylphenoxy) aniline [26] cured properly but those employing 4-ethynylaniline failed to do so. N-(4'-ethynyl phenyl)-2-carboxybenzamide , 3, as studied as the model for the curing reaction [29].



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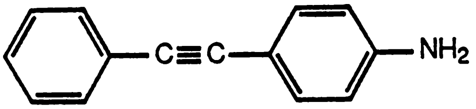
This work showed that the acetylenic group in the 4-position is converted to an acetyl group by hydration with water evolved during thermal imidization of the amic acid. Other ethynyl substituted anilines have been employed as end-capping reagents for ATI's such as 3-phenylethynyl aniline, 4, and 3-phenyl diacetylene, 5, as well as several other compounds [27].



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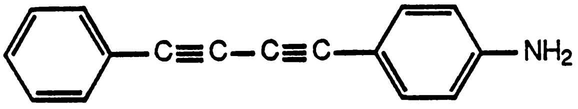

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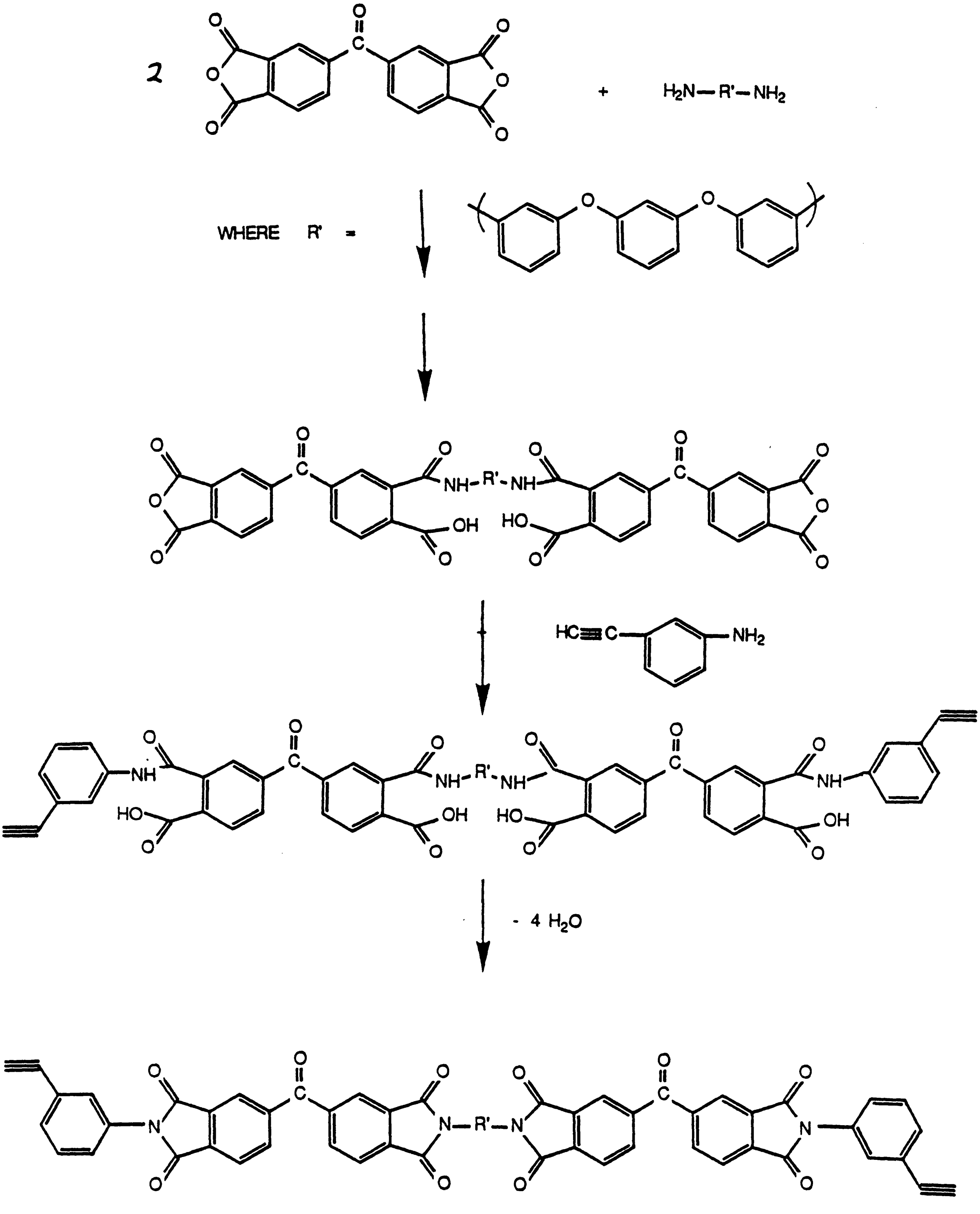


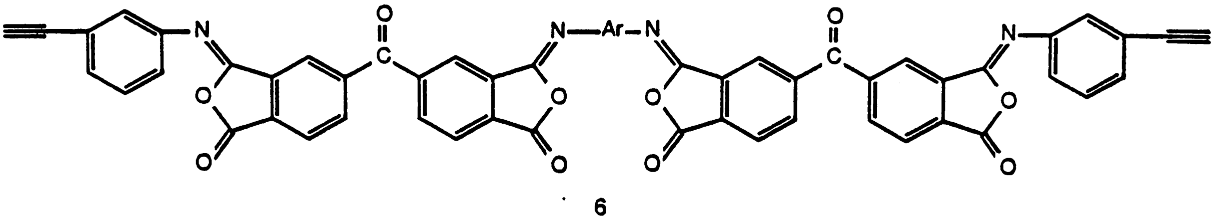
(18)

ATI's have also been synthesized by reacting 3-ethynylphthalic anhydride with amine terminated amic acids [30].

When ATI's are heated, the acetylenic endgroups undergo an exothermic reaction which can be monitored by differential scanning calorimetry (DSC) as seen in Figure 3. This behavior is typical of acetylene containing compounds in general. The first scan shows the oligomeric T_g (not indicated) and the curing exotherm. The second run shows the T_g for the cured sample [6]. The regular placement of the acetylene groups and the distance between them -- essentially the $<M_c>$ for the network -- allows for more careful examination of the system's structure-property relationships.

The properties of Thermid-600 were greatly improved over those of H-Resin [31,32]. It could be processed into unidirectional graphite fiber reinforced composites and was evaluated as adhesive in joining titanium to titanium [33,34]. In spite of this, major processing problems have plagued ATI's as well as certain other acetylene terminated heterocyclic oligomers. The ethynyl groups begin to react prior to formation of a complete melt or soft state and this inhibits the flow and wetting of the resin. This becomes even more serious due to heat transfer problems in larger sample sizes.

An attempt to circumvent the flow and solubility problems was to convert acetylene terminated polyamic acid oligomers to acetylene terminated isoimide oligomers, 6, using dicyclohexyl carbodiimide [35].



6

At high temperatures (≅300°C), the ethynyl groups react while the isoimide rearranges to the imide. This isoimide was reported to have better solubility and processability than ATI's. The

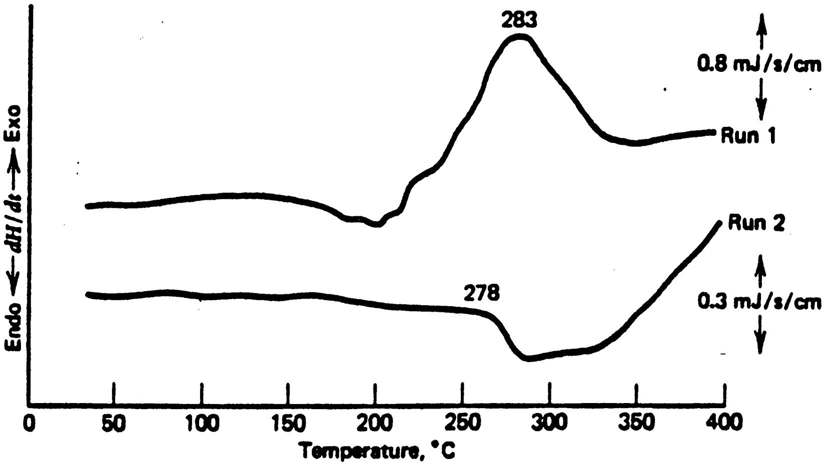


Figure 3: Differential scanning calorimetric curves of Thermid-600; sample weight: 43 mg, weight loss after heating to 400°C: 6.9%, atmosphere: nitrogen, heating rate: 20°C/min. [6]

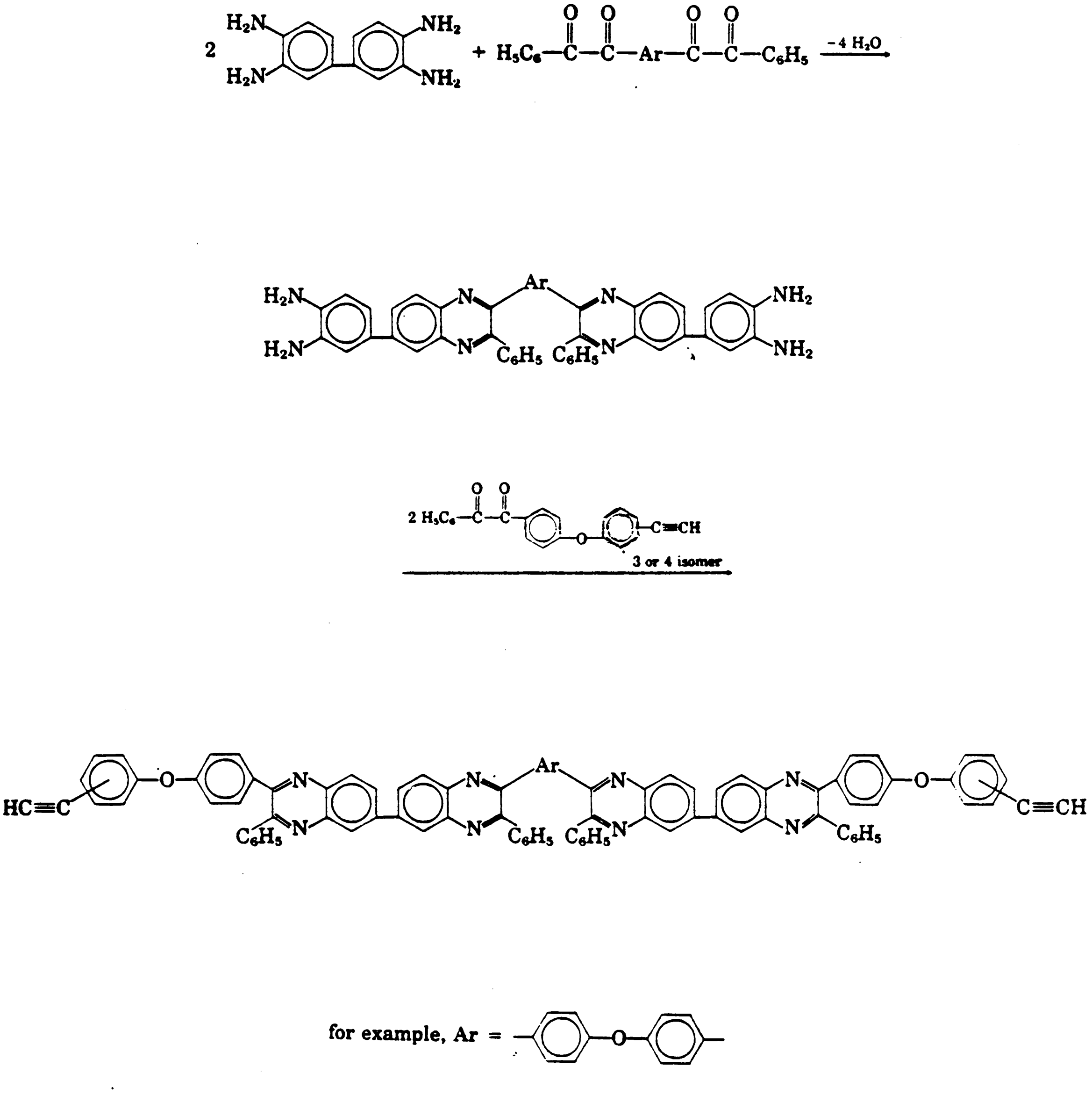
adhesive and composite properties of cured ATI's and acetylene terminated isoimide oligomers were comparable.

Another linear, high T_g thermoplastic family which could readily be functionally terminated were the poly(phenyl quinoxalines) or PPQ's. Acetylene terminated PPQ oligomers (ATPQ) were initially prepared from the reaction of 2 moles of an aromatic bis(phenyl-α-diketone), such as 4,4′-oxydibenzil (ODB) and 1 mole of 3,3′4,4′-tetraaminobiphenyl (TAB) to yield a benzil terminated oligomer. Then an end-capping reaction of the oligomer with 3-(3′,4′-diaminophenoxy) phenylacetylene provided the ATPQ [36]. Alternately, a 2:1 molar ratio of TAB to ODB has been successfully employed, and end-capping of the 1,2-diaminophenyl-terminated PPQ oligomers has been carried out with either 4-(4′-) or 4-(3′-ethynylphenoxy)benzil as illustrated in Scheme 1 [33,34]. The cure behavior and properties of the ATPQ's and their cured forms produced by the two methods are very similar. Torsional braid analysis (TBA) illustrates an intense damping peak in the 200°C range accompanied by a decrease in the relative rigidity (Figure 4). This may be due to melting, softening, or both in the ATPQ oligomer. The damping index decreases as the relative rigidity increases due to the cure process. As one approaches the T_g of the cured oligomer, the damping index again rises as the relative rigidity again decreases. Upon heating to 400°C in a nitrogen atmosphere, a T_g of 348°C was obtained [6].

As the length of the ATPQ increased, both the thermo-oxidative stability and the adhesive strength of the cured ATPQ at room temperature and 260°C increased [39]; however, processability decreased. Additionally, the acetylene terminated heterocyclic oligomers were found to be less stable under a thermo-oxidative environment than the parent linear polymer.

The modification of poly(arylene ether sulfones) with terminal acetylene groups was performed to preserve their attractive features, such as toughness and thermoformability, and to improve their solvent resistance, especially in a stressed condition. Linear poly(arylene ether sulfones), e.g. UDEL P-1700, are excellent engineering thermoplastics, but are sensitive to certain solvents, especially when under load; this precludes their use in certain applications. The neat resin or composites prepared from unmodified materials undergo stress cracking and crazing with

SCHEME 1



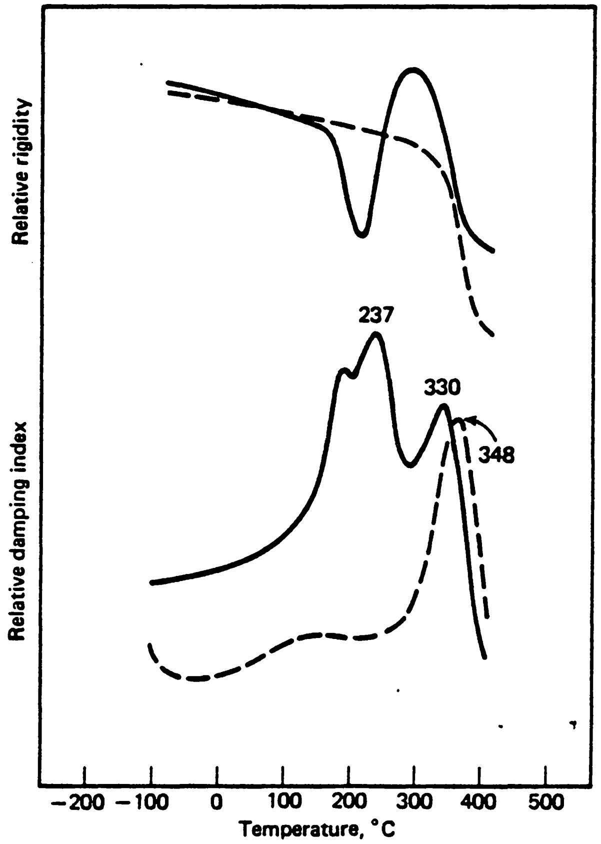


Figure 4 Torsional braid analysis curves of acetylene-terminated phenylquinoxaline oligomer; nitrogen atmosphere, ——— run 1, — — — run 2, heating rate: 3°C/min. [6]

eventual loss of mechanical integrity under chemical exposure to commonly used compounds such as jet fuels, paint strippers, deicing and hydraulic fluids.

Ethynyl terminated sulfone oligomers, ETS, have been prepared by several different methods [40,41]. The Vilsmeier reaction has been used to convert terminal acetyl groups on arylene ether sulfone oligomers to acetylenic groups [42]. Post reactions of this type may be unfavorable since most reactions are generally not quantitative (typical Vilsmeier yields ≅ 80%). Furthermore, it is difficult, if not impossible, to separate any unreacted starting oligomer or mono-acetylene adduct from the diacetylene terminated oligomer.

Improved synthetic schemes take advantage of the ease of preparing phenolic hydroxyl terminated poly(arylene ether sulfone) oligomers. Various molecular weight oligomers, $<M_n> =$ 3000 to 26,000 g/mole, of this nature can be prepared and end-capped with either 4-ethynylbenzoyl chloride [43] or 4-bromobenzoyl chloride [44]. The former reaction directly yields the ETS while the latter method results in a bromobenzene terminated oligomer. A subsequent reaction with trimethylsilylacetylene using a palladium catalyst, followed by cleavage of the trimethyl group with weak base provides the ETS oligomer. In general, the less steps one can use in the preparation of a functionally terminated oligomer, the better the chances are of obtaining the targeted system cleanly. The first end-capping method presented is more direct and hence the method of choice for an ETS oligomer synthesis.

There is, however, a slight drawback even with the direct approach. Residual palladium catalyst is contained in 4-ethynylbenzoyl chloride from its synthesis. This is known to catalyze the curing reaction of ethynyl groups, and, as a result, the peak exotherm temperature obtained in DSC or TBA is not due solely to ethynyl group reactions. For example, an ETS oligomer, $<M_n> =$ 12,000 g/mole, containing 80 and < 10 ppm palladium exhibits exothermic peaks at ≅255 and 280°C in the DSC, respectively (heating rate 20°C/min) [6]. The palladium residues will also lower the thermo-oxidative stability of the cured resin.

The relationship between the crosslink density, $<M_c>$, and solvent resistance is again evident in ETS systems of varying $<M_n>$. After curing has occured, an ETS oligomer with a lower molecular weight linear segment, for example $<M_n> = 3000$ g/mole, produces a resin which exhibits a higher T_g and better solvent resistance to chloroform than a cured ETS with a higher linear molecular weight segment, e.g. $<M_n>$ = 26,000 g/mole. It follows that the resin produced from the lower molecular weight oligomer will contain a higher crosslink density or lower $<M_c>$. The less densely crosslinked network, produced from the higher molecular weight ETS oligomer, will more freely allow solvent molecules to penetrate into the matrix than would the resin produced from a lower molecular weight oligomer.

Some preliminary mechanical property comparisons of thin films, adhesive specimens and graphite composites made from cured ETS oligomers, $<M_n>$ = 12,000 g/mole and UDEL have been reported [45]. Among the improvements of cured ETS films over those of UDEL were higher tensile modulus at 93°C, higher strength adhesive specimens at 177°C, increased flexural modulus at 177°C and improved solvent resistance to tricresyl phosphate and methylene chloride.

Another acetylene terminated system can be prepared with phenolic hydroxyl terminated polyarylates using procedures similar to those in the ETS systems [46]. Properties of these cured oligomers are quite similar to those of high molecular weight polyarylates; however, little work has been published in this area.

One last approach used to produce acetylenic containing materials is quite interesting even if it does not produce difunctional materials. First a phenolic hydroxyl terminated poly(arylene ether sulfone) oligomer is prepared. It is then reacted with an aromatic diacid chloride which contains a pendant ethynyl group [47]. The polymerizable groups in the resulting polymer are still at (relatively) known intervals approximately equal to the $<M_n>$ of the starting oligomer. This results in a system in which the $<M_c>$ can still be calculated to a high degree of accuracy. The only drawback of this system is that acetylene groups may not be as mobile to react under curing conditions as in the case where they are found exclusively at the chain ends. In the case of a $<M_n>$ = 4000 g/mole sulfone segment treated in this manner, then cured at 250°C in air, a network with properties very similar to those of a 4000 g/mole cured ETS resulted.

Acetylene containing polymers and oligomers represent a new class of high performance structural resins with excellent processability, solvent and moisture resistance and attractive mechanical properties. Considerable research and development is in progress and success of any specific system will depend heavily on its price, processing and desired end use properties.

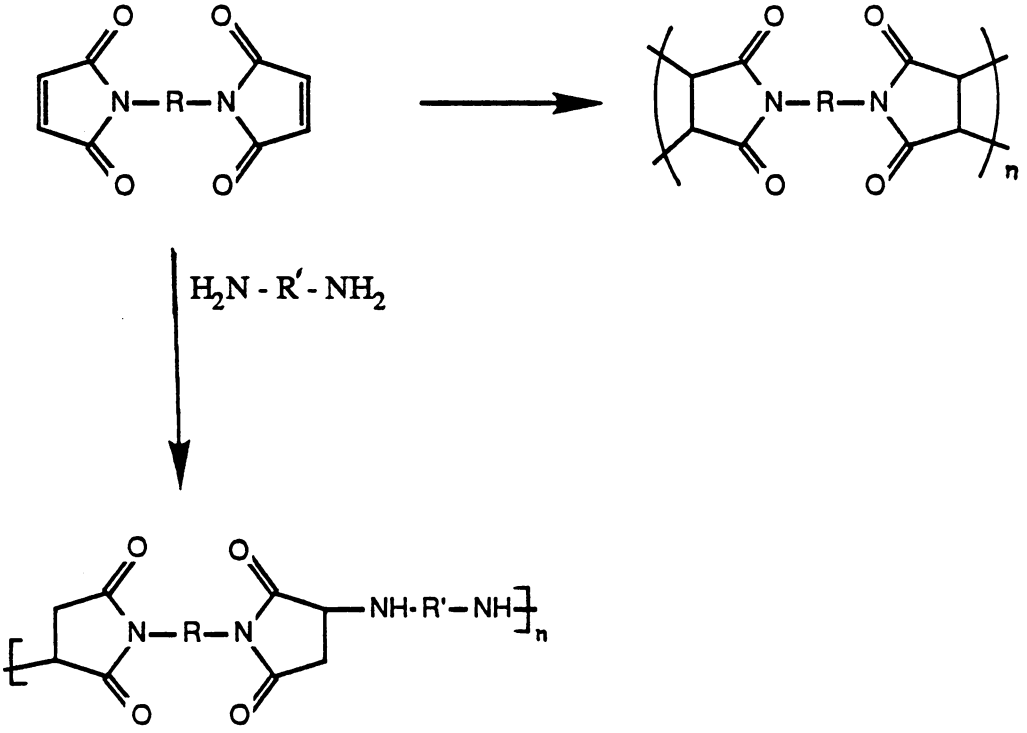
2.1.2 *Bismaleimide Terminated Prepolymers*

Bismaleimides represent another widely used class of thermally polymerizable materials [48-65]. These were first commercially introduced in the early 1970's, however, there had been interest in this area for quite some time [49]. Bismaleimides or BMI's are produced from the reaction of maleic anhydride with a diamine to yield an amic acid followed by either chemical or thermal cyclodehydration in about 70-80% yield [50]. Bismaleimides possessing widely different properties can be obtained by varying the diamine employed [51]. A crucial limitation is that the crude BMI produced must be purified, most often by recrystallization from a suitable solvent. This seriously limits the molecular weight range of BMI's to about 1000 g/mole or less. It is quite difficult, if not impossible, to separate isomeric fumarates or mono-maleimide adducts from the true BMI in systems originating from oligomeric diamines ($<M_n>$ = 1000-5000 g/mole). Hence, the focus has not been on quantification of the cyclodehydration step, but on other, less well-defined approaches.

Bismaleimide chemistry is represented in Scheme 2. Curing can be accomplished thermally through the unsaturation in the maleimide or by way of the Michael reaction, in which an appropriate curing agent such as an aromatic diamine reacts across the activated double bond. The thermal polymerization route follows first order kinetic laws as shown by differential scanning calorimetry [52] and infrared spectroscopic analysis [53].

Some attempts at higher molecular weight BMI's involve reacting a diamine with an excess of a low molecular weight BMI to produce ideally a BMI terminated prepolymer by the Michael addition pathway [54-57]. An example of this is commercially available as Technochemie H 795 resin and its synthesis is outlined in Scheme 3; the diamine employed is m-aminobenzoic acid hydrazide [54]. The molar proportion of the BMI and diamine is such that the idealized bisimide is formed as well as other intermediates in the reaction mixture. These materials contain an appreciable number of amide (and secondary amine) functionalities, which may catalyze the vinyl

SCHEME 2

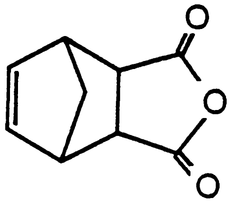


crosslinking reaction or react to become crosslink points in the resulting network [56]. Often, reactive "diluents" such as α-amino-ω-maleimido compounds are included in BMI systems [57]. Improvements in cured BMI resin properties have also been realized by the copolymerization of BMI and other vinyl compounds such as 1,2-polybutadiene [58], vinyl ester resins [59], allyl phenols [60], phosphorous containing diamines [61-63] and siloxane containing materials [64].

Although there exists one report in the literature of a BMI terminated arylene ether sulfone [65], virtually all BMI systems contain components which undergo both reaction pathways depicted in Scheme 2. Even though BMI's represent a very important class of materials, the majority of commercial materials do not fall in the category of difunctionally terminated oligomers. Recently, a quantitative solution cyclodehydration [66] of a diamine terminated poly(arylene ether ketone) oligomer to its corresponding bismaleimide has been reported [67]. This may open the door to the development of well-defined, higher molecular weight bismaleimide oligomers.

2.1.3 *Norbornene Terminated Oligomers*

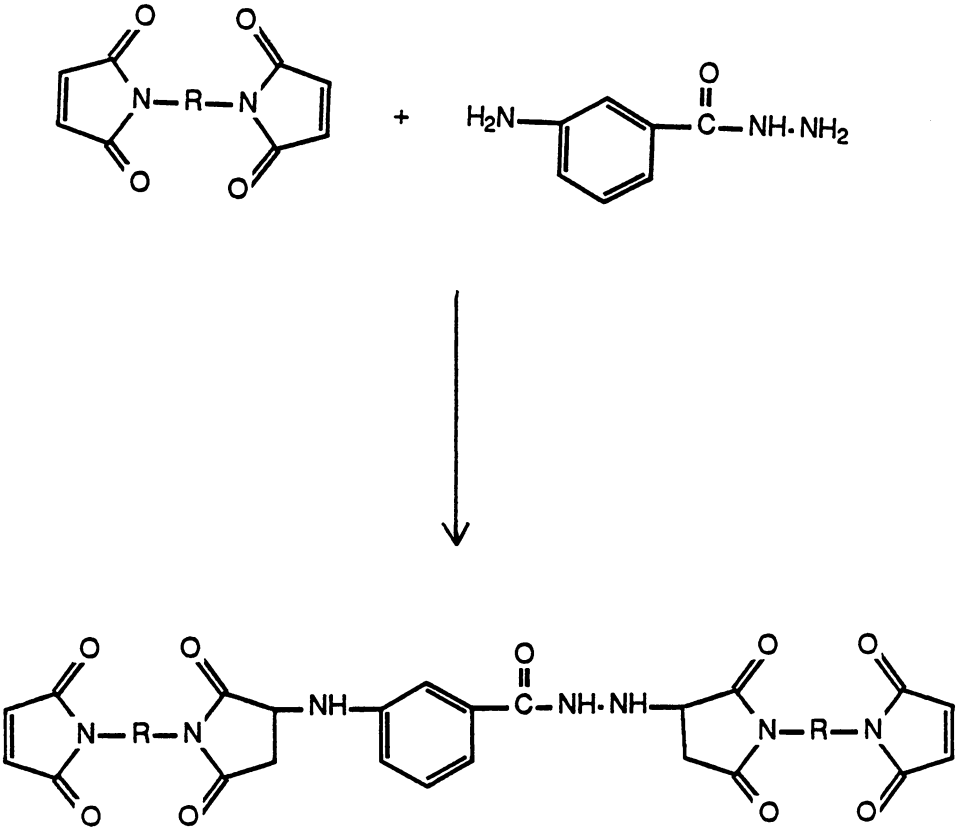
Norbornene, or more commonly referred to as Nadic, terminated materials have become widely recognized as resins which thermally cure without loss of volatiles. Early studies centered on nadic termination of oligomeric polyimides (1-2000 g/mole) since polyimides possessed many desirable properties. Nadic anhydride or 5-norbornene-2,3-dicarboxylic acid anhydride, 7, was primarily used as the endcapping reagent of choice [68-70].



7

Nadic terminated polyamic acids are thermally cyclodehydrated at ≅270°C. The endgroups begin to react at that temperature with the evolution of a small amount (1-2%) of cyclopentadiene. This thermal chain extension, referred to as pyrolytic polymerization, occurs through a combination of

SCHEME 3



addition reactions involving the unsaturation of the nadic moiety and the maleimide + cyclopentadiene, formed from a reverse Diels-Alder reaction. While these system represented improvements, the curing reaction increased the molecular weight which caused a decrease in flow and hence, incomplete imidization. Complete imidization prior to polymerization through the nadic endgroups may not occur but researchers have varied the oligomer molecular weight and cure cycle to obtain prepregs, adhesives and composite systems with excellent properties [71-77].

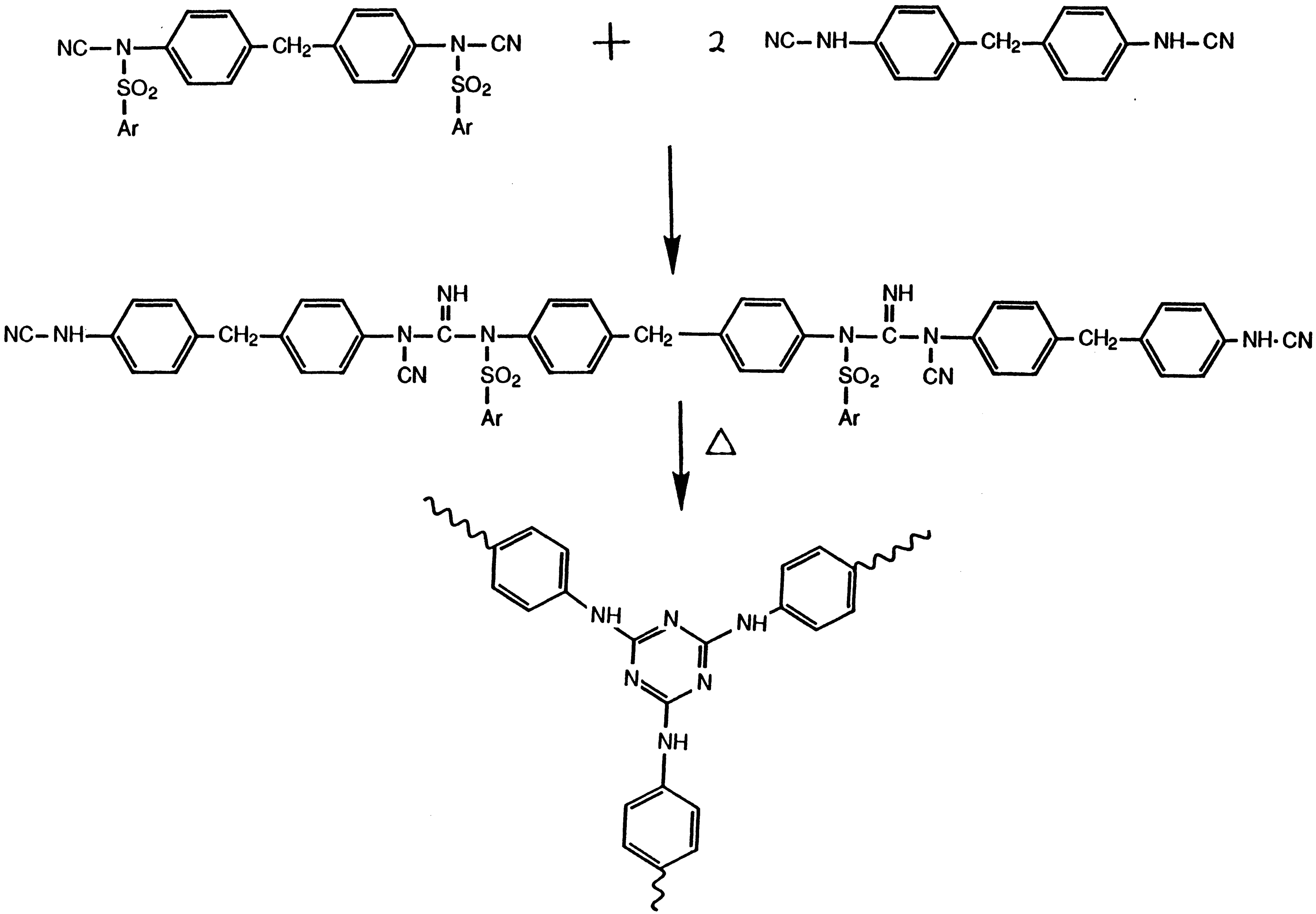
Nadic terminated bisphenol A based poly(arylene ether sulfone) oligomers were reported in the literature in 1980 [78]. The arylene ether sulfone segment used was $<M_n>$ = 20,000 g/mole. This high molecular weight linear segment did not result in a sufficiently dense network upon curing to prevent loss of mechanical properties under long term exposure to methylene chloride [79].

2.1.4 *Cyano-Terminated Oligomers*

Cyanamides represent a fairly new class of reactive functionally terminated oligomers. Scheme 4 shows the reaction between a bis (arylene sulfonyl cyanamide) and a bis cyanamide. Proper stoichiometric control results in a soluble oligomeric mixture which may be thermally cured to yield a network structure containing stable s-triazine moieties [80-81].

A similar approach was used by Lin [82] to prepare N-cyanourea terminated oligomers. Cyanamide reacted with an isocyanate capped prepolymer to form this thermally polymerizable system (Scheme 5). At room temperature, these oligomers polymerize in a linear fashion, but upon heating at > 100°C, a complex system consisting of s-triazine units, carbodiimides and many other groups is obtained. Although poly(caprolactone) was used in this study, any hydroxyl terminated oligomer capable of undergoing an isocyanate capping reaction may be employed.

A reactive functionally terminated oligomer is initially formed and subsequently cured to yield a highly crosslinked system are the cyanate terminated systems [83]. Cyanate chemistry initially involved the dicyanate of bisphenol A but more recently has been extended to include other systems [84-87]. Cyanates have also found use as co-reactants in systems containing other thermally polymerizable functionalities. The cyanate of bisphenol A has been used in blends with various bismaleimides and the curing behavior has been studied [88,89]. These BT materials (B =



NC—N—SO2—Ar
CH2
N—CN
SO2
Ar
+
2
NC—NH
CH2
NH—CN
NC—NH
CH2
N—C—N
NH
CN
SO2
Ar
CH2
N—C—N
NH
SO2
Ar
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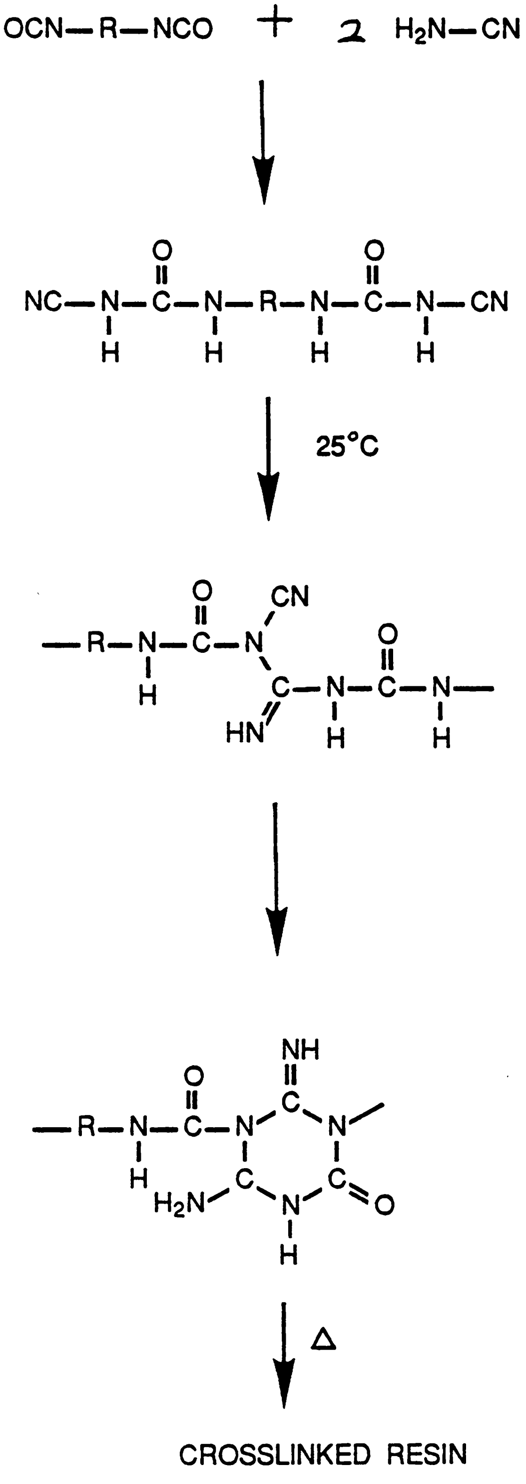
CH2
NH·CN
△
NH
N
NH
N
N
NH

SCHEME 4

SCHEME 5



bismaleimide, T = triazine) have been evaluated in composites and offer an excellent temperature use range.

2.1.5 *Miscellaneous Functionally Terminated Oligomers*

There exists a potentially large number of thermally polymerizable, functionalized oligomers if one envisions various polymeric systems terminated with allylic or vinyl groups. To date however, there exist only a few literature reports on such systems. Matsumoto and coworkers [90] have developed glycol based bis (allyl phthalates) as well as diallyl terminated carbonates in controlled fashion to yield difunctionally terminated materials with a range of molecular weights. Other groups have focused on placing either pendant or terminal styrenic groups on arylene ether sulfone oligomers [91]. Vinyl groups have also been quantitatively placed on both ends of a poly(isobutylene) chain via "inifer" techniques [92].

Biphenylene end-caps have been used to functionally terminate imides [93,94], quinoline [95,96] and quinoxaline [96] based oligomers. This endgroup requires very high curing temperatures, >300°C, even in the presence of catalysts. This limits its use to polymeric systems which will not degrade at these temperatures.

An interesting system that has been recently developed utilizes diamine terminated poly (arylene ether ketone) oligomers. The amine functionality will attack backbone carbonyl groups to form an imine group with the loss of water. Under moderate temperatures and pressures, an insoluble, crosslinked network results [97].

A very important trade-off in desired properties exists in all the systems presented here. The crosslink density (inversely proportional to $<M_c>$ of a system) will often determine its ductile/brittle failure mode and its solubility (or solvent resistance). If one desires good solvent resistance, a high crosslink density or low $<M_c>$, is necessary. This inevitably will lead to sample brittleness. To obtain a more ductile material, a lower crosslink density may be desirable; however, this may decrease solvent resistance to an unacceptable level.

One approach towards solving this dilemma is to employ an oligomer and a monomer bearing identical functional groups. In this case, one can view the procedure in two ways; (1) adding small amounts of functionalized oligomer to the curing of a low molecular weight compound "dilutes" the crosslink density (increases $<M_c>$), resulting in a more ductile system, or, (2) reacting small amounts of a low molecular weight compound in the curing of a functionalized oligomer will "tighten" the resulting network, which should aid in obtaining better solvent resistance. In practice, it is often easier to develop mixtures such as these in which each component can be varied to obtain optimum properties. Commercially available bismaleimides often contain 2, 3 or more components depending on requirements for curing or the end use of the material [56,98,99].

2.2 *FUNCTIONALLY TERMINATED OLIGOMERS FOR COPOLYMER SYNTHESIS*

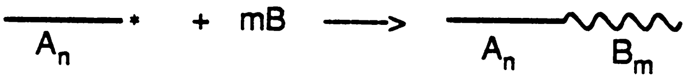
2.2.1 *Introduction and Background*

Copolymers are prepared from chemically bonding two dissimilar repeating units via any one of a large number of existing synthetic techniques. This class can be further subdivided into random or alternating copolymers, graft and block copolymers. Various thermosetting materials may also be thought of as copolymers if they have been modified with functionalized oligomers. Block copolymers represent an important field of polymer science which has been known about for some time [100-114]. The depth of the field was not appreciated until elastic linear polyurethanes were developed which were composed of "soft" polyester or polyether segments and "hard" polyurethane or carbamate sequences.

Block, segmented, graft and ion-containing copolymers offer several distinct advantages over polymer blends or alloys even though they are more costly to prepare. The majority of homopolymer pairs are immiscible with one another and give rise to low strength materials due to the lack of interfacial adhesion between the separate phases. Since copolymers are covalently linked together, macroscopic incompatability at the interface in minimized. These copolymers can be used to strengthen blends of immiscible polymers by serving as emulsifiers [100-103]. Molecular architecture can also be designed to produce novel materials.

We will primarily be concentrating on copolymers with "blocky" architecture or block copolymers. The simplest designation for two dissimilar repeating units combined together at one point (1-chemical bond) is referred to as an A-B diblock. The 'A' block, by convention, is the first polymeric species formed and 'B' is the second. Other common systems include A-B-A triblocks and $-(A-B)_n$ - multiblocks. There exists a large number of different copolymer architectures such as starblocks, overlap tapered, etc. which will not be treated in this survey.

There are two general methods available to synthesize block copolymers. In the first, active sites on a macromolecular chain are created which then initiate the polymerization of a monomer. The polymerization in principle may be radical, anionic or cationic, and for one active site, can be represented as:



(19)

The second method, which is usually step-growth or condensation, is the reaction between chemically different functional groups present at the ends of different macromolecular species, schematically represented in equation (20).

(20)

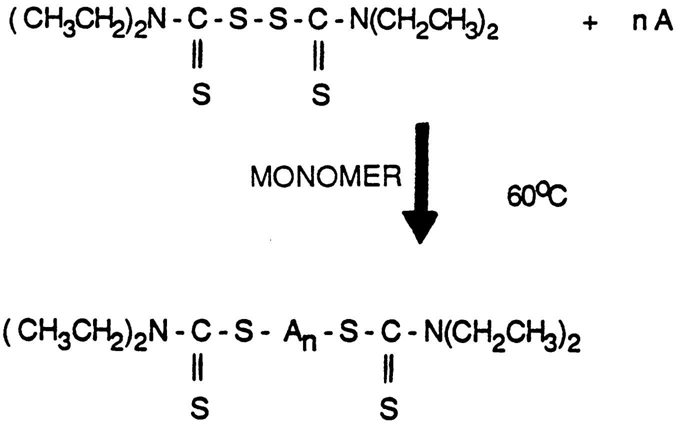
Equation (20) represents the formation of an A-B diblock copolymer. When difunctional species are used, these reactions lead to multiblock copolymers $-(A-B)_n$- which also can be referred to as segmented copolymers. Optionally, two small difunctional monomers can be used in addition to the A or B blocks, which results in a system also called a random or segmented copolymer.

Although a large number of block copolymers have been prepared using both approaches outlined here, some more well-defined than others. Such a vast array of copolymers cannot be treated individually with any depth herein. Many excellent sources for specific syntheses, characterization and mechanical properties of block copolymers exist [100-132, 136-162, 166-185]. Therefore, the focus of this section will be to present the methodologies employed in different polymerization modes (anionic, free-radical, etc.) which can be used to prepare functionally terminated oligomers.

2.2.2 *Block Copolymers Utilizing Radically Initiated Polymerizations*

In free radical polymerization, the simultaneous copolymerization of two monomers A and B are characterized by their reactivity ratios, r_A and r_B. The probability of forming long sequences of A or B is very small. Accordingly, the free radical polymerization of a mixture of monomers usually does not lead to a block copolymer. It is known, however, that use of a large amount of peroxide initiator can lead to oligomeric species with initiator fragments on both chain ends [115]. Also, the creation of free-radical sites or radical generating species, such as azo or peroxide, on a given polymer can then initiate polymerization of a second monomer [119-120]. One example of this is the capping of the terminal hydroxyl groups of a poly(oxyethylene glycol) with a percarbonate [116]. Free radicals are generated upon heating which are able to initiate styrene, and some B-A-B triblock structures of polystyrene-poly(oxyethylene glycol)-polystyrene results.

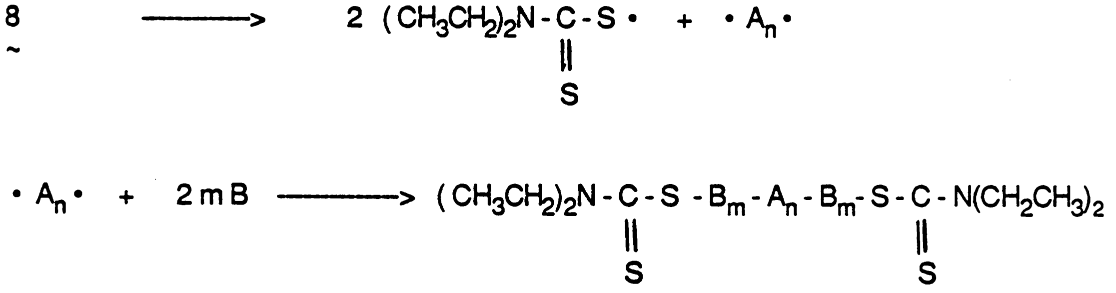
A more recent approach involves interferters, or *ini*tiator trans*fer* agents (inifers) and/or *ini*tiator *ter*minators (initers) [117-118]. Through a thermal initiation of tetraethylthiuram disulfide, two free radicals result, and in the presence of monomer A, the radicals undergo the following reaction to yield an α,ω-difunctional oligomer, 8.



$$(CH_3CH_2)_2N-\underset{\underset{S}{\|}}{C}-S-S-\underset{\underset{S}{\|}}{C}-N(CH_2CH_3)_2 \quad + \quad nA \xrightarrow[60^{\circ}C]{\text{MONOMER}} (CH_3CH_2)_2N-\underset{\underset{S}{\|}}{C}-S-A_n-S-\underset{\underset{S}{\|}}{C}-N(CH_2CH_3)_2 \qquad (21)$$

8

The S-A bond is photolabile and in a second step, these oligomers may be photolyzed in the presence of a second monomer.



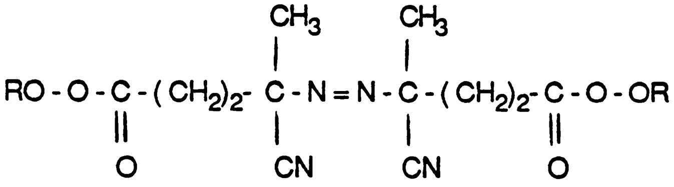
$$\underset{\sim}{8} \longrightarrow 2\ (CH_3CH_2)_2N\text{-}\underset{\underset{S}{\|}}{C}\text{-}S\bullet + \bullet A_n\bullet$$

$$\bullet A_n\bullet + 2mB \longrightarrow (CH_3CH_2)_2N\text{-}\underset{\underset{S}{\|}}{C}\text{-}S\text{-}B_m\text{-}A_n\text{-}B_m\text{-}S\text{-}\underset{\underset{S}{\|}}{C}\text{-}N(CH_2CH_3)_2$$

(22)

Chain propagation of monomer B occurs only on the macroradical whereas the microradical apparently recombines to terminate the chain. A-B-A triblocks consisting of poly(methyl methacrylate)-poly(styrene)-poly(methyl methacrylate), PMMA-PS-PMMA, and poly(ethyl acrylate)-PS-poly(ethyl acrylate) have been synthesized by this technique [118].

Another means to generate a functionalized oligomeric precursor is to use radical initiators with at least two different potential initiation groups. These groups can be of different types, as shown in $\underset{\sim}{9}$, or of the same type with different rates of decomposition.



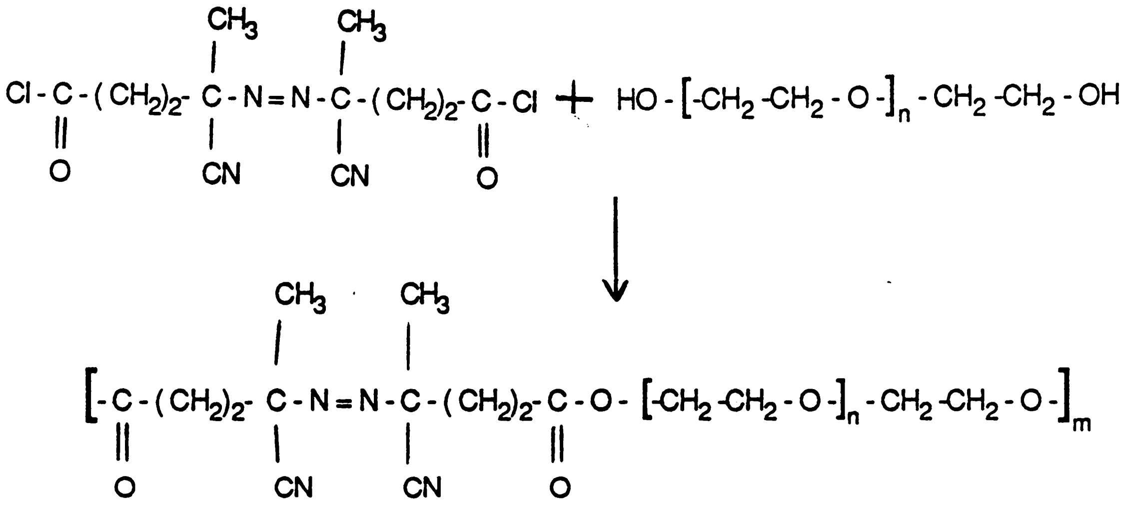
$$RO\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_2\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}}\text{-}N{=}N\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}}\text{-}(CH_2)_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\text{-}OR$$

$\underset{\sim}{9}$

Azo decomposition occurs first to initiate polymerization and the peroxy-groups become the chain ends. Materials of this type have been used with various R-groups [119-122] to prepare block copolymers centered around PMMA.

The use of polymers with endgroups that can be converted into radicals by organometallic compounds has been another effective approach [123]. Manganese and rhenium carbonyls, with additives such as tetrafluoroethylene have been used to prepare a difunctional block of PMMA [124], followed by thermal initiation of a block of acrylonitrile. Di- and triblocks have also been prepared using an organoaluminum such as triethylaluminum, TEA [125]. A thermal polymerization of styrene in the presence of TEA, which acts as a chain transfer agent, will terminate the PS chains. These endgroups react with benzoyl peroxide and generate polystyrene free-radicals which can initiate the polymerization of a second monomer, acrylate, methacrylate or acrylonitrile at low temperatures.

Polymers have also been prepared with initiator groups present in the polymer chain rather than at the ends. This internal functionalization can be used to prepare block copolymers. The general formula of such initiators is $-(R-N=N-R-N=N)_n-$ where R can be either a low molecular weight species or an oligomer.



$$\mathrm{Cl-\underset{\underset{O}{\|}}{C}-(CH_2)_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}}-N=N-\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}}-(CH_2)_2-\underset{\underset{O}{\|}}{C}-Cl} + \mathrm{HO-[-CH_2-CH_2-O-]_n-CH_2-CH_2-OH}$$

$$\downarrow$$

$$\mathrm{\Big[-\underset{\underset{O}{\|}}{C}-(CH_2)_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}}-N=N-\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}}-(CH_2)_2-\underset{\underset{O}{\|}}{C}-O-[-CH_2-CH_2-O-]_n-CH_2-CH_2-O-\Big]_m}$$

$\underset{\sim}{10}$

Prepolymer $\underset{\sim}{10}$ is primarily a homopolymer of poly(ethylene oxide), PEO which upon thermal degradation of the azo linkages in the presence of vinyl chloride yields a block copolymer. Prepolymers like this have been used to prepare block copolymers containing a range of PEO from 2-20% [126]. When the R-group is a low molecular weight species, the number of free-radical initiator fragments is large and gives rise to ill-defined sequence arrangements and molecular weights. Block copolymers of N-vinylacetamide and styrene or methyl acrylate have been prepared using this approach [127-128].

There have been reports on the preparation of block copolymers using living radicals [129-132]. This occurance is based on the fact that some polymers are insoluble in their monomers, so when polymerizations are carried out in bulk (or with a poor solvent), occluded macroradicals are produced. Copolymers have been prepared with PMMA and acrylonitrile [129] and PS-Pt-butylstyrene-PS-triblocks [130] have also been synthesized. The effect of complexing agents on these macroradicals has also been studied in a few cases [131,132].

Free-radical polymerization syntheses provide for a great deal of variety in block copolymer synthesis due to the great number of vinyl monomers polymerizable by this method. It is also quite useful for polar monomers that cannot be polymerized cleanly by anionic techniques. The methods presented, however, result in products that are generally polydisperse in molecular weight, composition and structure, and may include a significant percentage of homopolymer.

2.2.3 *Block Copolymer Synthesis Using Anionic Polymerization*

Anionic polymerization since its discovery [133] has become one of the preferred techniques for the preparation of monodisperse homopolymers and well defined block copolymers. The lack of termination or transfer steps (living polymerizations) allows the preparation of block copolymers possessing controlled molecular weights, composition and structure. Block copolymers prepared by this method have certain advantages over other techniques; (1) di-, tri- or multiblock block copolymers of low polydispersity or of defined heterogeneity can be prepared by suitable coupling reagents or with difunctional initiators, (2) successive polymerizations of different monomers (often termed a sequential monomer addition method) or by polymerizing the second monomer with functionalized prepolymers of the first monomer or (3) functionalized block copolymers can be obtained with suitable initiators (difunctional center block formation) or with specific deactivation reagents (ethylene oxide, then protonic source). This technique also has drawbacks; ultrapure reagents and solvents, high vacuum or purified blanketing gas and usually low temperatures are required. There are also a limited number of monomers, mainly dienes, styrenes and cyclic ethers, which polymerize well by this technique.

The primary block copolymers produced by anionic polymerization are based on polystyrene (PS), polyisoprene (PI), polybutadiene (PBD) and poly(α-methylstyrene) with monofunctional initiators such as butyllithium and cumyl potassium (phenyl isopropyl potassium). Difunctional initiators such as the classic alkali metal naphthalides or DDPE + s-butyl lithium have also been used [134,135]. Thus, the monofunctional initiation of styrene followed by addition of a second monomer, isoprene, will yield a block copolymer upon termination of the living anionic endgroups. However, when all the isoprene has been reacted, more styrene can be added to produce an A-B-A triblock material. The same polymer can be prepared by the difunctional initiation of isoprene, and when it has been consumed, addition of more styrene monomer. Some important considerations are solvent effects and complexation. Solvent significantly influences reactivities of the endgroups in anionic polymerizations [136] as well as the microstructure obtained [137]. Both subjects have been extensively reviewed [138,139].

Various cyclic ethers, sulfides, epoxides, siloxanes and lactams can be polymerized by anionic methods [140,141]. Thus, block copolymers can be prepared in which the first sequence is a vinyl or dienic monomer and the second block is a polymer such as polyethylene oxide or PEO [142-145]. An interesting improvement in block copolymer synthesis employs ε-caprolactone to form the third block. The polymerization of ε-caprolactone involves the attack of base on the carbonyl carbon which generates an alkoxide endgroup. Therefore, instead of initiating the lactone with polybutadienyl lithium directly, improved results are observed if one first converts the carbanion chain end to a less basic alkoxide group with ethylene oxide [146]. Care must be taken to effectively terminate the triblock to avoid degradation of the aliphatic polyester.

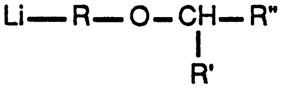
(23)

Conversion of the growing species to an aluminum alkoxide chain end has been reported to improve the situation.

It is possible to obtain functionalized polymers and/or block copolymers by deactivation with appropriate compounds. Endgroups such as hydroxyl, vinyl, ether, ester, carboxylic acid and acid chloride have been obtained by proper deactivation [147]. Dihydroxyl-terminated polybutadiene [148] prepared in this manner could be endcapped with an isocyanate to prepare various polyurethanes. They could also be further converted into N-acyllactam endgroups by reaction with caprolactam which permits subsequent polymerization to yield Nylon 6 blocks.

Living polystyryl or polybutadienyl lithium polymers can be reacted with oxirane/H_2O, and effectively endcapped [150]. Difunctional initiation of isoprene followed by reaction of CO_2 in tetrahydrofuran can result in dicarboxylic acids [151] or the chain end can be converted to the di-tetrabutyl ammonium salts [152] which initiates the ring opening polymerization of pivalolactone. Nakahama and co-workers [159,160] have utilized the reaction of polymeric anions with a trimethylsilyl-protected imine to prepare amine terminated polymers. Quirk, *et al.* [161,162] has reported a direct amination of polystyryl lithium utilizing the reagent generated from methoxyamine and methyl lithium [163]. The highly difunctional oligomer could be isolated by column chromatography. These functionalized prepolymers, also called telechelic polymers, are able to further react with either monomers for further anionic polymerization [149-163] or with other telechelic prepolymers via step-growth reactions.

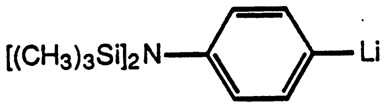
Another method to introduce endgroup functionality into a polymer chain is through the use of a blocked initiator. A typical example is an initiator of the general formula in 11 [164].



$$Li{-}R{-}O{-}\underset{\displaystyle R'}{CH}{-}R''$$

11

Polymerization with such initiators leads to a chain bearing an acetal endgroup, which by acid hydrolysis can be transformed into a hydroxyl group. Similarly, polydienes have been prepared by using an initiator such as 12.



12

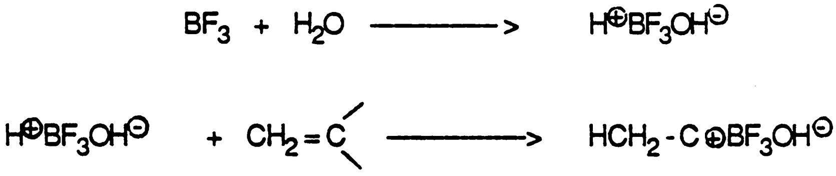
Following polymerization, the living anions are coupled and the bis(trimethylsilyl) amine groups can easily be converted to amine groups by hydrolyzing with dilute acid [165].

2.2.4 *Block Copolymer Synthesis Utilizing Cationic Polymerization*

For many years, copolymers prepared by cationic polymerization were ill-defined in structure and contaminated to a large extent with homopolymers. In the last two decades, procedures have improved to the point where control over each different step of the synthesis is realized and a wide variety of copolymers have been devised [166-185].

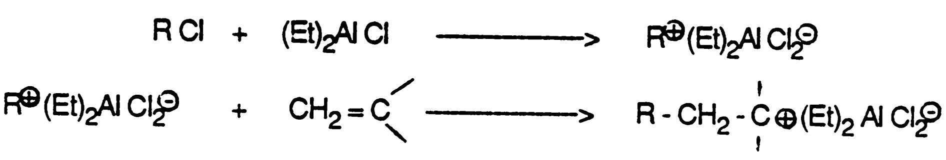
Cationic initiation conventionally utilized a Lewis acid such as BF_3, $AlCl_3$, etc., with protic impurities, commonly water. This resulted in a system with poor control over reproducibility along with an unreactive head group (Scheme 6).

SCHEME 6



Controlled initiation and head group functionality can be obtained by using certain alkylaluminum compounds, eg. Et_2AlCl, Et_3Al, Me_2AlCl, with tertiary benzylic or allylic chlorides (Scheme 7). Protic impurities do not adversely effect this system. Extension of this principle to include certain halogenated polymers as co-initiators (where R-Cl is a halogen terminated polymer) with Lewis acids is now utilized to prepare di- and triblock copolymer systems as well as various grafted architectures.

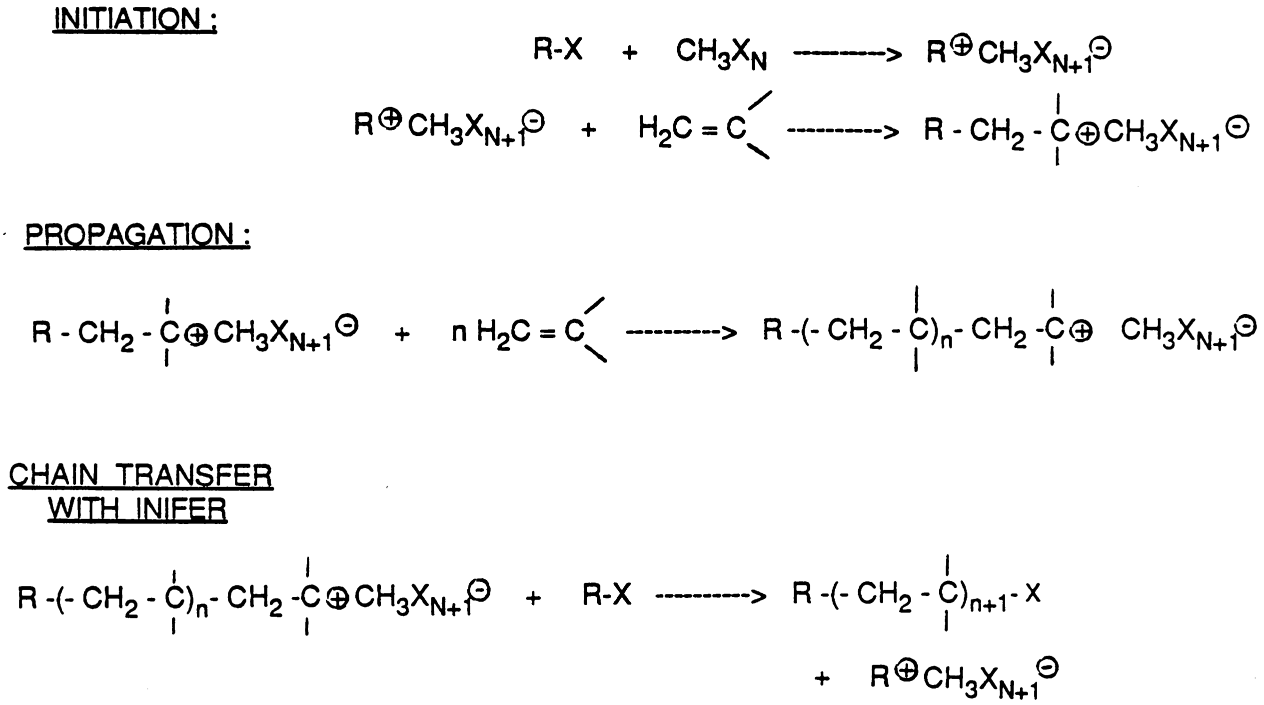
SCHEME 7



Another key feature in block copolymer or functionalized oligomer synthesis via cationic polymerization is the propagation step. The crucial requirement is to maintain uninterrupted propagation by avoiding chain transfer reactions, especially to monomer. Quasi living polymerization is a recently discovered polymerization system in which termination is absent or reversible and chain transfer to monomer is strongly suppressed [170]. This is achieved by maintaining monomer addition and consumption of the monomer equal so that 100% conversions are obtained throughout the polymerization. Chain transfer to monomer can be largely eliminated by the use of extremely basic but non-nucleophilic, sterically hindered amines, eg. 2,6-di-tert-butylpyridine. Compounds such as these exhibit extraordinary specificity towards a free proton, but are sterically hindered towards reactions with carbocations. Hence, polymers produced using these "proton traps" exhibit very narrow molecular weight distributions. This method of controlling chain transfer has been exploited for efficient preparations of block and graft copolymers [172].

An interesting method used to prepare α,ω-functionalized polymers is by the "inifer" technique. This involves special functional *ini*tiating and trans*fer* agents which may be mono-, di-, tri- or multifunctional in nature. Scheme 8 outlines this concept for a monofunctional inifer where CH_3X is a Lewis acid and X is a halogen.

SCHEME 8



Thus well-defined macromolecules carrying both head and tail groups from the inifer are obtained when the rate of chain transfer to inifer is greater than that of chain transfer to monomer. In the case where CH_2X_2 is used, a difunctional oligomer may be obtained. These telechelic polymers are useful initiators for the block copolymerization of olefins (with alkylaluminums) and cyclic ethers (generally using silver salts). The terminal tertiary chloro-group of a polyisobutylene rubber obtained in this manner can also be converted into other groups, eg. hydroxyl, olefin, epoxide, carboxylic acid, ionomeric groups and silane for further application in block copolymer syntheses [169].

Controlled termination is also widely used in functionally terminating polymeric chains. Highly defined, uniform endgroups result only when the rate of termination is higher than the rate of chain transfer to monomer. An example of a chain transfer agent can be seen in Equation 25.

$$A_n^{\oplus} \quad + \quad R\,Me\,X_n^{\ominus} \text{ ---------> } A_nR \quad + \quad Me\,X_n \tag{25}$$

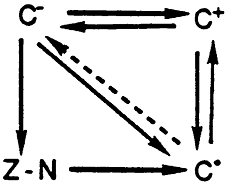
R may be either reactive, eg., Cl^-, Br^-, $CH_2=CH$- and suitable for block copolymer synthesis or unreactive, eg., H- or CH_3-.

Hence, by having control over initiation, propagation, chain transfer and termination reactions, a wide variety of functionally terminated materials can be prepared based on polyisobutylene, and subsequently, a large number of block and graft copolymers [172-185].

Poly(tetramethylene oxide) oligomers prepared by the ring opening polymerization of tetahydrofuran is also of interest [186]. Under the proper conditions, ″poly THF″ can be synthesized via living oxonium ion polymerization, which yields oligomers of predictable molecular weights and narrow molecular weight distributions. By careful consideration of the initiating species, eg., $AgPF_6$, followed by hydrolysis or amination, dihydroxyl- or diamino-terminated oligomers have been obtained. These oligomers have become extensively used in block copolymer syntheses [186] and are described in the references contained therein.

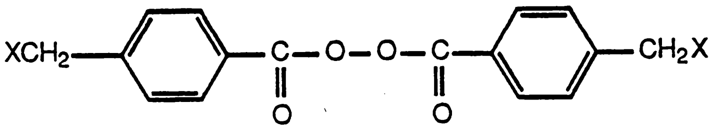
2.2.5 *Transformation Reactions*

Recently much research has been centered on the preparation of block copolymers using combinations of two (or more) different polymerization mechanisms. This is due, in part, to the advantages realized in the polymerization of certain monomers using a polymerization mechanism which optimizes the preparation of a well-defined, functionally terminated oligomeric species. This approach, often termed transformation reaction, has the potential to greatly extend the range of potential monomer combinations in block copolymers. Thus, it might be feasible to devise processes in which the polymerization mechanism can be changed at will, to best suit the monomer being polymerized. In most cases, these materials can be envisioned as reactive, functionally terminated oligomers, even though some terminally are oligomers are used in situ in the block copolymer synthesis. The possible combinations can be represented schematically by



where Z-N refers to Ziegler-Natta catalysts, C- is anionic, C^+ is cationic and $C^\bullet$ is free radical polymerization mechanisms.

The first such transformation reaction to be discussed will be anionic to free radical. This procedure is based on the deactivation of the living anionic polymer sequence with different reagents which are able to initiate radical polymerization of a second monomer. For example, living polystyrene and polyisoprene have been deactivated with 4,4′-bis (halomethylbenzoyl peroxide, 13, and the thermal decomposition of the peroxide groups has been used to initiate the polymerization of methyl methacrylate and vinyl chloride [187-188].



13

This can again be thought of as an internally functionalized oligomer. 2,2′-Azobisisobutyronitrile (AIBN) has been used in an analagous manner [189] to yield PS-b-PMMA and PS-b-PVC.

Other reagents that have been successfully utilized for the deactivation of anionic polymeric species include metal salts of lead [190], silver [191,192] and mercury [193]. The carbon-metal bonds in these cases are unstable and can be decomposed either chemically, as with Ag, or thermally, as in the case of Pb and Hg, to yield free radicals which can initiate the polymerization of a second monomer.

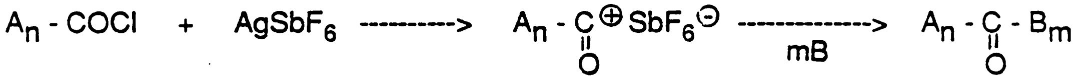
The most widely studied transformation system is that of anion to cation. The functionalization of the negative species with a halogen or halogenated derivative can be achieved by using an excess of different reagents such as α,α′-dibromoxylene [194], bromine, 1,2-dichloroethane or 1,4-dibromobutane [195]. Greater yields have been realized in the functionalization reaction by treating the living polymer with anhydrous $MgBr_2$ to form a polymeric Grignard reagent [196] which then reacts with a halogenated species.

$$\begin{array}{l} A_n^{\ominus}Li^{\oplus} + MgBr_2 \text{ -------> } A_n - MgBr + LiBr \\ A_n - MgBr + X - R - X \text{ -------> } A_n - R - X + MgBrX \end{array} \qquad (26)$$

PS-b-PTHF and PS-b-PBD-b-PTHF copolymers have been produced using this mechanistic approach [197].

The functionalization of the living polymer may also be achieved by reaction with phosgene, leading to an acid chloride endgroup [197]. This endgroup is then reacted with a suitable co-initiator, $AgSbF_6$, to yield an insoluble silver chloride salt and a carbocationic initiating species (27).

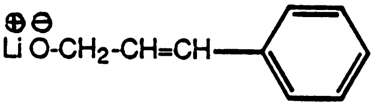
$$A_n^{\ominus}Li^{\oplus} + COCl_2 \text{ -------> } A_n - COCl + LiCl \qquad (27)$$



$$A_n - COCl + AgSbF_6 \text{ ---------> } A_n - \underset{\underset{O}{\|}}{C}{}^{\oplus}SbF_6^{\ominus} \xrightarrow[mB]{\text{-----------}} A_n - \underset{\underset{O}{\|}}{C} - B_m$$

Highly successful syntheses of PS-b-PTHF and PS-b-PBD-b-PTHF copolymers have been achieved using this method [197]. These last two approaches, unfortunately will not yield difunctionally terminated oligomers due to the obvious coupling reactions involving a polymeric dianion.

The cation to anion transformation reaction can be achieved by two approaches. The first involves treating the living "poly(tetrahydrofuran)" cation with the lithium salt of an alcohol possessing a styryl unit, eg., cinnamyl alcohol, 14, to terminate the polymers with a functional group which can react with a strong nucleophile, ex., butyllithium [198].

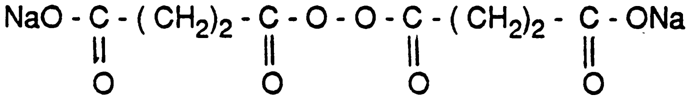


14

Styrene and isoprene can then be polymerized as the second monomer. Unfortunately, serious side reactions limit the yield.

The second approach consists of the functionalization of living cationic "poly THF" with a primary amine. The amino-terminated polymer thus obtained is metallated, creating a terminal nitranion which has been used to initiate styrene [199]. Similarly, a dicationic "poly THF" oligomer can be reacted with aniline, followed by addition of sodium/naphthalene which provides proper functional termination for the polymerization of methyl methacrylate, yielding a PMMA-b-PTHF-b-PMMA triblock copolymer [200]. However, none of these reactions are quantitative.

Cation to free-radical transformation reactions utilize the same synthetic methodology as with the anion to free radical case. A living cationic species is deactivated with the disodium salt of succinic acid peroxide, 15, which, upon decomposition, yields free radicals able to initiate polymerization of a second monomer [201].



$$NaO-\underset{\underset{O}{\|}}{C}-(CH_2)_2-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-(CH_2)_2-\underset{\underset{O}{\|}}{C}-ONa$$

15

Anion to Ziegler-Natta transformations have been achieved by deactivation of the living anion with $TiCl_4$ to form the Ti-C bond. This bond is active towards ethylene and a polystyryl lithium anion treated with this reagent can be used to polymerize ethylene linearly to yield a block copolymer [202].

Ziegler-Natta to free radical [199] transformations have been achieved only with difficulty. Presently, only free radical to anionic transformations have not been achieved [200]. What we have seen is that is is possible to transform one mechanism into another. The methods presented here might be extended to difunctional anionic or cationic polymeric species and/or α,ω-difunctional pre-polymers by utilizing either difunctional initiating species or suitable coupling reagents. In such cases, the reactive functionally terminated polymeric species can be further reacted to produce multiblock copolymers possessing alternating or random distributions of the different sequences.

2.3 *CONDENSATION AND COUPLING REACTIONS*

Condensation techniques for preparing block copolymers are often relatively simple to carry out. One limitation is that increasing the molecular weight of the precursor polymer sequence decreases the concentration of the endgroups and can decrease the reaction rate. An increase in the molecular weight of these oligomers might also lead to a macroscopic phase separation because of polymer-polymer incompatability. The latter phenomenon could also influence the reaction rate and sequence distribution. In addition to solution polymerizations of various functionalized oligomers, interfacial condensation reactions have been utilized. In this procedure, two functionally terminated oligomers A_n-X and B_m-Y, are selectively dissolved in 2 immiscible solvents, S_A and S_B respectively. The nature of the reactive endgroups is such that they are attracted to the interface of the two liquids so that the reaction occurs between X and Y, localized at the interface [203]. If the reaction cannot effectively be carried out by this approach, reagents known as phase transfer catalysts or PTC's may be employed. The most commonly used PTC's are tetra-alkyl ammonium halides. A further extension of this method includes a procedure known as a pseudo-interfacial polymerization [204] which will be discussed in further detail in a later section.

Condensation or step-growth polymerization can also be used to prepare functionally terminated oligomers of controlled molecular weights by proper knowledge of the Carothers equation. In the solution polymerization of functionalized oligomers, several different approaches can be used to obtain various architectures. First, two difunctional oligomers may be directly reacted together, yielding $(A - B)_n$ type systems [205-212], such as with polybutadiene diols and diacid chloride terminated polystyrene [206]. A second example is when two difunctionally terminated oligomers possess mutually non-reactive endgroups and are coupled together with a low molecular weight component [213-217]. A good example of this is the reaction between a poly THF diol, a poly vinyl chloride diol and 4,4′-methylene diisocyanate [215]. A closely related series exists where one diol can be replaced by an oligomeric diamine [218-220] and a diisocyanate coupling agent can still be employed. The third broad classification includes systems which contain one functionally terminated oligomer, a monomer possessing the same functional endgroups and a coupling reagent to react with both components [218,221-222]. Finally, one may use condensation techniques to couple two monofunctionally terminated prepolymers [206,223-224], a monofunctional oligomer, monomer and coupling agent [225,226] or various combinations thereof [227-229].

2.4 *GENERAL ASPECTS OF POLY(ARYLENE ETHERS)*

Poly(arylene ethers) are members of a class of materials known as engineering thermoplastics. These are tough, ductile and rigid materials possessing good thermal and mechanical properties. These are useful in applications requiring toughness under load bearing conditions and can be used over a wide temperature range approaching their glass transition temperature (T_g). Conventional methods such as extrusion or injection molding can often be employed to produce products having excellent thermal, hydrolytic and dimensional stability. This section reviews the development of poly(arylene ethers), synthetic routes and structural variability.

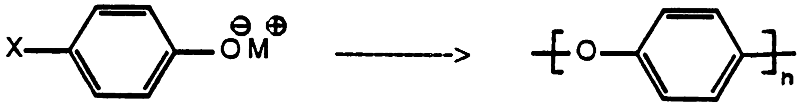
Aromatic moieties such as benzene or naphthalene are recognized for their thermal stability, originally as coal by-products and later as integral components in polymeric backbones. The utilization of other thermally stable groups such as $-SO_2-$, -CO- or -O- in conjunction with aryl groups can lead to a controlled amount of flexibility or intractability which can enhance ductility and processability. In addition to these desirable engineering thermoplastic properties, alternate synthetic pathways become available as these functional groups are introduced into the polymer backbone.

In the class of poly(arylene ethers), the predominant linkage is the ether group and hence the characteristics of the C-O bond become paramount. The C-O-C linkage has a lower barrier to rotation, exclusion volume and Van der Waals interaction forces as compared to a C-C bond. This therefore leads to a greater backbone mobility, contributing to a greater ease of chain coiling and uncoiling which may impart chain flexibility to the system. An aryl ether bond also possesses greater hydrolytic stability as compared to other polar functional groups such as esters and amides.

Only in the last few decades have the synthetic techniques been developed for the production of useful, high molecular weight polymers [230]. The preparation of poly(arylene ethers) from a mechanistic point of view utilizes only three synthetic approaches. These are oxidative coupling, nucleophilic aromatic substitution and electrophilic aromatic substitution. Oxidative coupling is generally restricted to the polymerization of substituted phenols. The other two methods permit a wide variety of polymeric materials to be synthesized.

2.5 *POLY(PHENYLENE ETHER)*

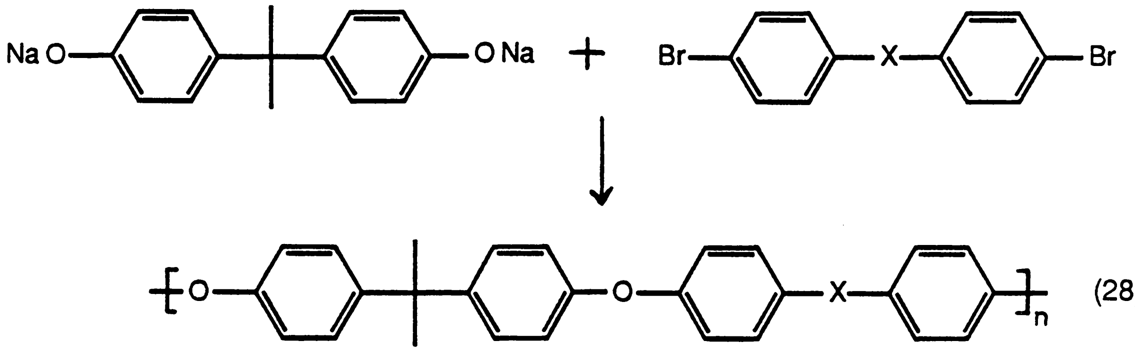
The structurally simplest polymer in the poly(arylene ether) family is poly(phenylene ether),



where X = I or Br, M = Na or K. The Ullmann ether synthesis is used to prepare ethers in this fashion [231,232]. Presently, most investigators have been able to synthesize low molecular weight materials [232-235]. Stamatoff [236,237] employed a modification of the Ullmann condensation with the sodium salt of p-bromophenol to produce high molecular weight material. An inert, high boiling solvent such as benzophenone or dimethoxy benzene must be employed to provide the high reaction temperatures necessary. The reaction is catalyzed by an organic base complexed with copper compounds. Water and oxygen must be rigorously excluded from the reaction in order to produce high molecular weight material. Dutch workers [238] reproduced Stamatoff's work and studied some of the polymer's physical characteristics [239]. Various other investigators have utilized this material to perform more in-depth mechanical property studies [240-245]. The major drawback of the Ullmann condensation reaction was that even high molecular weight materials appeared to be physically different than the expected structures. Traces of oxygen were known to cause a free radical side reaction resulting in possibly branched and crosslinked products [246]. Recent workers have been able to prepare PPE as well as a variety of 2,6-disubstituted derivatives by electro-oxidative means [247].

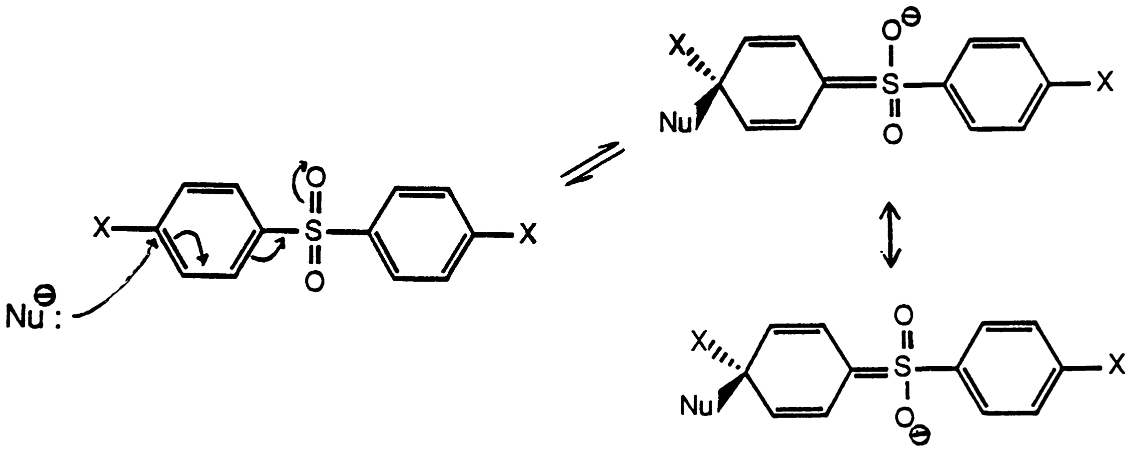
2.6 *POLY(ARYLENE ETHERS)*

A major problem in the synthesis of poly(phenylene ether) was its high crystallinity. By working with monomers that would result in an amorphous system, Robeson *et al.* [248] reacted sodium bisphenates with aromatic dihalides under conditions similar to those used in PPE synthesis and successfully synthesized linear high molecular weight polymers. This technique had been outlined earlier in the patent literature [249] and involved the reaction of sodium bisphenates with aromatic dihalides under similar conditions to those used in PPE synthesis.



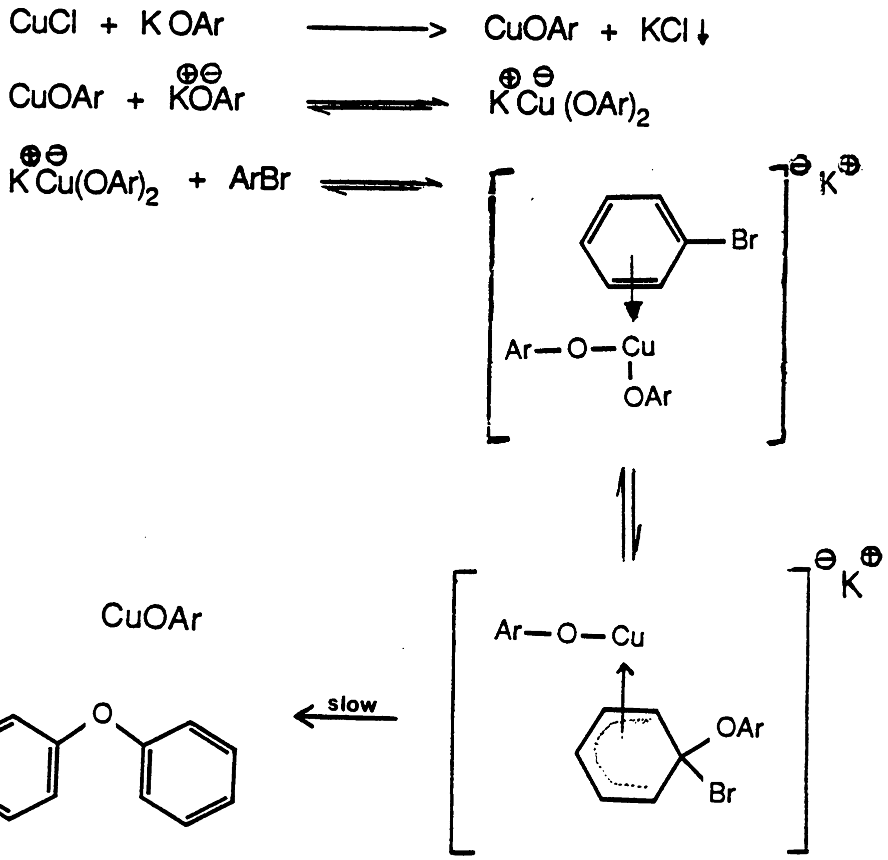
(28)

where X = 0, phenyl or chemical bond. The electronic effect of X dictates which synthetic pathway may be best utilized for obtaining high yields of polyethers. The reaction will proceed by a substitution mechanism using the Ullmann ether syntheses as outlined here or it can proceed via nucleophilic aromatic substitution such as is the case with electron withdrawing groups in which X = -SO_2- or $\rangle C=O$. The Ullmann ether synthesis utilizes aryl halides which are termed "non-activated", in reference to nucleophilic aromatic substitution. Aryl halides possessing electron withdrawing groups are activated towards nucleophilic aromatic substitution due to the resonance stabilization of the intermediate formed.



Although the Ullmann condensation reaction had been known since 1904 [231], it was not until 1951 that Bunnet and Zahler proposed a nucleophilic aromatic substitution mechanism for the reaction. Although the reaction explained experimental observations, it was somewhat incomplete [250]. Bacon studied the salts of various transition metals and found the salts of copper to be uniquely active in this reaction [251,252]. Further studies conducted by Weingarten [253,254] resulted in a more detailed synthetic mechanism.

SCHEME 9



Several important points were noted in this work.

1. Copper (I) was believed to be the catalytically active form.

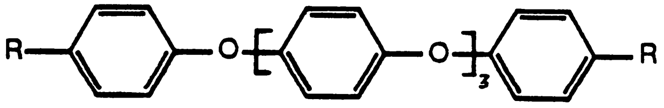
2. The halogen reactivity decreases in the order I > Br > Cl > > F.

3. The nature and position of substituent effects were similar to previously studied aromatic nucleophilic substitution.

4. The reaction was found to be first order in catalyst and in aryl halide, but a variable order was noted for potassium phenoxide.

The copper (I) in Scheme 9 is envisioned to first interact with the electrons of the aromatic halide. The validity of this mechanism has further been substantiated by the isolation of cuprous ion-benzene complexes [255]. The role of solvent in the polymer forming reaction does not appear critical [238,248] provided it is inert and high boiling. The rate of the reaction was markedly affected by temperature [238]. At a reaction temperature of 170°C, the reaction was found to be seven times slower than at 200°C. Additionally, in the PPE system, at 170°C, linear but very low molecular weight product could be obtained as a precipitate from the reaction mixture. The Ullmann reaction can be accompanied by side reactions such as reductive dehalogenation [256], Ullmann coupling [232] and branching or crosslinking due to free radical formation [246]. Hence, the reaction conditions, solvent and nature of the aromatic halide play an important role in the relative contributions to the main and side reactions. Some of the polymers prepared with this method are shown in Table 1.

Some workers have utilized the Ullmann ether reaction to prepare oligomeric PPE's where R can be either -OH or -Br [257].



(29)

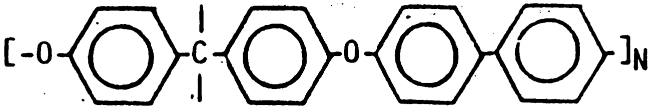
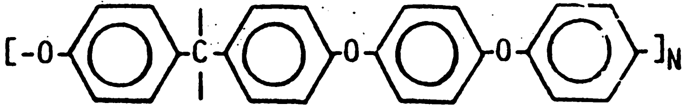
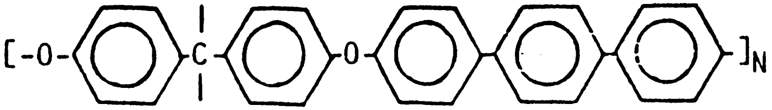
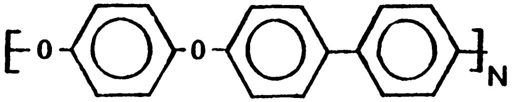
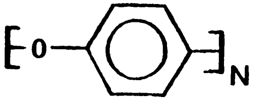
These oligomeric materials can be used to prepare high molecular weight PPE or various copolymers. Still others have utilized 3-bromophenol to prepare amorphous low molecular weight PPE for heat transfer fluids and stationary phases for gas chromatography [258].

2.7 *POLY(ARYLENE ETHERS) VIA OXIDATIVE COUPLING*

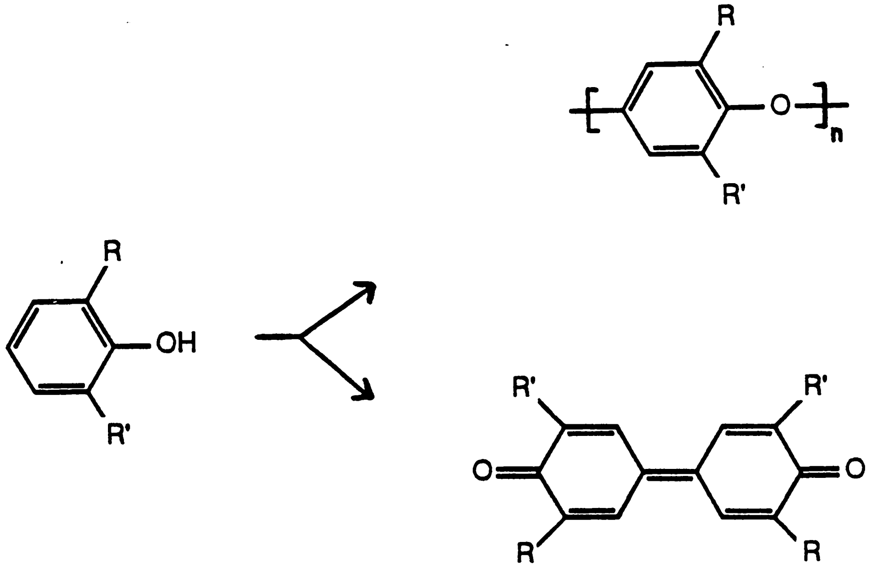
Oxidative coupling of 2,6-dimethylphenol is an important route to poly(2,6-dimethylphenylene oxide) or DMPPO. Hay [259] initially discovered that

TABLE 1

Polyethers Prepared with the Ullmann Ether Reaction

Polymer Repeat Unit	η_{sp}/C 0.2 gm/dl $CHCl_3$, 25°C	T_g°C	T_m°C	REF.
	0.70	154	—	248
	0.50	122	—	248
	1.1	182	—	248
	0.29	—	365	245
	1.15	90	286	238

2,6-dimethyl phenol could be effectively oxidized to yield a tough, flexible polymeric material. The general reaction scheme given below shows the polymer forming reaction along with the competitive side reaction.



(30)

(31)

Diphenoquinones were obtained as the major or minor product depending on the substituent R. The effect of several different substituents are shown in Table 2.

Reactions of unsubstituted and monosubstituted phenols yielded crosslinked or branched polymers. The reaction has been most successful with phenols having small electron donating groups in both ortho positions. When bulky groups such as t-butyl are present, carbon-carbon coupling predominates, producing mainly a diphenoquinone product.

In general, the substituted poly(phenylene oxides) exhibit good thermal stability but are prone to free radical oxidation at the benzylic methyl group. A wide variety of substituted 1,4-phenylene oxide polymers have been prepared and are summarized in Table 3.

The mechanism of oxidative coupling for 2,6-dimethyl phenol involves an initial formation of aryloxy radicals by oxidation of the phenol with the oxidized form of the copper-amine complex. The aryloxy radicals couple to form cyclohexadien-one which undergoes enolization and redistribution [260]. This is shown in Scheme 10.

In the first step, the dimer (II) is formed by enolization of the quinone ether (I). Oxidation of the dimer produces the dimer radical, which can couple with other radicals. If it couples with

Table 2

Effect of Ortho Phenol Substituents on the Product of Oxidative Coupling [223]

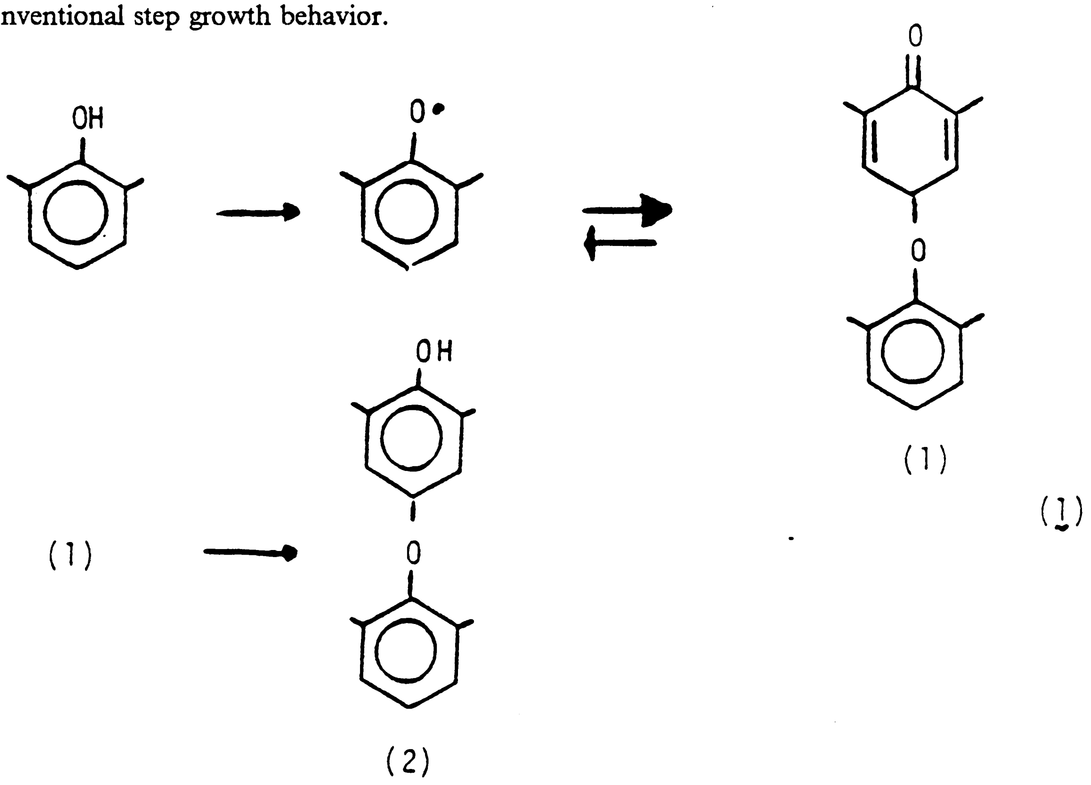
R	R'	Principal Product
Methyl	Methyl	Polymer
Methyl	Ethyl	Polymer
Methyl	t-butyl	Diphenoquinone
Methyl	Phenyl	Polymer
Ethyl	Ethyl	Polymer
i-Propyl	i-Propyl	Diphenoquinone
t-Butyl	t-Butyl	Diphenoquinone
Chloro	Chloro	Polymer
Methoxy	Methoxy	Diphenoquinone
Nitro	Nitro	No Reaction

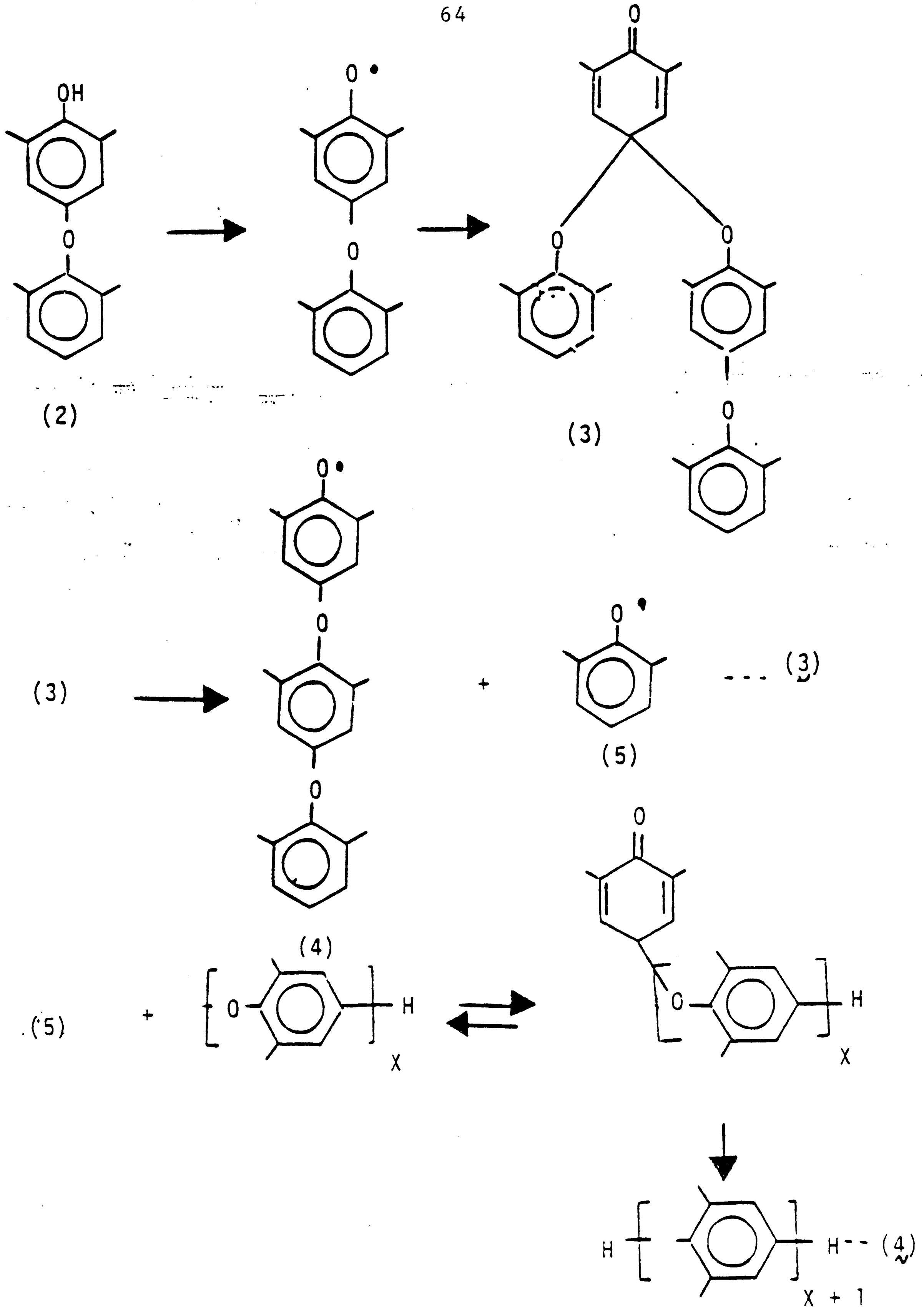
Table 3

Glass Transition and Melting Behavior of 2,6 Substituted 1,4 Poly(Arylene Oxides) [240]

R	R′	T_g°C	T_m,°C
CH_3	CH_3	211	268
CH_3	C_6H_5	169	-
CH_3	$CH_2C_6H_5$	99	-
CH_3	$CH(CH_3)_2$	144	-
OCH_3	OCH_3	167	-
Cl	Cl	228	269
C_6H_5	C_6H_5	230	480
C_6H_5	m. Tolyl	219	-
C_6H_5	p. Tolyl	281	-
C_6H_5	4-t-butyl phenyl	240	-
C_6H_5	α-napththyl	234	-

the 2,6-dimethyl phenoxy radical to form a quinol ether, enolization produces the trimer. Oxidation of the trimer followed by coupling with 2,6-dimethyl phenoxy radical produces the trimer. This procedure continues until high molecular weights are achieved. However, the polymerization does not proceed only by step-growth addition of one unit at a time to the growing chain, since coupling can occur between any combination of oligomers. For example, 2 dimer radicals may couple to form a ketal (III) or larger radicals may couple to form the analogous higher molecular weight species. Such a ketal dissociates to form a trimer radical (IV) which can again couple with a 2,6-dimethyl phenoxy radical to form a tetramer. These distribution reactions of oligomers by ketal formation and subsequent dissociation generate terminal quinol ethers which enolize to the more stable phenol. The enolization aids the attainment of high molecular weight by providing the driving force for the coupling of two oligomeric radicals to form a phenol terminated oligomer of higher molecular weight, and also by furnishing phenolic endgroups which undergo oxidation to form a new aryloxy radical which can enter into the redistribution-enolization scheme. This vast array of reactions such as oxidation, radical coupling, dissociation and enolization eventually increase the molecular weight in a manner reportedly resembling conventional step growth behavior.



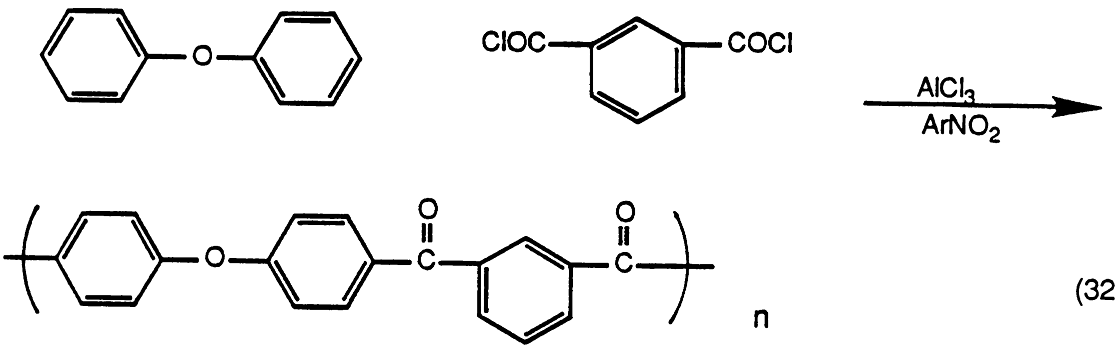

OH
O•
(2)
(3)
(3)
+
(5)
--- (3)
(4)
(5)
+
H
X
X
H
H -- (4)
X + 1

A wide variety of pyridine and pyridine derivatives have also been used as catalysts [261-264] as well as inorganic bases such as NaOH [265] and NH_4OH [266]. In all cases, the ratio of organic base to metal complex has been high. A host of transition metal salts have been used, such as cobalt [267], manganese [268-270] and most commonly, copper [271-275]. The reaction is generally carried out at room temperature for 3-6 hours utilizing common solvents such as benzene, chlorobenzene, toluene or chloroform.

2.8 *POLY(ARYLENE ETHERS) VIA POLYETHERFICIATION*

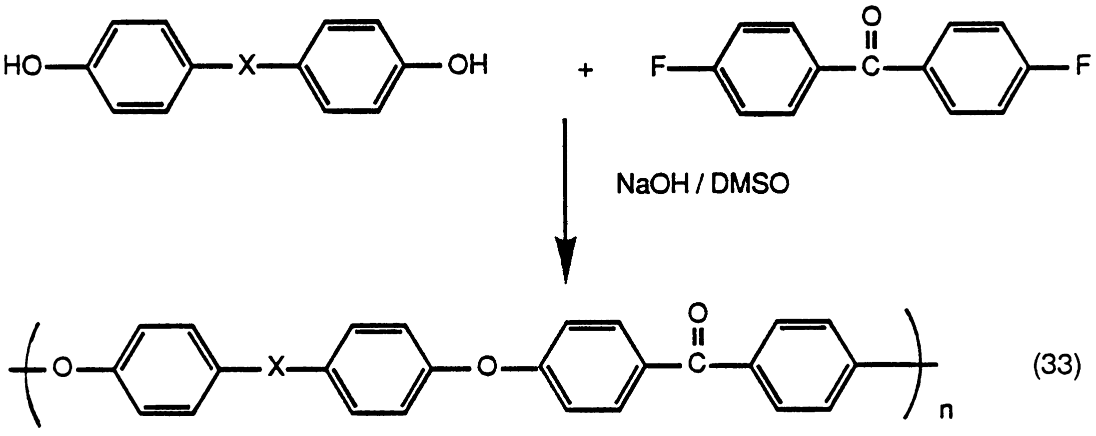
The last two sections dealt with the ether linkage as the principal functional group between aromatic groups in the polymer backbone. This section reviews macromolecules containing either sulfone or carbonyl groups in addition to the ether link. Earlier, it was mentioned that incorporation of these two groups into the reaction scheme increased the number of synthetic methods available for polymeric preparation. The choice of the sulfone group is based on the thermal stability of diphenylsulfones and their sulfonylation chemistry. In principle, poly(arylene ether sulfones) can be synthesized by polysulfonylation or polyetherficiation. Polysulfonylation involves the formation of the sulfone linkage between ether containing monomers and proceeds via electrophilic aromatic substitution in the presence of a Friedel-Craft catalyst [276-278]. In polyetherfication, the sulfone group is already present in one or both of the monomers and the ether link is formed via nucleophilic aromatic substitution in a dipolar aprotic solvent.

When the carbonyl group is present, a poly(arylene ether ketone) can be produced, again by two potential routes. Friedel-Craft acylation with aluminum chloride [279,280] could be used to obtain polymeric materials. However, side reactions, such as branching and problems



(32)

with highly crystalline materials are the main drawbacks to this method. Polyetherfication can be successfully used in the synthesis of amorphous poly(arylene ether ketones) via nucleophilic aromatic substitution in a dipolar aprotic solvent.



(33)

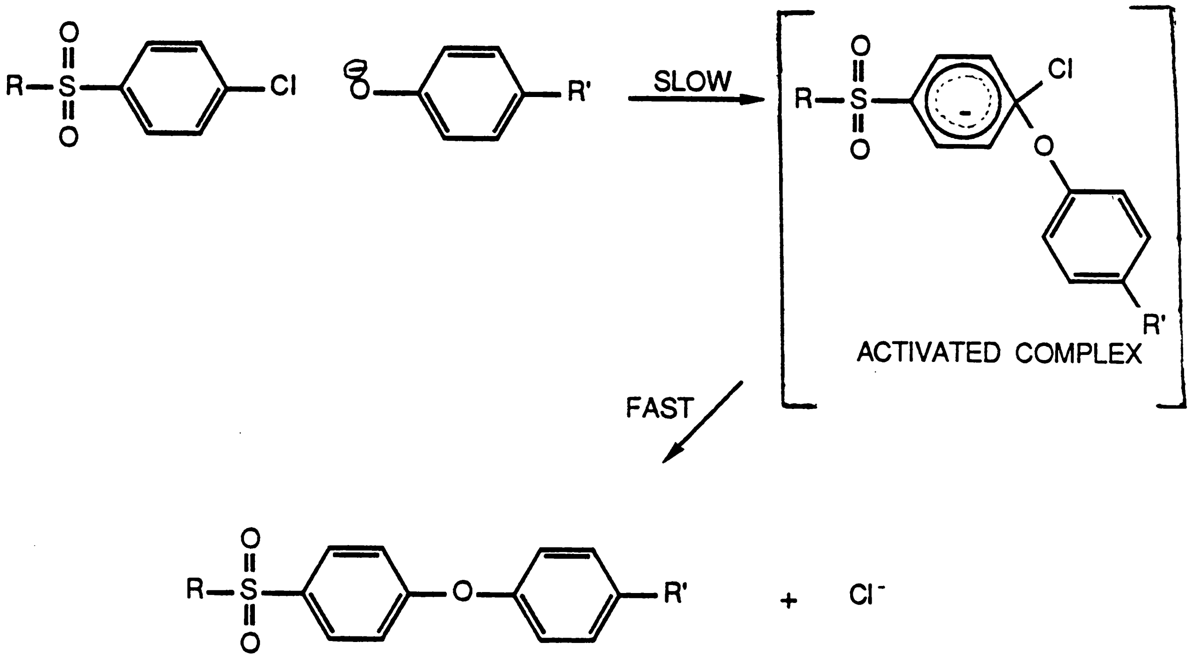
High molecular weight semi-crystalline polymers of this type were first prepared by Rose *et al.* [281] by using a high boiling solvent, diphenylsulfone, to facilitate the nucleophilic reaction of hydroquinone phenates with 4,4′-difluorobenzophenone.

2.9 *POLY(ARYLENE ETHER SULFONES)*

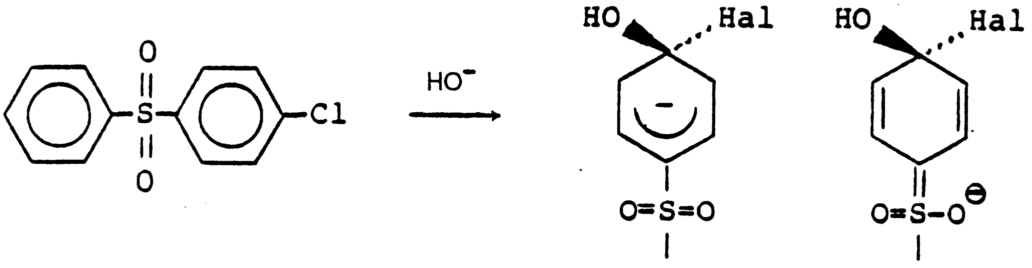
Since the main focus of this dissertation is on poly(arylene ether sulfone) oligomers, a short discussion of the synthesis of these materials via polyetherfication will be presented.

In 1967, Johnson *et al.* [282] described the synthesis of a large number of high molecular weight poly(arylene ether sulfones) via condensation of bisphenates with activated aromatic halides. An important consequence of this work was the synthesis and subsequent commercialization of bisphenol-A polysulfone (UDEL Polysulfone by Union Carbide). In this reaction, the ether bond is formed by the displacement of halide by the phenoxide. Thus, although the bisphenol may contain the sulfone group, this group forms an essential part of the dihalide monomer. The electron withdrawing nature of the sulfone group activates the dihalide, thus facilitating nucleophilic aromatic substitution.

Bunnett and Zahler proposed an aromatic nucleophilic substitution for similar monofunctional model compounds [250]. Schulze studied the kinetics of the polymer forming reaction and concluded that the observed rate constant was first order in phenoxide and activated halide concentration [283]. Rose *et al.* [281] studied the effect of substitution on the polymer forming and hydrolysis reaction. Based on their observations and the known kinetic data, they proposed the following mechanism.



The reaction is envisioned to take place in two steps, and involves an activated complex as an intermediate. The first step is the slow, rate determining step, which accounts for the overall second order reaction. The sulfone group plays a very important role in activating [284] the halide and forming the stabilized intermediate complex [285].



The order of reactivities of the halides in the activated systems has been observed to be F > Cl > > Br, I and p- > o- > > m- [281,285]. Aromatic halides which do not contain powerful electron withdrawing groups are unreactive via this mechanistic pathway. The more basic (less acidic) phenols are more reactive in halide displacement. A wide variety of poly(arylene ether sulfones) can be prepared by this method [281,282,286-296].

Chapter 3

EXPERIMENTAL PROCEDURES AND PURIFICATION

3.1 *GENERAL CONSIDERATIONS OF STEP-GROWTH POLYMERIZATION*

Step-growth polymerizations are characterized by the formation of linear long chain macromolecules via stepwise intermolecular condensations of reactive monomeric components. All step-growth polymerizations fall into two categories depending on the type of monomer(s) employed. The first, an A-B system, involves a single monomer unit which contains both types of functional endgroups. The second, an A-A/B-B system, involves two different bifunctional monomers in which each monomer possesses only one type of functional group. The following discussion will focus primarily on the A-A/B-B monomer system.

A primary concern in homopolymer syntheses is molecular weight control. The physical and mechanical properties of a polymer depend primarily on its molecular weight and molecular structure. Very low molecular weight polymers will not exhibit desirable properties while very high molecular weight materials are difficult and costly to process due to high viscosities. Consequently, a compromise between processability and optimum polymer properties must be achieved.

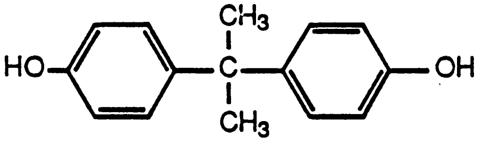
The importance of monomer and solvent purity and correct stoichiometry to achieve high molecular weight has already been discussed but should once again be stressed. The ability to synthesize functionalized oligomers of controlled molecular weight by either addition of a monofunctional reagent or by use of a stoichiometric imbalance of monomers has also been presented. These oligomers may not exhibit optimum properties by themselves, but their difunctional nature makes them valuable as ″macromonomers″ in copolymer syntheses.

The following section deals with the purification of various monomers and solvents along with experimental techniques for oligomer syntheses and their subsequent post reactions.

3.2 *MONOMER PURIFICATION*

3.2.1 *Bisphenol A* [2,2-Bis(4-hydroxyphenyl) propane]

Source:	Dow Chemical
Empirical formula:	$C_{15}H_{16}O_2$
Molecular weight:	228.27
Structure:	



Procedure: Bisphenol-A (200 g) was added to 800 ml toluene in a 1500 ml erlenmeyer flask. The solution was heated to 100°C with stirring until complete dissolution occured and 2 g activated charcoal and 100 ml toluene was added[1] . The dark solution was stirred for 20 minutes and filtered through a porcelain buchner funnel using Celite® to remove the charcoal[2] . The clear, colorless solution was reheated to dissolve the bisphenol-A and was reduced in volume by ca. 100 ml. The solution was slowly cooled to room temperature. The white crystals were filtered and dried under vacuum at 50°C for 12 hours. In order to remove any trapped solvent, the dried crystals were crushed and dried another 8 hours at 80-90°C in a vacuum oven[3] . Yield 80%, M.P. = 154-155°C (Lit. M.P. = 155°C).

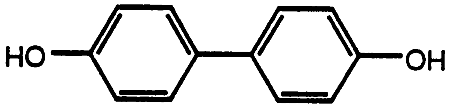
---

[1] The solution is near saturation under these conditions. The addition of 100 ml toluene dilutes the solution to facilitate filtration without affecting the yield

[2] The use of Celite® is essential to remove the charcoal completely.

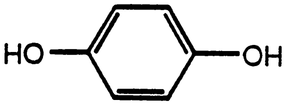
[3] This is particularly important as otherwise a substantial amount of toluene (0.5%) is trapped in the crystals.

3.2.2 *Biphenol* (4,4′-dihydroxybiphenyl)

Source:	Buffalo Chemical Corporation
Empirical formula:	$C_{12}H_{10}O_2$
Molecular weight:	186.22
Structure:	

The purity of this commercial sample was very high and was used without further purification, M.P. = 279°C (dec).

3.2.3 *Hydroquinone*

Source:	Eastman Kodak
Empirical formula:	$C_8H_6O_2$
Molecular weight:	110.12
Structure:	

Procedure: 600 ml high purity acetone was placed in a 1 ℓ erlenmeyer flask and covered with aluminum foil. Dry argon or nitrogen was bubbled through it for 15 minutes and the solution was then boiled[4]. 90 g hydroquinone was then added and the solution was cooled to room temperature. The gas inlet was removed and the flask was immediately stoppered to maintain the inert atmosphere over the solution. The colorless solution was cooled in a freezer and the crystals were filtered and dried in a vacuum oven at 30°C for 6 hours. Yield 75%[5] M.P. = 171-172°C (Lit. 171°C).

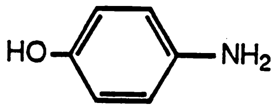
---

[4] Hydroquinone is easily oxidized to the quinone; therefore, acetone must be completely deoxygenated before use.

[5] Purified hydroquinone should be stored in a dark bottle under a nitrogen atmosphere.

3.2.4 *4-aminophenol*

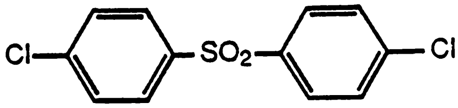
Source:	Aldrich
Empirical formula:	C_6H_7NO
Molecular weight:	109.129
Structure:	



25 g of 4-aminophenol were added to a 500 ml erlenmeyer flask with 50 ml deoxygenated distilled water and heated to boiling. Deoxygenated 95% ethanol was added until solution was effected. The solution was filtered under nitrogen and was allowed to cool. The off-white crystals obtained were filtered and dried under vacuum at 50°C for 4 hours. It was then placed in a sublimator and heated to 100°C/0.3 mm Hg. The white product obtained was dried under vacuum and stored in a sealed brown bottle in a dessicator[6] Yield 40% M.P. 190.5-191.0°C (Lit. M.P. = 190°C).

3.2.5 *4,4′-Dichlorodiphenyl sulfone*

Source:	Union Carbide
Empirical formula:	$C_{12}H_8Cl_2O_2S$
Molecular weight:	287.16
Structure:	



Procedure: 4,4′-dichlorodiphenyl sulfone (500 g) and toluene (800 ml) were placed in a 1500 ml erlenmeyer flask and heated to boiling with stirring. Two grams of activated charcoal was added and allowed to stir for 20 minutes. The dark colored solution was filtered through Celite® using a porcelain filtering funnel. The clear filtrate was boiled to reduce the volume and allowed to cool

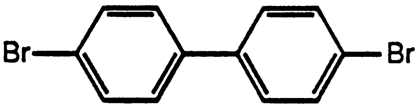
---

[6] 4-aminophenol readily oxidizes and cannot be exposed to air or stored for more than one week prior to use.

to room temperature overnight. The white crystals were filtered and washed with cold toluene. This procedure was repeated, but the activated charcoal step was omitted. The white crystalline solid obtained was dried under vacuum at 80°C for 8 hours. The crystals were crushed and dried again under vacuum at 90°C for 12 hours. Yield 75%, M.P. = 146.5-147.0°C (Lit. M.P. = 148°C).

3.2.6 *4,4'-Dibromobiphenyl*

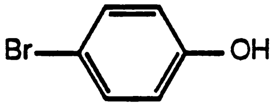
Source:	Fisher Scientific
Empirical formula:	$C_{12}H_8Br_2$
Molecular weight:	312.02
Structure	



Dibromobiphenyl (15 g) was placed in a 2 ℓ erlenmeyer flask and 1400 ml methanol was added. Following dissolution, the solution was vacuum filtered and slowly cooled to room temperature. The white crystals were collected by filtration, washed with cold methanol and dried. The process was repeated and the purified material was dried under vacuum at 50°C for 4 hours. The crystals were crushed and redried at 70°C for 8 hours. This monomer was stored in a dessicator. Yield 70%, M.P. = 163.5-164.5°C (Lit. 164°C).

3.2.7 *4-Bromophenol*

Source:	Fisher Scientific
Empirical formula:	C_6H_5BrO
Molecular weight:	173.02
Structure:	



4-Bromophenol (50 g) was dissolved in 65 ml chloroform in a 125 erlenmeyer flask with heating. One gram activated charcoal was added and stirred for 10 minutes. The solution was filtered through Celite® and the deep red solution was reduced in volume to 40 ml. It was then placed in a refrigerator and after 3 hours, a seed crystal was added. Reddish platelets were obtained which were filtered and washed with cold chloroform.[7] The procedure was repeated two or three times until the supernatant liquid was lightly colored (or colorless) and the large platelets obtained were white. Then they were dried under vacuum at 25°C for 4 hours, crushed and redried for 24 hours and stored in a dessicator[8] Yield after 3 recrystallizations 40%, M.P. = 63.0-64.0°C (Lit. 64°C).

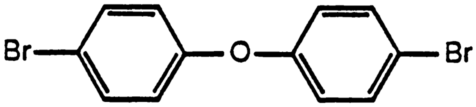
---

[7] The supernatant liquids from all recrystallizations were saved, reduced in volume by 50%, and seeded to obtain a second crop in 45% yield, M.P. = 62.0-64.0°C.

[8] 4-bromophenol was still pure after being stored in a tightly sealed sample bottle in a dessicator 3 months.

3.2.8 *Bis(4-bromophenyl) ether*

Source:	Kodak
Empirical formula:	$C_{12}H_8Br_2O$
Molecular weight:	328.01
Structure:	



20 gms of BPE were added to a 250 ml erlenmeyer flask and dissolved in 95% ethanol. The solution was filtered and cooled to room temperature. The white crystals obtained were again crystallized from 95% ethanol. The BPE was collected by filtration and dried 3 hours at 50°C under reduced pressure. The crystals were then dissolved in benzene (or toluene), filtered and slow cooled to obtain the purified product. It was dried in vacuo for 24 hours at 25°C and stored in a dessicator. Yield = 60%, M.P. = 61.0-62.0°C (Lit. M.P. = 62.0°C).

3.3 *PURIFICATION OF SOLVENTS*

Poly(arylene ether sulfones) are synthesized by the reaction of bisphenates with activated aromatic halides in a dipolar, aprotic solvent under anhydrous conditions. These solvents are hygroscopic, high boiling and usually sensitive to strong alkali, especially at high temperatures. The solvents used in these studies were N-methyl-2-pyrollidone (NMP), dimethyl sulfoxide (DMSO) and N,N′-dimethyl formamide (DMF). These solvents were distilled using the apparatus assembly shown in Figure 5 and were stored under nitrogen unless otherwise noted.

Poly(arylene ethers) synthesized with the Ullmann aryl ether synthesis utilized non-activated aromatic halides and require a high boiling, inert solvent. The solvents used in these systems were benzophenone, 1,4-dimethoxybenzene and 1,3-dimethoxybenzene.

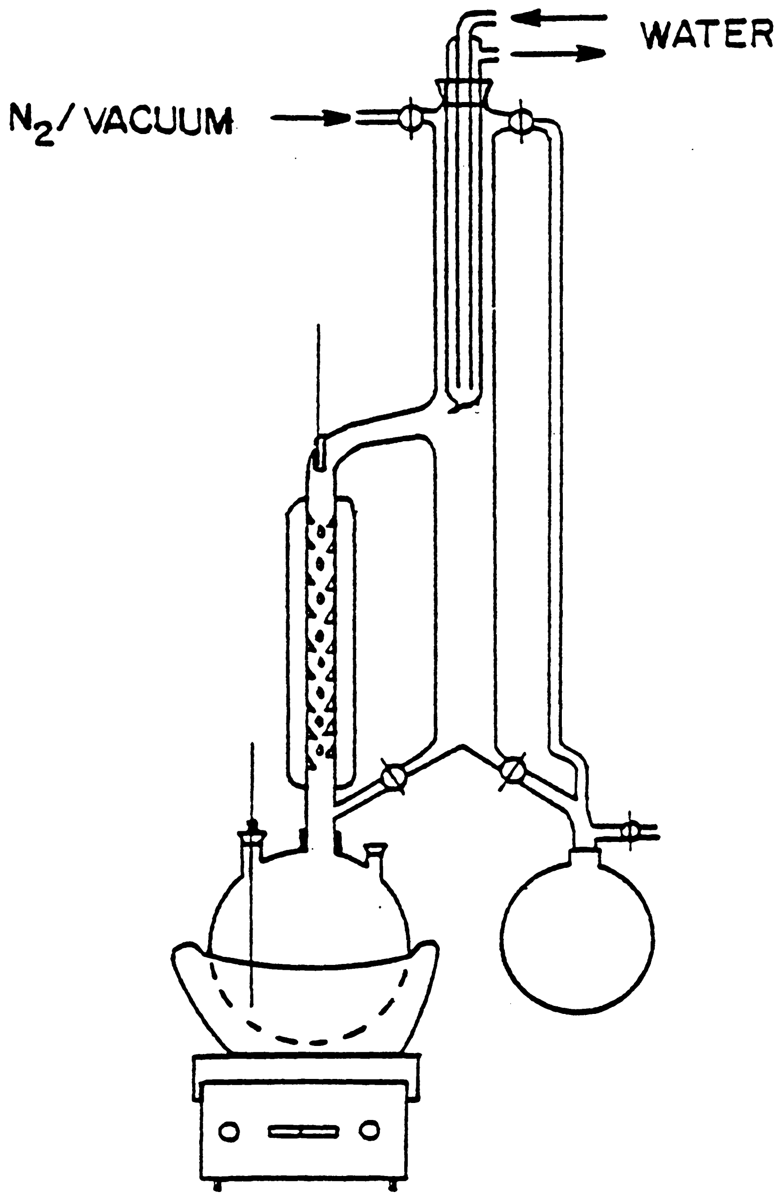
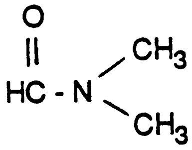


Figure (5) : Apparatus assembly used for solvent distillation

3.3.1 *N,N'-dimethylformamide* (DMF)

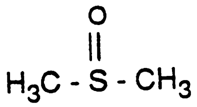
Source:	Fisher Scientific
Dielectric constant:	37
Density (20°C):	0.9487
Boiling point (1 atm.):	153°C, 40°C/10 mm
Structure:	



DMF (150 ml) was stirred over ≅ 2 g crushed calcium hydride for 12 hours and distilled under reduced pressure. A low boiling fraction, ≅ 20 ml, was removed and discarded. A constant boiling fraction, ca. 100 ml, was obtained as a colorless liquid and stored over a large piece of calcium hydride in a 250 ml round bottom flask fitted with a drying tube. Purified DMF could not be stored for periods greater than 1 week due to excessive formation of amines.

3.3.2 *Dimethyl sulfoxide* (DMSO)

Source:	Fisher Scientific
Dielectric constant:	47
Density (20°C):	1.1014
Boiling point:	190°C, dec. ≥ 160°C, 85°C/20 mm
Structure:	

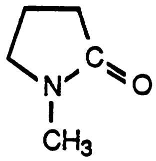


$$H_3C - \overset{\overset{O}{\|}}{S} - CH_3$$

DMSO (800 ml) was stirred over ≅3 g crushed calcium hydride for 24 hours and then distilled under nitrogen at reduced pressure. After discarding the first 30 ml, 700 ml of a constant boiling fraction was obtained as a clear, colorless liquid. It was stored over calcium hydride or over pretreated 5 Å molecular sieves in a flask fitted with a drying tube. DMSO could not be used as a polymerization solvent after periods of 2 or 3 days and hence should be freshly distilled before use.

3.3.3 *N-methyl-2-pyrollidone* (NMP) [90]

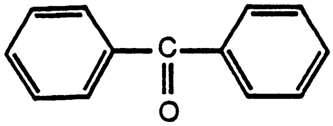
Source:	GAF or Fisher Scientific
Dielectric constant (25°C):	32.2
Density (25°C):	1.026
Boiling point:	202°C, (dec.), 100°C/24 mm
Structure:	



NMP (1700 ml) was stirred over ≅3 g crushed calcium hydride for 24 hours. It was distilled under vacuum, discarding the first 50 ml and collecting a constant boiling 1500 ml fraction. NMP could be stored for extended periods of time over either calcium hydride or pretreated 5 Å molecular sieves in a flask fitted with a drying tube. As long as the NMP remained colorless, it was essentially polymer grade solvent.

3.3.4 *Benzophenone*

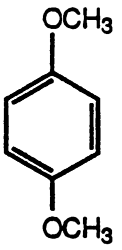
Source:	Aldrich or Fisher Scientific
Dielectric constant (50°C):	11.4
Density (20°C):	1.146
Boiling point:	306°C, M.P. = 48.5-49.0°C
Structure:	



Technical grade benzophenone (500 g) was dissolved in 600 ml methanol in a 1500 ml erlenmeyer flask. Activated charcoal was added and stirred for 20 minutes. The dark solution was filtered through a Celite®-packed Buchner funnel. The clear filtrate was reheated to reduce the volume and then was cooled to room temperature. After 8 hours, the flask was placed in the freezer. The recrystallization was then repeated, omitting the activated charcoal. The white crystals were dried under vacuum for 8 hours at room temperature, crushed and re-dried for 24 hours. Yield = 65%, M.P. = 48.0-48.5°C.

3.3.5 *1,4-Dimethoxybenzene*

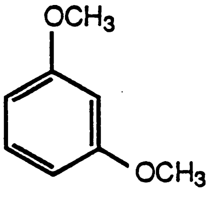
Source: Fisher Scientific
Dielectric constant (50°C): 13.5
Density (55°C): 1.0526
Boiling point: 212°C, M.P. = 58.0°C
Structure:



Dimethoxybenzene (500 g) was recrystallized from 600 ml methanol in a 1500 ml erlenmeyer flask. White crystals were obtained and dried under vacuum at 25°C for 24 hours and then stored in a tightly sealed sample bottle. Yield 75%, M.P. 57.5-58.0°C.

3.3.6 *1,3-Dimethoxybenzene*

Source: Kodak (Veratrole)
Dielectric constant (25°C): 14.3
Density (25°C): 1.0552
Boiling point: 218°C, M.P. = -19.0°C
Structure:



Veratrole (250 ml) was extracted twice with 200 ml aqueous NaOH (10% w/w) and then twice with 200 ml distilled water using a separatory funnel. The veratrole was dried over barium oxide and fractionally distilled under reduced pressure. A fore cut, ≅ 10%, was discarded and 200 ml of a constant boiling middle fraction was obtained as a colorless liquid. It was stored in a flask fitted with a drying tube.

3.4 *MISCELLANEOUS PURIFICATIONS*

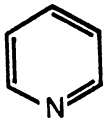
3.4.1 *Potassium Carbonate*

Source	Fisher Scientific

A fresh 500 g bottle of certified K_2CO_3 was placed in a vacuum oven at 75°C for 16 hours. It was then stored in a dessicator until needed.

3.4.2 *Pyridine*

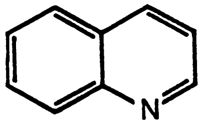
Source:	Fisher Scientific
Density (20°C):	0.9831
Molecular weight:	79.10
Boiling point:	116°C
Structure:	



Pyridine (50 ml) was refluxed with 5 g solid KOH for 2 hours. It was then fractionally distilled, taking a constantly boiling middle fraction of 25 ml. It was stored in a sealed serum vial.

3.4.3 *Quinoline*

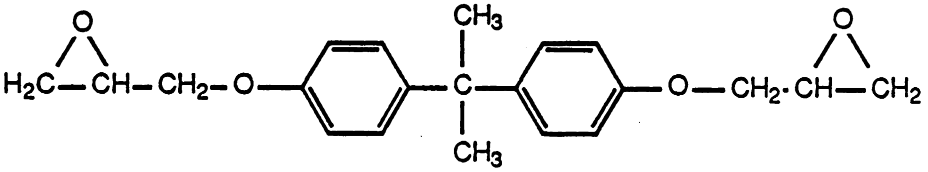
Source:	Aldrich
Density (20°C):	1.0937
Molecular weight:	129.16
Boiling point:	236°C, 112°C/16 mm
Structure:	



50 mls of the yellowish quinoline was stirred over 1 g sodium sulfate in a flask fitted with a drying tube for 24 hours. It was then filtered into a 50 ml 1 neck round bottom flask and 1 g zinc dust was added. The solution was heated with stirring and distilled under vacuum using a "cow" distillation apparatus. A broad boiling (48-110°C/16 mm) yellowish liquid was obtained first. 25 ml of a constant boiling fraction (116°C/16 mm) was obtained as a clear liquid. This was stored in a sealed brown serum vial under an argon atmosphere.

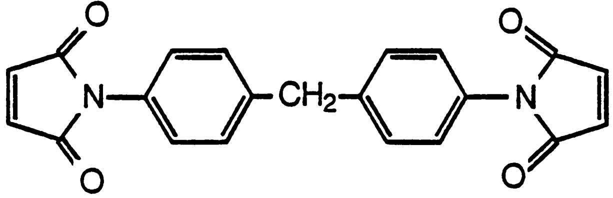
3.4.4 *Diglycidylether of Bisphenol-A* (DGEBA)

Source:	Dow Chemical (DER 332)
Empirical formula:	$C_{21}H_{24}O_4$
Molecular weight:	340.42
Melting point:	48-50°C
Structure:	



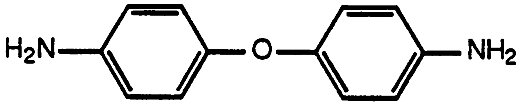
A 60/40 mixture of methyl isobutyl ketone and 2-ethoxyethyl ether was used to dissolve the DER 332. The solution was filtered and placed in the refrigerator for up to 3 days. The white crystals obtained were washed several times with hexanes and dried under vacuum at 20°C for 24 hours and then crushed and re-dried for 48 hours. Prior to use, it was again dried at 20°C for 24 hours.

3.4.5 *1,1′-(Methylenedi-4,1-phenylene) bismaleimide* (BMI)

Source:	Aldrich
Empirical formula:	$C_{21}H_{14}N_2O_4$
Molecular weight:	358.36
Structure:	

50 gms of the yellow BMI were dissolved in 400 ml of a 1:1 (V/V) mixture of methanol/chloroform. The solution was filtered and placed in the refrigerator. The fine yellow crystals were collected by filtration and the process was repeated. In the second recrystallization, the solution cooled slowly to room temperature. Thin layer chromatography was performed by dissolving the BMI in acetone and eluting with 95/5 methylene chloride-methanol. Yield 45-50%, M.P. (DSC) = 158.1-158.9°C (Lit. M.P. = 158°C).

3.4.6 *(4-aminophenyl) ether* [oxydianiline-ODA]

Source:	Fisher Scientific
Empirical formula:	$C_{12}H_{12}N_2O$
Molecular weight:	200.24
Structure:	

125 gms of brown ODA were placed in a 2-ℓ erlenmeyer flask with 1200 ml 95% ethanol and 600 ml water[9] were added and heated to reflux[10] It was cooled rapidly to 5°C and filtered. The black solution was discarded. The filtered solid was dissolved in degassed 70/30 ethanol-water mixture

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[9] Both solvents need to be degassed prior to use.

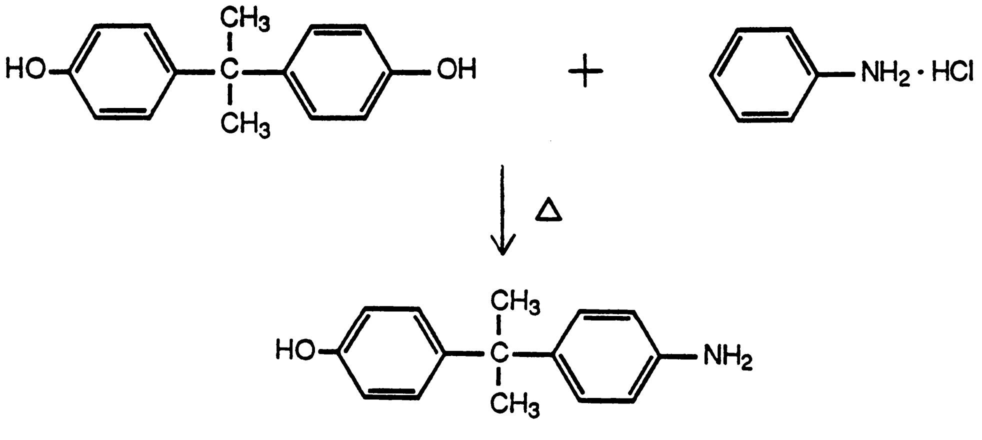
[10] All the ODA did not dissolve in this step.

and stirred with activated charcoal at ≅60°C for 6 hours. The solution was filtered through Celite®, reduced in volume and the purple solution slowly cooled to room temperature[11] The off-white crystals obtained were filtered, washed with cold ethanol and dried under vacuum at 80°C for 5 hours. The ODA was then sublimed in vacuo onto a cold finger at 160-170°C/.9-1 mm. It was stored in a sealed brown sample jar in a dessicator. Yield 30%, M.P. = 191.0-191.5°C (Lit. M.P. = 192°C).

3.5 *MONOMER SYNTHESIS*

3.5.1 *Synthesis of Monoamino Bisphenol-A (MBA)* [310]

2,2′-(4-aminophenyl-4-hydroxyphenyl) propane (MBA)
Empirical formula: $C_{15}H_{17}NO$
Molecular weight: 227.35
Reaction:



Procedure: Aniline hydrochloride salt (0.30 mole) and purified bisphenol-A (0.10 mole) were charged to a 1 ℓ-4 neck flask. The flask is heated to 140°C where the mixture begins to melt. It is rapidly heated to 180°C under a fast argon flow. Phenol can be seen condensing in the Dean Stark trap as well as evolving out the top of the reflux condensor. After 30 minutes at 180°C, water was slowly added, 1 ml at a time, to the reaction flask. Water and phenol vigorously reflux into the

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[11] The crystals should be filtered as soon as possible since the crystals became noticeably darker with time.

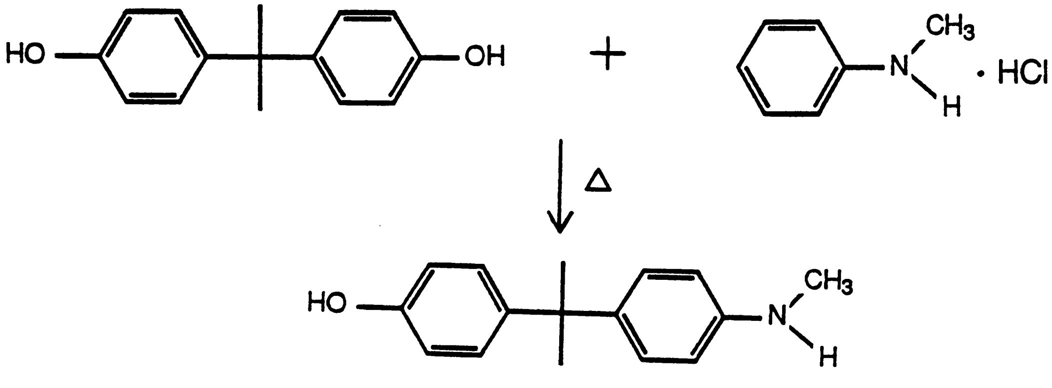
dean stark trap and this process was repeated for 5 minutes. The heating was discontinued and additional water was added to the flask to prevent solidification of the reactants. The reaction was cooled to 25°C and transferred to a 4-ℓ flask. 50% NaOH (or KOH) was added portionwise until pH = 12. Additional water, ≅ 2ℓ, was generally needed to keep the salts in solution. A small upper layer containing unreacted aniline was separated in a separatory funnel and the blue aqueous layer was extracted twice with toluene[12] The aqueous solution was then acidified with 10% HCl to pH = 6,[13] whereupon the off-white crude MBA precipitates. It was collected by filtration, washed several times with water and dried. It was recrystallized from ethanol-water[14] to obtain white needles, M.P. = 192.0-192.5°C in 70% yield.

3.5.2 *Synthesis of N-methyl MBA*

2-(4-(N-methyl) aminophenyl)-2-(hydroxyphenyl) propane

Empirical formula:	$C_{16}H_{19}NO$
Molecular weight:	241.39

Reaction:



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[12] The aqueous layer must be at room temperature as an appreciable quantity of MBA becomes dissolved in toluene at elevated temperatures. The toluene layer may be dried over $MgSO_4$, filtered, and vacuum distilled to remove toluene and aniline. The diamino derivative of bisphenol-A can be obtained by recrystallization of the crude pot residue from water. M.P. = 133-134°C.

[13] A white solid precipitates at pH = 8-9 but redissolves on stirring. Below pH = 5, MBA will form the hydrochloride salt and becomes soluble in water. Bisphenol-A is difficult to separate from MBA by recrystallization. Hence, one may choose to make the solution pH = 2, where all the MBA dissolves and filter off any bisphenol-A. The solution's pH may then be adjusted to pH = 6 and the MBA worked up as usual.

[14] Depending upon the color and melting point of the MBA, a second recrystallization may be necessary. If the material is initially light brown or pink, activated charcoal should be used.

Procedure: The same procedure was used as described above for MBA with the exception that distilled N-methyl aniline and reagent grade HCL were used to form the salt *in situ*. Yield 50%, M.P. = 133.0-134.5°C.

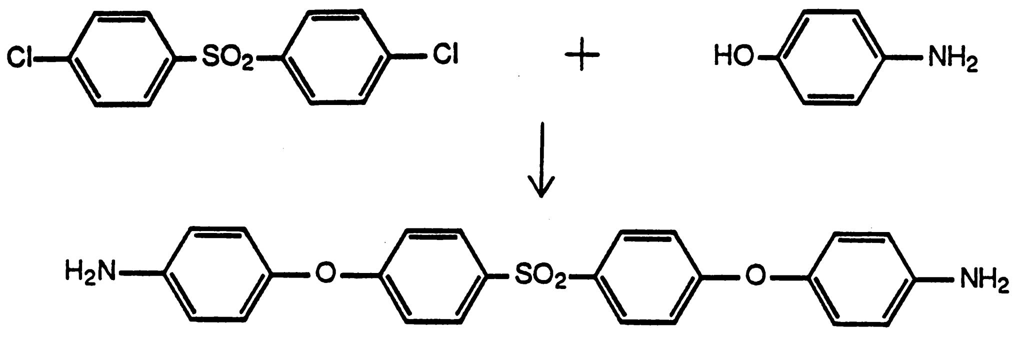
3.5.3 *Synthesis of N,N′-dimethyl MBA*

2-(4-(N,N′-dimethyl) aminophenyl)-2-(hydroxyphenol) propane
Empirical formula: $C_{17}H_{21}NO$
Molecular weight: 255.42

Procedure: The same procedure was again employed in this synthesis, but using N,N′-dimethyl aniline and HCl. It was run only for 20 minutes at 180°C due to the strong activating effects of the N-methyl substituents towards electrophilic aromatic substitution [321].

3.5.4 *Sulfone Ether Diamine (SED) of p-aminophenol*

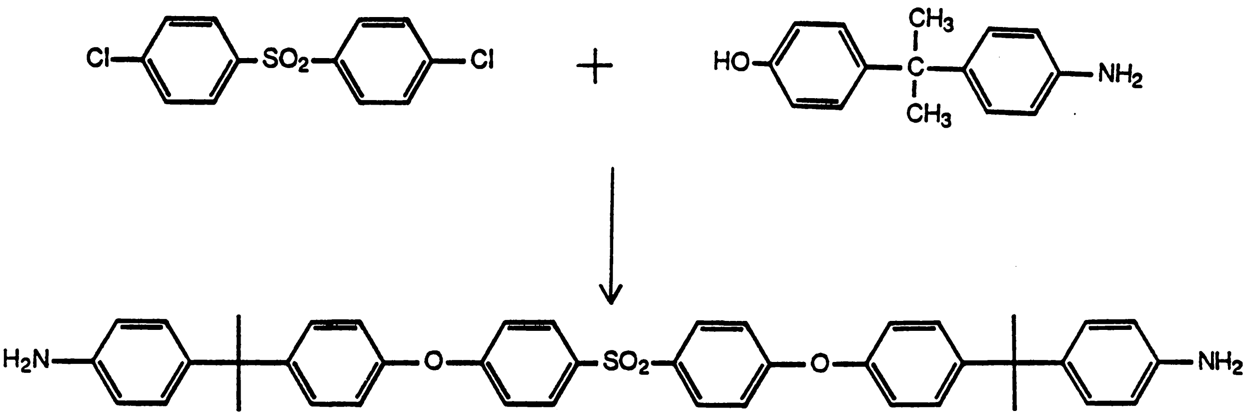
Bis[4-(aminophenoxy)phenyl] sulfone
Empirical formula: $C_{24}H_{20}N_2O_4S$
Molecular weight: 432.62
Reaction:



Procedure: Purified p-aminophenol (0.21 mole) and 4,4′-dichlorodiphenyl sulfone (0.10 mole) were charged to a 1-ℓ 4 neck flask as shown in Figure 6. The reactants were dissolved in 300 ml distilled NMP and 125 ml of toluene were added. Crushed K_2CO_3 (0.20 mole) was added and the reaction was heated to 150°C, whereupon a toluene/water azeotrope began. The reaction was maintained at 155°C for 4 hours. An inert atmosphere, argon or nitrogen was maintained throughout the reaction. After 4 hours at 155°C, the reaction mixture was cooled to 80°C, filtered to remove the inorganic salts and was coagulated into an aqueous solution of 2% Na_2CO_3 and 1% sodium sulfate [298]. The pink powder was washed several times with warm (80°C) water, dried and recrystallized from n-butanol. A very light pink powder was obtained in 90% yield, M.P. = 192-193°C. M.W. by titration = 434 g/mole. ^1H NMR and FT-IR spectra confirmed the structure.

3.5.5 *Sulfone Ether Diamine (SED) of MBA*

Empirical formula: $C_{42}H_{40}N_2O_4S$
Molecular weight: 668.98
Reaction:



Procedure: Purified MBA (0.21 mole) and DCDPS (0.10 mole) were charged to a 1-ℓ flask and dissolved in 450 ml of distilled NMP. Crushed K_2CO_3 (0.20 mole) and 200 ml toluene were added and the reaction was heated to 150°C under an inert atmosphere. After 1 hour, the stoichiometric quantity of water had been removed from the system and the reaction was heated to 165°C for 3 hours. It was cooled to 80°C, filtered, and precipitated in an aqueous solution of 5% Na_2CO_3 and 1% sodium sulfate. The tan colored powder was washed with warm water until neutral to pH paper. A suitable recrystallizing solvent could not be found. The SED was too soluble in most solvents and attempts to use a binary solvent system inevitably resulted in an oil.

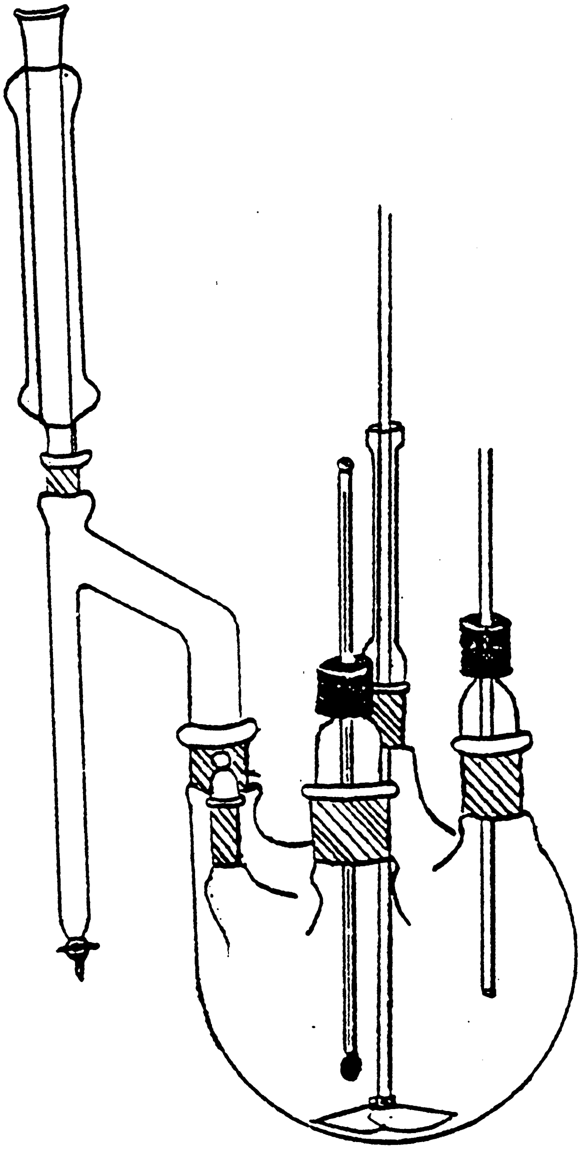
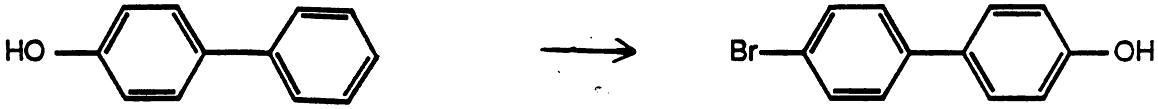


Figure (6) : Typical reaction assembly used for the synthesis of Polymers.

Polymeric grade monomer was obtained by dissolving the SED in toluene, extracting with aqueous NaOH (5%) to remove unreacted MBA and then with water. The toluene solution was dried over $MgSO_4$, filtered and reduced in volume to obtain a light brown powder in 98% yield, M.P. = 155-156°C, molecular weight by amine titration = 670 g/mole. ^1H NMR and FT-IR spectra confirmed the structure.

3.5.6 *Attempted Preparation of 4-Bromo-4-Hydroxybiphenyl*

Empirical formula: $C_{12}H_9BrO$
Molecular weight: 249.11
Reaction:



Procedure: 4-phenyl phenol (0.05 mole) was added to 60 ml of chloroform at 0°C. Very little dissolution occurred. Bromine was added via syringe and the solution became brightly colored. After the color faded, more Br was added until a slight excess had been used (0.30 mole Br_2). The solution became very light in color and very little solid remained. The solution was filtered and then heated to volatilize any remaining bromine. The solution was reduced in volume and cooled to 25°C. White crystals were obtained which were dried, M.P. = 145-167°C. T.L.C. was performed on silica gel plates using 50/50 hexane/ethyl acetate. The sample was spotted against 4-phenylphenol and the sample contained ≅10-20% unreacted material. Two subsequent recrystallizations from $CHCl_3$ did not noticably affect the melting point or T.L.C. The target molecule could not be separated from its starting compound and this approach was abandoned.

3.6 *SYNTHESIS OF DIAMINE TERMINATED POLY(ARYLENE ETHER SULFONE)*

3.6.1 *Poly(Arylene Ether Sulfone) Oligomers* (Scheme 11)

Bisphenol-A-based
M.W. Repeat unit = 442

Procedure: Purified bisphenol-A (0.1612 moles), DCDPS (0.1800 moles) and MBA (0.0399 moles) were charged to the reaction vessel and dissolved in 650 ml NMP. Crushed K_2CO_3 (0.25 moles) was added to the colorless solution along with 250 ml toluene. It was heated to 155°C for 2 hours in order to dehydrate the system. Approximately 210 ml toluene were removed from the system and the reaction was heated to 170°C for 8 hours. The reaction became green and viscous and was cooled to ≅80°C. It was vacuum filtered to remove inorganic salts and was coagulated in isopropanol,[15] acidified with a few drops of glacial acetic acid. A tan powder was obtained by filtration, washed several times with IPA and allowed to dry. It was then stirred in hot water (90-95°C) for 4-8 hours to remove any trapped salts. It was then filtered, washed with alcohol and dried under vacuum at 60°C for 8 hours. The material was then redissolved in methylene chloride, filtered and reprecipitated in IPA. It was again stirred in hot water, filtered, washed with IPA and dried under vacuum at 100°C for 15 hours.

3.6.2 *Hydroquinone Based Diamine Terminated Poly(Arylene Ether Sulfone) Oligomers*

M.W. Repeat unit = 324
Reaction: Scheme 8

Procedure: The same synthetic procedure could be used for hydroquinone, biphenol or 50/50 molar mixtures of the two monomers.

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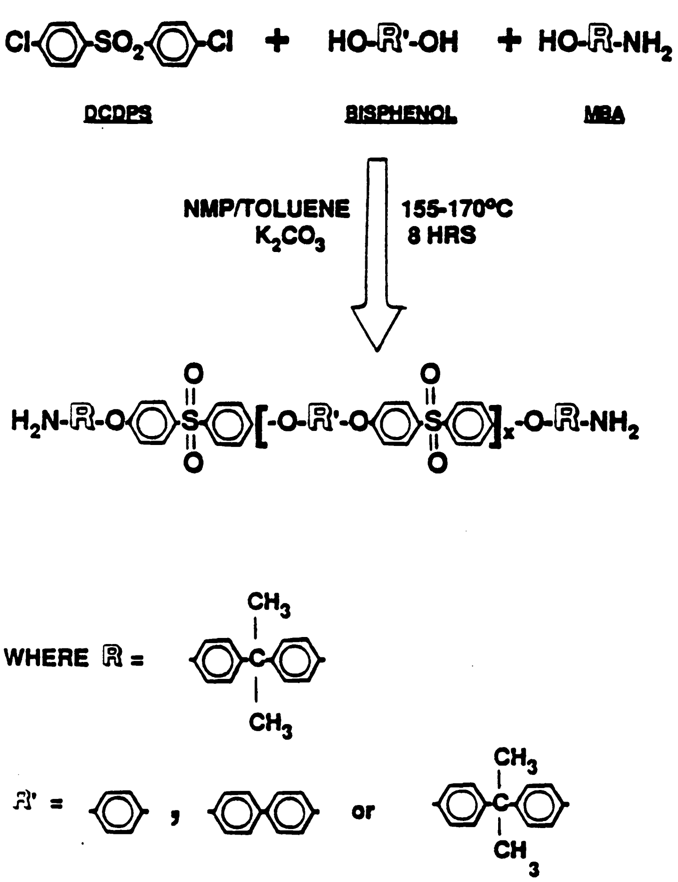
[15] Methanol should be used to precipitate and wash oligomers of $<M_n> = 5000$ g/mole or greater. The molar values of monomers presented here resulted in an oligomer of $<M_n> = 4100$ g/mole.

SCHEME 11


DCDPS
BISPHENOL
MBA
NMP/TOLUENE
K_2CO_3
155-170°C
8 HRS
WHERE R =
R' =
or

3.6.3 *Biphenol Based Diamine Terminated Poly(Arylene Ether Sulfone) Oligomers*

M.W. Repeat unit = 400
Reaction: Scheme 11

3.6.4 *Hydroquinone/Biphenol Based Diamine Terminated Poly(Arylene Ether Sulfone) Oligomers*

M.W. Repeat unit = 362
Reaction: Scheme 11

3.6.5 *Attempted Synthesis of Bisphenol-S Based Poly(Arylene Ether Sulfone) Oligomers*

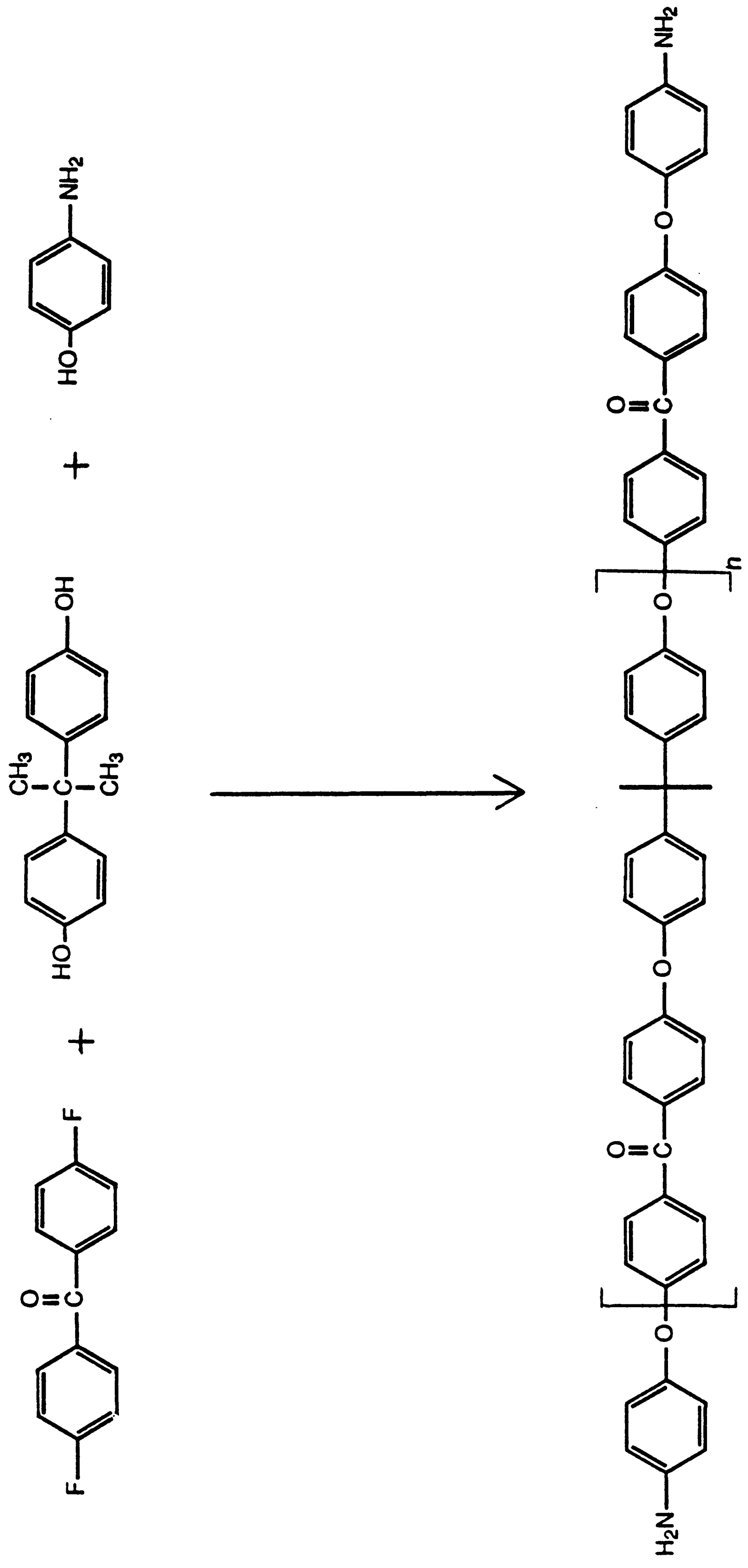
M.W. Repeat unit = 464
Reaction:

Procedure: Calculated amounts of DCDPS, Bisphenol-S and MBA were used for a $<M_N>$ = 10,000 g/mole oligomer. Under normal reaction conditions, the reaction did not turn its characteristic green color. Samples coagulated after 4, 6, 8, 10, 12, 14 and 16 hours did not appear any different from each other. After 16 hours, the reaction was stopped and a portion was worked up in the usual manner. Upon titration of the amine endgroups, the apparent $<M_N>$ = 26,000 g/mole. The powdery appearance of the material indicated a much lower molecular weight and a 2 point intrinsic viscosity measurement of 0.11 dl/g confirmed it. A second attempt using 4,4′ difluorodiphenyl sulfone was run. The same experimental observations, coupled with a high titration value and a low intrinsic viscosity measurement indicated that the reaction did not go to high degrees of polymerization and efficient end capping, possibly due to the slow reactivity of the bisphenol-S monomer, was not realized.

3.6.6 *Attempted Synthesis of Diamine Terminated Poly(Arylene Ether Ketone) Oligomers*

M.W. Repeat unit = 406.51
Reaction: Scheme 12

SCHEME 12

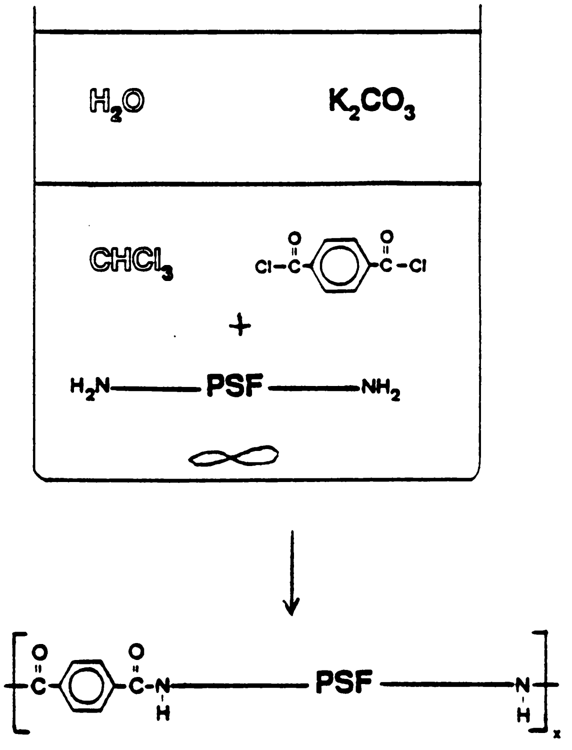


Procedure: The procedure of Kawakami *et al.* [298] was followed using proper molar quantities of bisphenol-A (0.0922), p-aminophenol (0.0166 moles, 2% excess) and purified 4,4′-difluorobenzophenone or DFB (0.1000 moles). The phenolic hydroxyl groups were first reacted with a stoichiometric quantity of NaOH (0.2000 mole) and the system was allowed to dehydrate for 5 hours. The activated aromatic halide, DFB, was added portionwise in a warm toluene solution via an addition funnel to keep the exotherm below 150°C. The purple-colored reaction was heated to 160°C for 2 hours, cooled to 100°C, vacuum filtered to remove inorganic salts and coagulated as previously described. Reactions of this dried oligomer with diacid chlorides did not result in polymeric materials. FT-IR of a solvent cast film revealed only a small amount of N-H stretching in the 3350 cm^{-1} region.

3.7 *POST REACTIONS OF DIAMINE TERMINATED OLIGOMERS*

3.7.1 *Chain Extension Reaction With Diacid Chloride Via Pseudo-Interfacial Techniques*

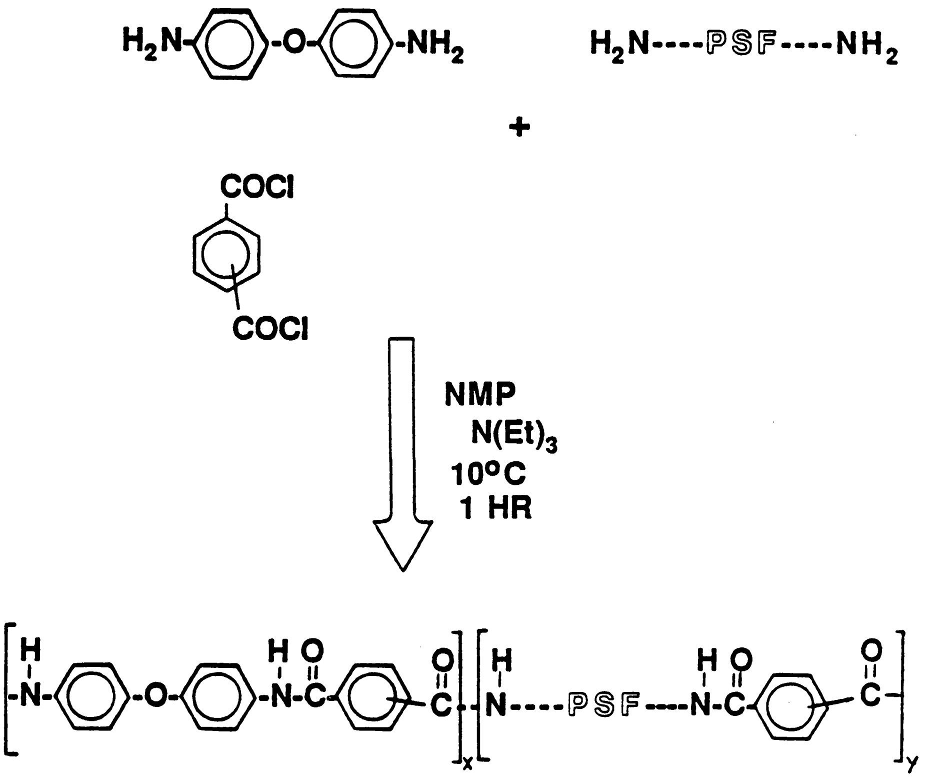
Reaction:



Procedure: Purified iso- (.001 mole) and terephthaloyl chloride (0.001 mole) were dissolved in 25 ml reagent grade chloroform. The solution was added to a Waring blender containing a solution of 0.002 moles of a diamine terminated oligomer in 30 ml $CHCl_3$ A solution containing 0.004 moles potassium carbonate in 30 ml water was added and vigorous stirring was applied for 20 minutes. After a few minutes, 30-100 ml of H_2O were added to keep the reaction temperature $\cong$30°C and to prevent the viscous material from being unevenly mixed. The reaction mixture was precipitated into a 50/50 MeOH/H_2O mixture containing a small amount of acetic acid. The fibrous polymer was washed with methanol, boiled in water for 2 hours, filtered and dried at 80°C for 6 hours under vacuum. The polymer was redissolved in $CHCl_3$ or THF, filtered to remove inorganic salts and the clear brown solution was reprecipitated into methanol. It was dried again under vacuum at 90°C for 12 hours.

3.7.2 *Block or Segmented Copolymers via Solution Polymerization*

Reaction:

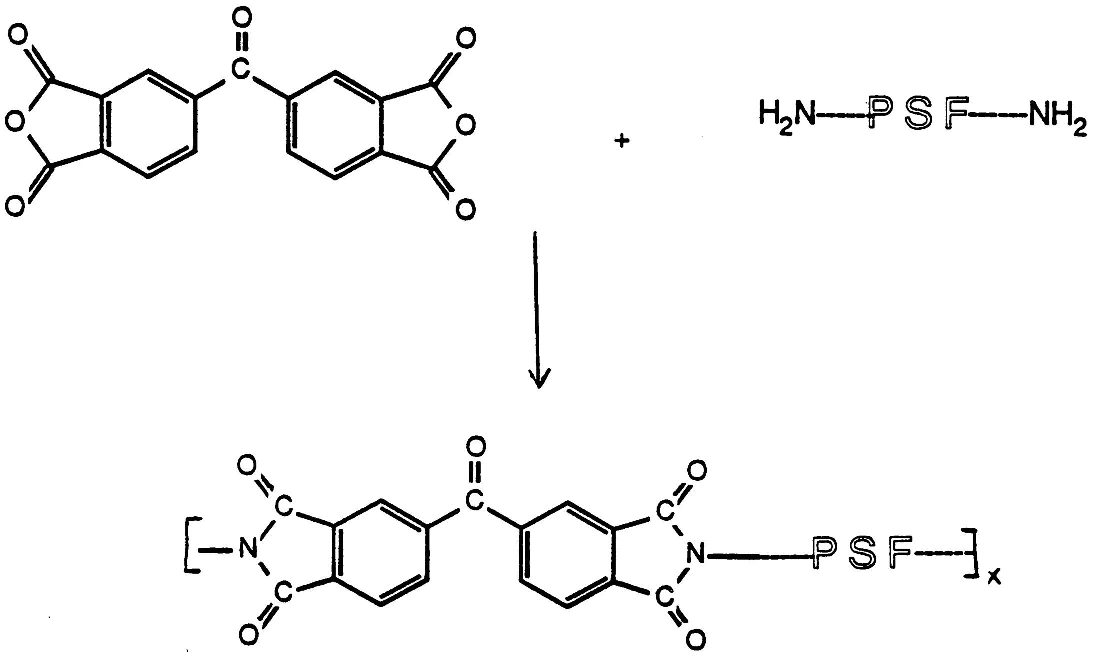


Procedure: Purified 4,4′-aminophenylether (ODA), 0.02 mole, and dry diamine terminated poly(arylene ether sulfone) oligomer, 0.001 mole were dissolved in freshly distilled, dry NMP. A 5% excess of dry, freshly distilled triethylamine (TEA), 0.044 moles, was added under an inert argon atmosphere. An addition funnel was filled with a solution of a 50/50 mixture of tere- and isophthaloyl chlorides (0.021 moles total) in dry, freshly distilled NMP. The acid chlorides were added dropwise to the diamine solution at 0-5°C. The solution became cloudy and slightly yellow as addition proceeded. After complete addition, the solution became so viscous that additional NMP was added to prevent the solution from "climbing up the stirbar". The reaction was heated to 50°C for 0.5 hours to ensure complete reaction. The reaction was filtered and the clear tan solution was precipitated into MeOH. The fibrous polymer was worked up as usual, redissolved in NMP, filtered, reprecipitated in MeOH, boiled in water and dried under vacuum at 100°C for 12 hours.

This reaction was performed at various times using only ODA, only an NH_2PSF, or only a SED.

3.7.3 *Synthesis of Poly(Imide Sulfones)*

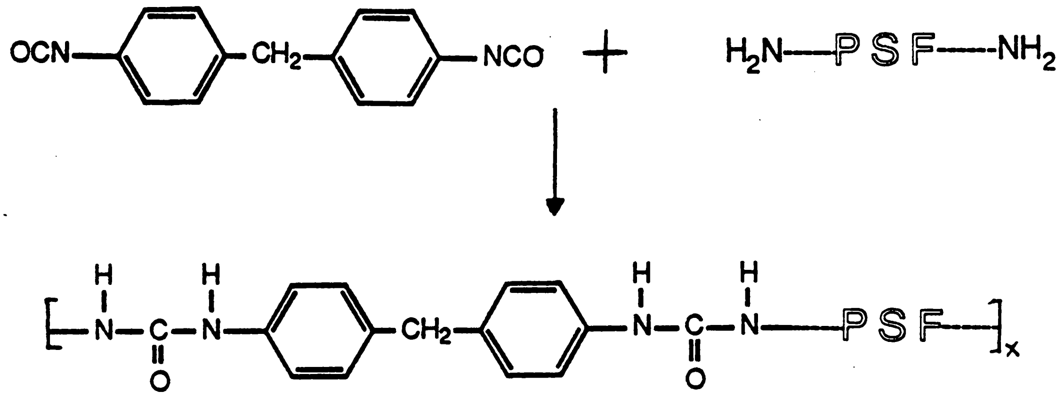
Reaction:



Procedure: Dried NH_2PSF (0.002 mole, $<M_N>$ = 3850 g/mole) was dissolved in dry DMAC to $\cong 15$ wt % solids. A 15 wt % solution of benzophenonetetracarboxylic dianhydride, BTDA (0.002 moles) in DMAC was added dropwise at 0°C to the diamine solution. After addition was complete, the reaction was allowed to come to room temperature and maintained that way for 24 hours. The viscous solution was cast onto a glass plate and subjected to a 3 stage curing procedure. The final temperature was 280°C. The final product was a flexible, creasable, yellow film which was soluble in THF, and dipolar aprotic solvents, such as DMAC and NMP.

3.7.4 *Synthesis of Poly(Urea Sulfones)*

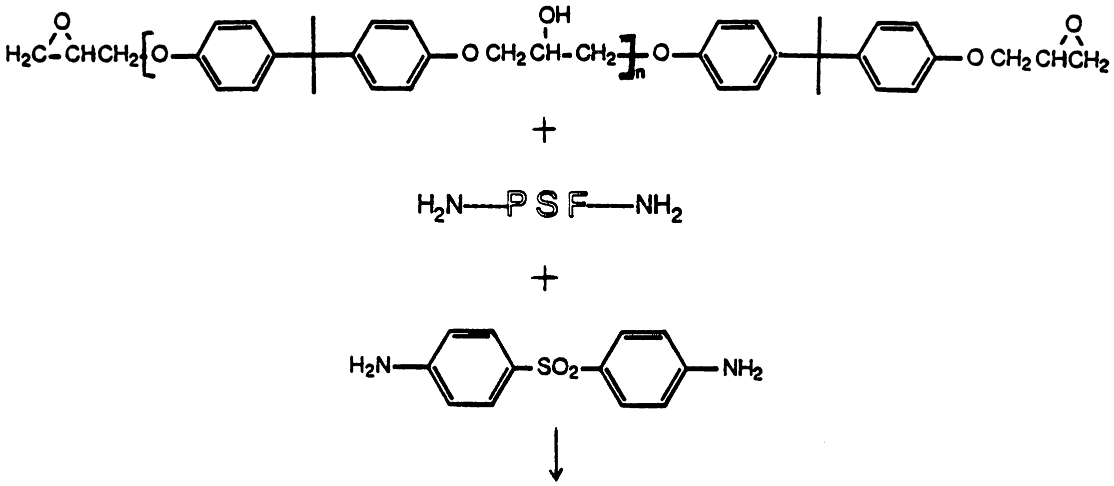
Reaction:



Procedure: Purified NH_2PSF (0.002 moles, $<M_N>$ = 6480 g/mole) was dissolved in dry, freshly distilled DMF and cooled to 0°C. Purified methylene diisocyanate (0.002 moles) in DMF was added dropwise. After complete addition, the reaction was brought to room temperature for 0.5 hr and then heated to 80°C for 0.5 hr. It was then cooled and precipitated in MeOH. The slightly fibrous polymer was filtered and dried. It was redissolved in THF, filtered and reprecipitated in MeOH. It was worked up as usual. An intrinsic viscosity in THF was run yielding a value of 0.82 dl/g.

3.7.5 *Synthesis of Amine Terminated Poly(Arylene Ether Sulfone) Oligomer Modified Epoxy Resins*

Reaction:



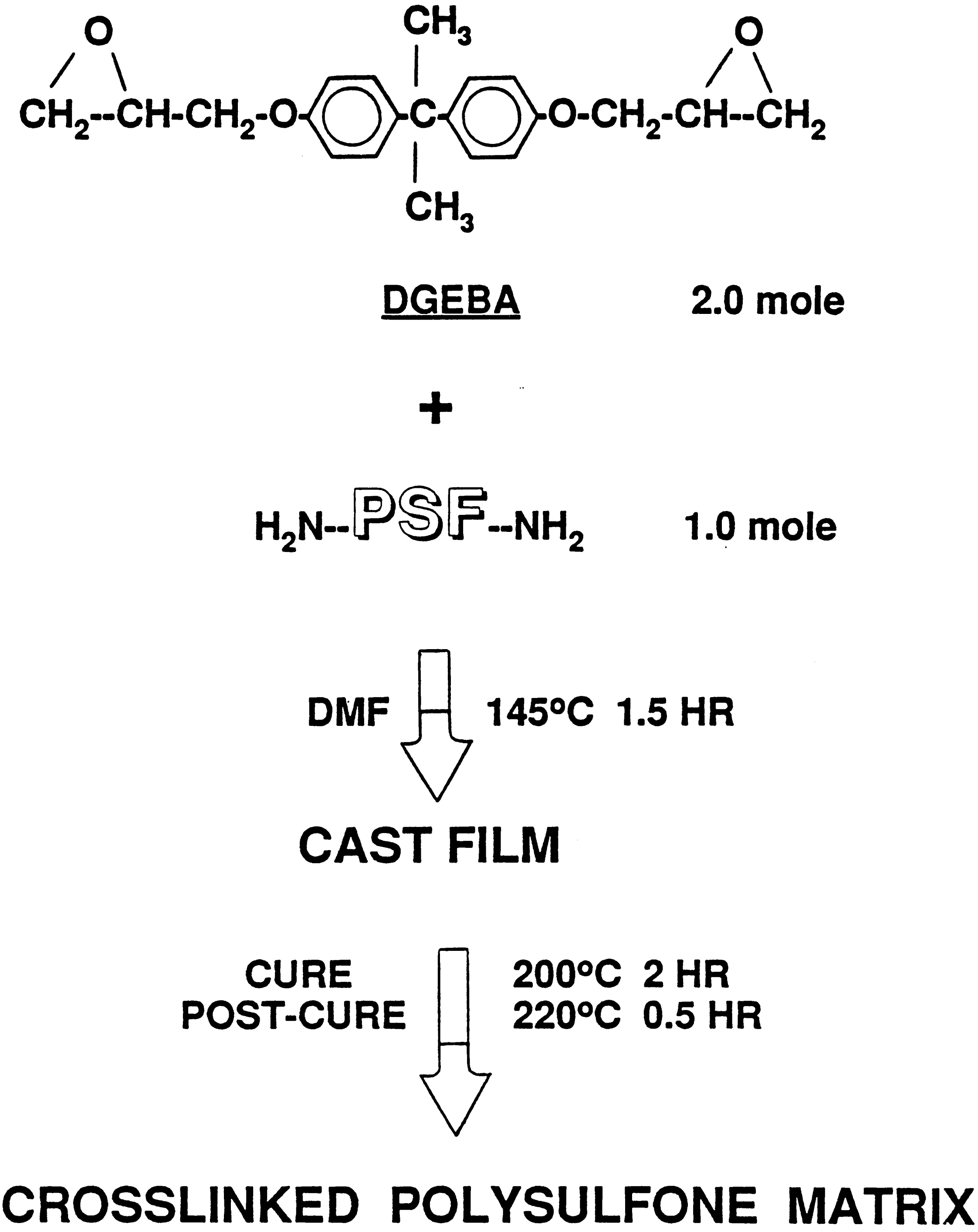
Procedure: Epon 828 (n = 0,1), (0.10 moles) was heated to 140°C in a stoppered 250 ml filter flask with stirring provided by a magnetic stirrer. Dry NH_2PSF (0.003 moles of 5000 g/mole or 12 wt %) was added to the Epon 828 and stirred until homogeneous. It was again degassed by stoppering the flask and applying a vacuum. After no more bubbling was evident, purified 4,4′-diaminodiphenyl sulfone (0.497 moles) was added to provide 2:1 overall stoichiometry. After the solution became homogeneous, it was poured into a preheated silicone mold which permitted preparation of test specimens for flexural modulus and fracture toughness. It was cured in an air circulating oven for 2 hours at 180°C and post-cured 0.5 hours at 205°C. The samples were transparent and brown in color.

3.7.6 *Synthesis of Lightly Crosslinked Amine Terminated Poly(Arylene Ether Sulfone) Oligomers*

Reaction: Scheme 13

Procedure: Purified NH_2PSF (0.002 moles) was dissolved in dry freshly distilled DMF to 20 wt % solids. It was heated to reflux with toluene to azeotrope any residual moisture. After all the

SCHEME 13



DGEBA 2.0 mole

+

H_2N--PSF--NH_2 1.0 mole

DMF 145°C 1.5 HR

CAST FILM

CURE 200°C 2 HR
POST-CURE 220°C 0.5 HR

CROSSLINKED POLYSULFONE MATRIX

toluene had been removed from the reaction vessel, diglycidyl ether of bisphenol-A, DGEBA (0.004 moles), was added and heated to 145°C for 1.5 hours. The reaction mixture became reddish-brown and viscous. Heating was discontinued and the reaction mixture was poured onto either glass plates, copper foil or aluminum foil and were cast into films of 15-25 mils thick. The films were placed in a vacuum oven at 60°C for 1 hour while the vacuum was held at 10 in Hg by "bleeding" the oven to the atmosphere[16] The temperature was raised to 80°C for 1 hour at 10 in Hg and then 1 hour at 80°C/20 in Hg. The temperature was then raised to 100°C/20 in Hg for 1 hour and finally 2 hours at 120°C and 30 in Hg[17] The films were then placed in an air circulating oven at 200°C for 2 hours and 220°C for 0.5 hours. The resultant films were brown, transparent and creasable.

3.7.7 *Synthesis of Poly(Aspartimides)*

Reaction: Scheme 14

Procedure: Purified BMI (0.05 moles) and ODA (0.0502 moles) were charged to a 250 ml flask and dissolved in 125 ml m-cresol. Glacial acetic acid (0.11 mole) was added and the mixture was heated to 100°C[18] After 24 hours, a portion of the reaction mixture was coagulated to yield a yellow, fibrous material. The reaction was stopped, cooled and precipitated into warm MeOH/H_2O solution (80:20 V/V). The polymer was washed several times, dried under vacuum, redissolved in DMF, filtered [19] and reprecipitated in methanol.

The same procedure was used in the preparation of linear polyaspartimides from various molecular weight NH_2PSF oligomers. The resultant polymer could be redissolved in CH_2Cl_2 or THF, filtered and reprecipitated.

Two model compounds, $\underset{\sim}{15}$ and $\underset{\sim}{16}$, were prepared by this method to investigate the effect of

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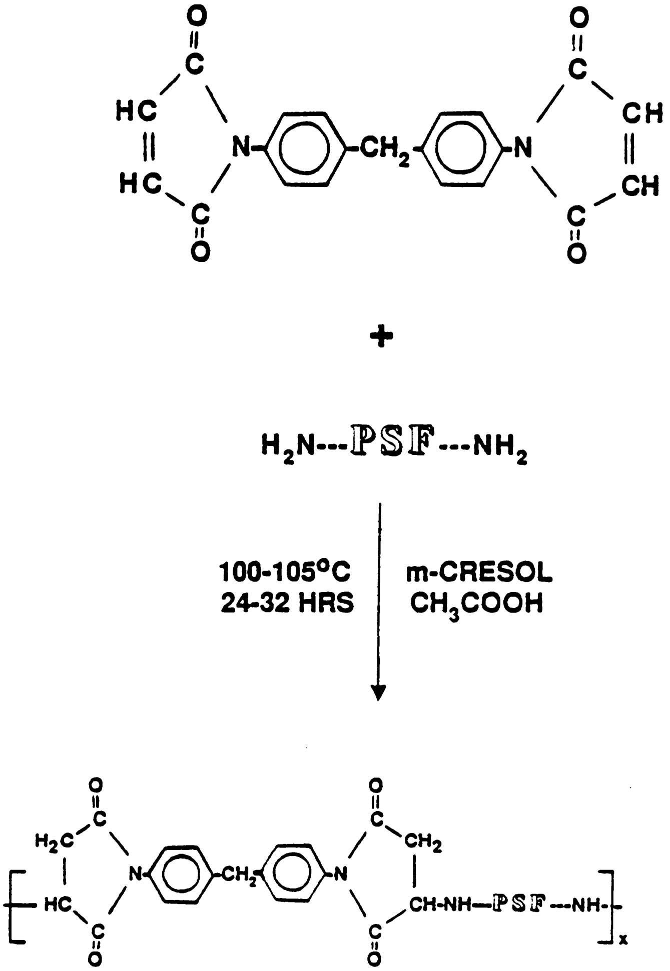
[16] Bleeding N_2 instead of air resulted in materials possessing the same color, T_g, solubility characteristics and thermal mechanical response.

[17] The slow increase in temperature and vacuum were necessary to prevent bubbling of the films.

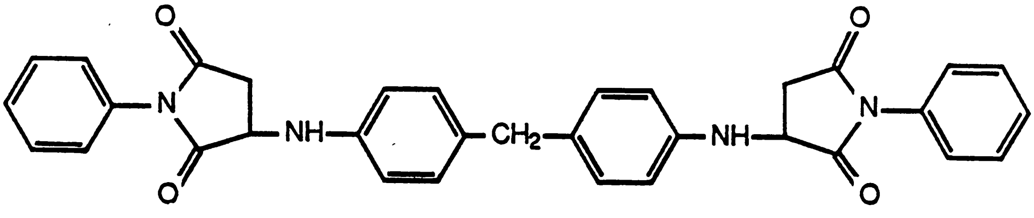
[18] At temperatures >110°C, exchange reactions with the phenolic hydrogen of m-cresol could be expected [299], hence temperature was maintained at ≤100°C.

[19] Invariably it seems, all polymers prepared by this method contain some gel fraction [300]. Due to an error in MW calculation, completely soluble polymers were prepared if an excess of amino groups were present. Hence, the unequal stoichiometry was used in all procedures.

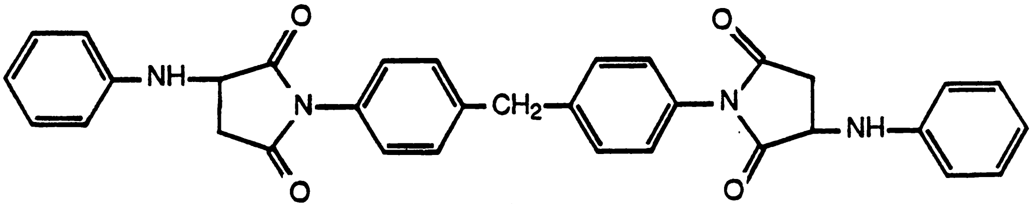
SCHEME 14


HC
HC
N
CH$_2$
N
CH
CH
O
C
C
O
+
H$_2$N---PSF---NH$_2$
100-105°C
24-32 HRS
m-CRESOL
CH$_3$COOH
H$_2$C
HC
CH$_2$
CH-NH—PSF—NH-
x

acetic acid on the rate of reaction, as well as the effect of solvent, protic or aprotic in nature.



15



16

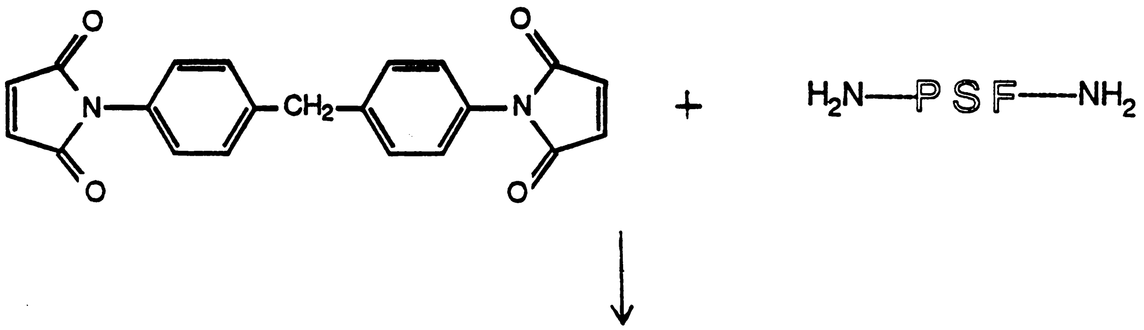
In the synthesis of 15, purified methylene dianiline, MDA (0.02 moles), and N-phenyl maleimide, N-PM (0.041 moles), were dissolved in either m-cresol or DMF to 20-22 wt % solids. The reaction temperature was kept constant at 100°C under an inert atmosphere. The molar ratio of glacial acetic acid to N-PM was varied from 1:2, 1:1, 2:1, 4:1 to 8:1. The reaction was followed by T.L.C. and the endpoint of the reaction was taken as the time when the MDA spot appeared negligable. At this point, the reaction was cooled and the product crystallized from solution. The crystals were filtered and could be recrystallized from o-dichlorobenzene or DMF. The time required for complete reaction (MDA disappearance) fell from over 3 days at a 1:2 molar ratio to ≅20 hours at 2:1, 4:1 and 8:1 in m-cresol. The yields remained constant at ca. 60%, M.P. = 175-177°C (Lit. 177-180°C) [299].

When the same reaction was run in DMF, T.L.C. showed the disappearance of N-PM at a faster rate than in m-cresol and it apparently was independant of acetic acid concentration. Also, this reaction produced a large number of products as evidenced by the large number of spots on the T.L.C. plate. The reaction mixture went through a viscosity maxima at 0.5-1.0 hour; shorter η_{max} for lower acetic acid content, higher η_{max} at higher concentrations. Disappearance of N-PM occured first and at that point, the reaction was stopped and cooled. Only a small amount of crystalline 15 was obtained. A portion of the gellaceous supernatant liquid was precipitated. It produced a brown powder which produced a gel upon attempted dissolution in DMF. The yields became greater as the amount of glacial acetic acid increased, but not substantially, 14 to 20%.

The preparation of 16 gave slightly better yields, 70-75% in m-cresol, than 15. Similar observations were obtained for reactions run in DMF. Compound 16 could be recrystallized from DMF to yield a yellowish powder, M.P. 221-225°C (Lit. 226-231) [299].

3.7.8 *Synthesis of Thermoplastic Modified Bismaleimide Resins*

Reaction:



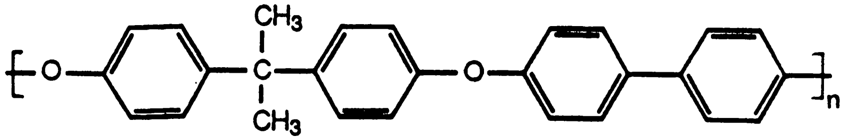
Procedure: Purified NH$_2$PSF oligomer was dissolved in freshly distilled DMF to about 20 wt % solids. Toluene was added to the reaction vessel and heated to azeotrope any residual water. After all the toluene had been removed, the temperature was lowered to ≅60°C and a solution of BMI in DMF was added all at once. The reaction was reheated to 140°C for 0.5 hr. where the viscosity had noticeably increased and the color had changed from brown to reddish brown. The reaction was cooled to ≅80°C, cast into thin films on glass plates and devolatilized in the same manner as with lightly crosslinked NH$_2$PSF oligomers. The curing of these resins required slightly higher temperatures with one stage of 200°C for 0.5 hour and a second stage of 250°C for 2 hours. The films obtained were clear and brown in color. They could be flexed, but not folded.

3.8 *SYNTHESIS OF POLY(ARYLENE ETHERS) VIA THE ULLMANN ETHER SYNTHESIS REACTIONS*

As discussed in the literature review section, poly(arylene ethers) prepared from non-activated aryl halides require a different synthetic approach than that employed in poly(arylene ether sulfone) or poly(arylene ether ketone) systems. The polymers prepared in this section use a modification of the Ullmann condensation reaction, differing in a few aspects from investigations already published [238,248]. Amorphous materials were obtained in systems based on bisphenol-A, and semicrystalline materials were prepared using 4-bromophenol.

3.8.1 *Synthesis of an Amorphous Polyether Based on 4,4′-Dibromobiphenyl*

Reaction:



Procedure: Purified 4,4′-dibromobiphenyl, DBB (0.10 moles), and bisphenol-A (0.10 moles) were charged to a typical reaction flask and rinsed into the flask with warm toluene. Solid benzophenone (150 g)[20] was added and the reaction was heated until the reaction became homogeneous. 0.20 moles of a standardized sodium hydroxide solution was added.[21] The colorless solution became yellow, then orange and then red upon complete addition of base. The addition funnel was rinsed with water to ensure quantitative addition of base. The reaction was heated to 110°C where a water-toluene azeotrope began. After 2.5 hours at 140°C, the system was dehydrated and the toluene was removed from the reaction via the Dean-Stark trap. The pot temperature reached 210°C as all the toluene was removed. The reaction mixture was cooled to 80°C and 10 ml of the CuCl/quinoline catalyst was added. A 1.0 molar solution of unpurified CuCl in purified

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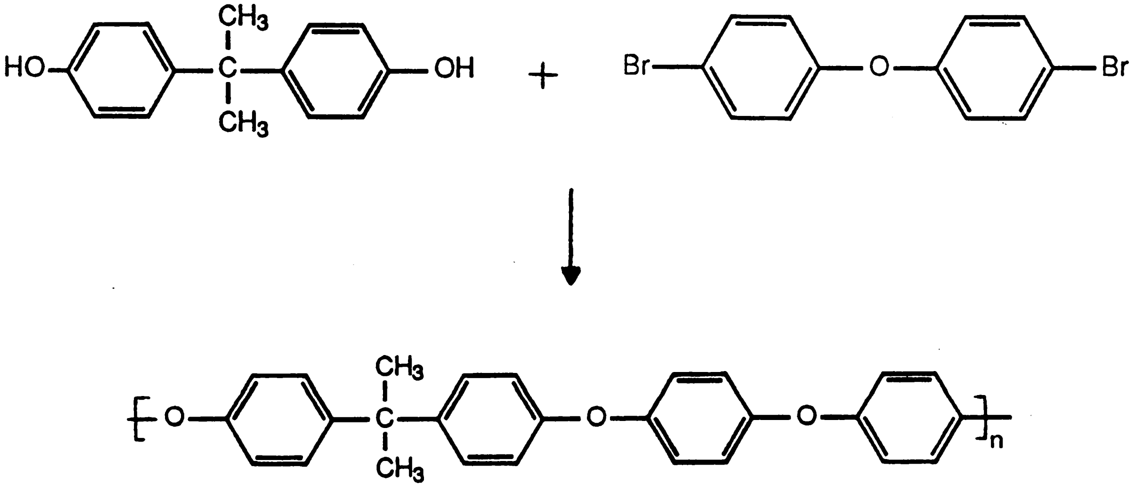
[20] Solid 1,4-dimethoxybenzene or 1,3-dimethoxybenzene, a liquid at room temperature, could also be used.

[21] In practice, the NaOH solution was often weighed first and then the proper molar quantities of the two monomers were calculated.

quinoline was prepared and stored in a brown serum vial until use. The Dean-Stark trap was removed and the reaction was heated to 195-200°C for 9 hours. The polymer was now deep brown and viscous,[22] and was diluted with 150 ml toluene and cooled to 80°C. It was precipitated into methanol, acidified with acetic acid and worked up in the usual manner. It was redissolved in chloroform and filtered through a fine glass frit. The clear tan colored solution was again precipitated into methanol, washed with acetone several times to remove trapped benzophenone, washed again with methanol and dried under vacuum at 100°C for 12 hours.

3.8.2 *Synthesis of a Poly(Arylene Ether) Based on Bis(4-Bromophenyl) Ether*

Reaction:



Procedure: The same procedure was used as in the previous case.

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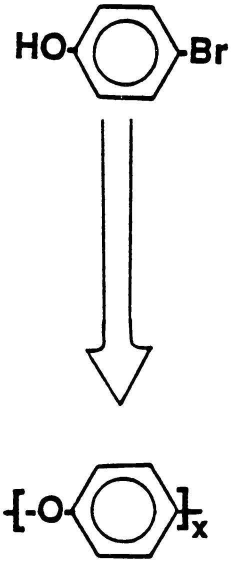
[22] At this point, it was optional to add 5 mole % bromobenzene to the reaction and continue heating for 1 hour to provide phenoxy-terminated polymers.

3.8.3 *Synthesis of Semi-Crystalline Poly(Phenylene Ether)*

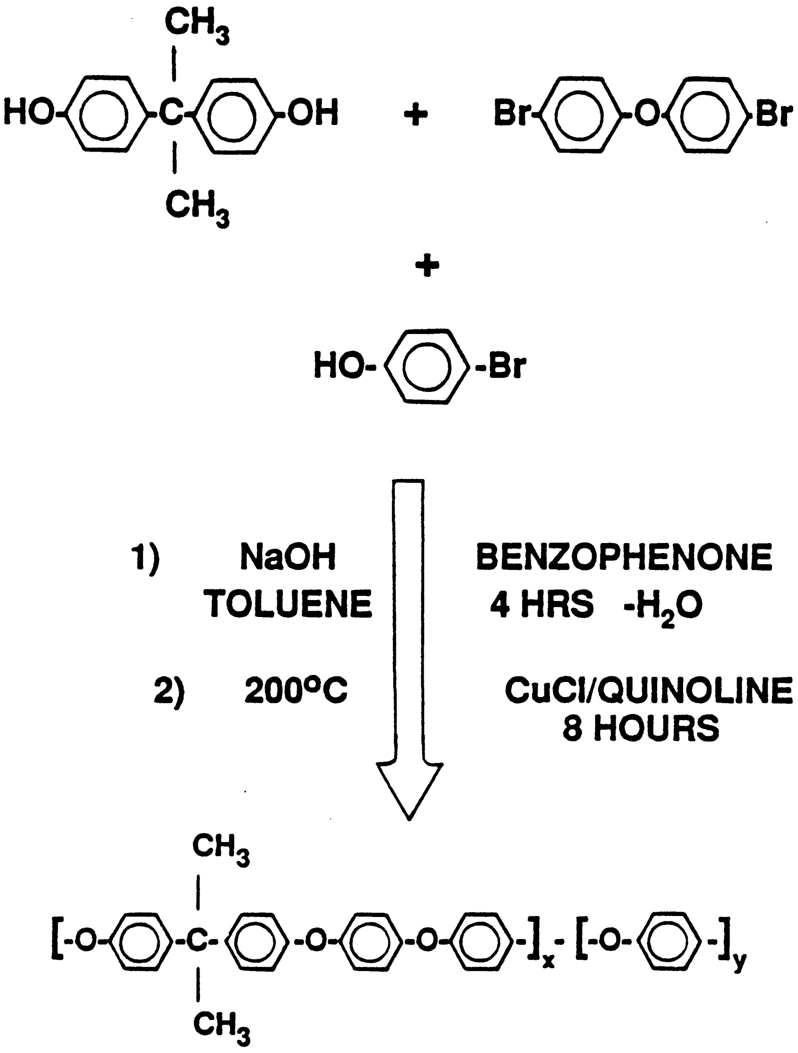
Reaction:



Procedure: 4-bromophenol (0.20 mole) was charged to a reaction flask, followed by benzophenone and toluene. The mixture was heated to form a homogeneous solution. An exact equivalence of sodium hydroxide was added as a standardized solution. The reaction was heated to remove water formed from phenate solution. The toluene was removed after 2 hours, raising the pot temperature to 200°C. It was cooled to 80°C and 3 ml of the CuCl-quinoline one mmolar solution was added. The reaction was heated to 200°C for 4 hours and then was raised to 210°, 220° and 230°C for 1 hour time periods. The dark-colored solution was cooled and precipitated in a acetone/methanol/water mixture (50/40/10 V/V/V). The brown powder was worked up as usual but it could not be easily redissolved except at > 140°C in NMP, o-dichlorobenzene or dinitrobenzene. It was placed in a Soxhlet extractor for 24 hours using acetone to remove any trapped benzophenone.

3.8.4 *Synthesis of a Semicrystalline Copolymer*

Reaction:



Procedure: A 1:1 stoichiometric ratio of Bisphenol-A and 4-Bromophenyl ether were used with a 0.10 mole % of p-Bromophenol. The remainder of the procedure was identical to that used to synthesize amorphous Bisphenol-A-based poly(arylene ethers)[23]

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[23] Higher reaction temperatures may be necessary to ensure reaction of the 4-bromophenol, which may polymerize to form semi-crystalline segments of the copolymer.

3.9 *CHARACTERIZATION*

3.9.1 *Dilute Solution Viscosity*

The theory of dilute solution viscometry has been presented elsewhere and will not be considered here [301,302]. The intrinsic viscosity, [η], of the oligomers, homo-, block, and segmented copolymers was determined in chloroform, THF or NMP at 25°C depending on the nature of the polymer. Comparison of [η] values for a series of similar oligomers provided an approximate idea of their molecular weight.

3.9.2 *End Group Analysis*

The oligomers produced in this study were either phenolic hydroxyl or aromatic amine terminated and rapid methods to determine the absolute number average molecular weight were developed in our laboratories. Phenolic hydroxyl terminated oligomers were titrated by potentiometric titration of the endgroups in a non-aqueous medium using tetramethyl ammonium hydroxide in methanol as the titrant [303]. Aromatic amine terminated oligomers were titrated using a modification of a technique used to titrate very weak bases ($pK_B < 10$) [304,305] or epoxides [306] and described below.

The Bisphenol-A based sulfone oligomers were dissolved in a 2:1 (V/V) ratio of chlorobenzene to glacial acetic acid and titrated potentiometrically with 0.02 N anhydrous HBr in glacial acetic acid. Oligomers prepared from hydroquinone, biphenol and 50/50 mixtures of each were not soluble in chlorobenzene and were titrated in a $CHCl_3$/glacial acetic acid solution, 90/10 V/V. The HBr/CH_3COOH solution was standardized by titrating potassium hydrogen phthalate in glacial acetic acid.

Procedure: The Fisher Automatic Titrimeter II was equipped with a double junction potential reference electrode and set at a gain of 70. An accurately weighed sample of oligomer (4 decimal point accuracy) was dissolved in 50 ml of distilled, dry chlorobenzene. [The amount of sample used should consume $\cong$4 ml titrant or $(.02N)(.004\ell) =$ moles titrant $=$ moles acid $=$ moles amine $=$ g oligomer/2] Glacial acetic acid, 25 ml, and a few drops of crystal violet indicator was added. After complete dissolution, the electrode and delivery tip were immersed in the solution. The endpoint was taken as the peak of the first derivative curve and the color change of crystal violet. The millivolt reading was taken at this point and a blank was run using this reading as the endpoint. A minimum of 3 titrations were run for each oligomer. Allowable deviations in molecular weight determinations were $<M_N> \pm 40$ g/mole for oligomers $< 10{,}000$ g/mole and $<M_N> \pm 80$ g/mole for oligomers $> 10{,}000$ g/mole.

3.9.3 *Gel Permeation Chromatography (GPC)*

The molecular weight distributions of the oligomers and polymers produced were determined using a Waters HPLC fitted with 6 columns ranging from 10^6 Å to 500 Å. Tetrahydrofuran solutions of approximately 0.1 wt/V % were injected into the chromatograph at a flow rate of 1 ml per minute at 30°C. Both ultraviolet and differential refractive index detectors were used. The MWD's were calculated using a cubic fit of the calibration curve based on 6 polystyrene standards. The cubic fit more closely represents true behavior for both very low or very high molecular weight polymers.

3.9.4 *Infrared Analysis*

Infrared spectra in the range 4000-500 cm^{-1} were measured using a Nicolet MX-1 spectrophotometer. Oligomeric samples were dissolved in $CHCl_3$ or CH_2Cl_2 and the solution was placed dropwise on a salt plate. It was evaporated to dryness and then placed in a vacuum oven at 25°C for 10 min., which produced a thin polymer film. For insoluble or non-film forming compounds, dry IR grade KBr was employed to make a pellet.

3.9.5 *Thermal Analysis*

Second order transitions of the oligomers and polymers synthesized in this study were studied with differential scanning calorimetry, DSC. A Perkin-Elmer, DSC model 2 was employed using a scanning rate of 10°C/min. and a sensitivity of 5 mcal/sec. Analyses were routinely run on dried, solvent-cast, polymer films. In most cases, the first heating removed any previous thermal history and hence, the second run was recorded.

3.9.6 *Nuclear Magnetic Resonance (NMR)*

Jeol FX-60-Q and FX-200Q instruments were used for obtaining the ^{13}C and ^{1}H NMR spectra of oligomers model compounds and monomers. Approximately 8% solutions in deuterated $CHCl_3$ or DMSO were used for the ^{13}C solution spectra and lower concentrations for ^{1}H NMR.

3.9.7 *Thermal Mechanical Analysis (TMA)*

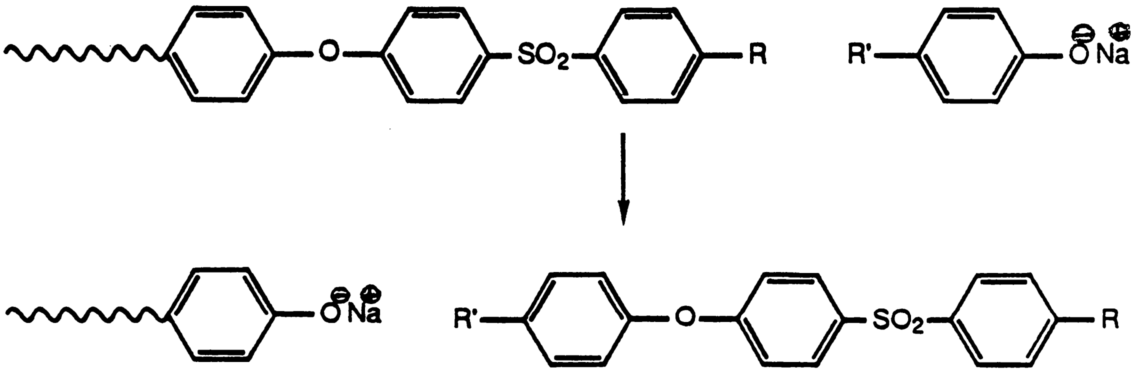
TMA was performed on copolymers using a Perkin-Elmer TGA model 2 in the TMA mode. Dried, solvent-cast, polymer films were measured with a micrometer to find samples with constant thickness for valid comparisons. The sample was heated in a nitrogen blanketed furnace at a rate of 10°C/min. The load placed on the probe in all cases was 10 gm.

Chapter 4

RESULTS AND DISCUSSION

The classical route for the synthesis of linear, high molecular weight poly(arylene ether sulfones) utilizes dimethyl sulfoxide and aqueous sodium hydroxide, a bisphenol, an activated aromatic halide and a suitable dehydrating agent such as chlorobenzene [282]. This method is not without limitations since it requires exact stoichiometric amounts of sodium hydroxide as compared with bisphenol. Even a modest 1% deviation in the base drastically decreased the reduced viscosity (R.V.) in $CHCl_3$ at 25°C of the resultant polymer from 1.8 dl/g to 0.6 dl/g [282]. A greater decrease in R.V. was observed for reactions in which a deficiency of alkali was used. Other workers [307] have postulated that unreacted phenolic groups can hydrogen bond with an equivalent amount of metal phenate ions, thus reducing the nucleophilicity of the phenate.

Although the ether bond is relatively stable to hydrolysis, the presence of excess strong base under these reaction conditions can cleave the activated ether linkage [245,250].



This hydrolysis reaction limits the scope of the reaction, particularly in the synthesis of block copolymers. The development of a synthetic scheme which utilized a weak base and N,N′-dimethylacetamide (DMAC), had been confined primarily to the patent literature [308] until an in-depth study was performed [309]. These studies indicated no hydrolysis occurred in the aromatic halide or to the polymer chain in the presence of excess weak base, potassium carbonate.

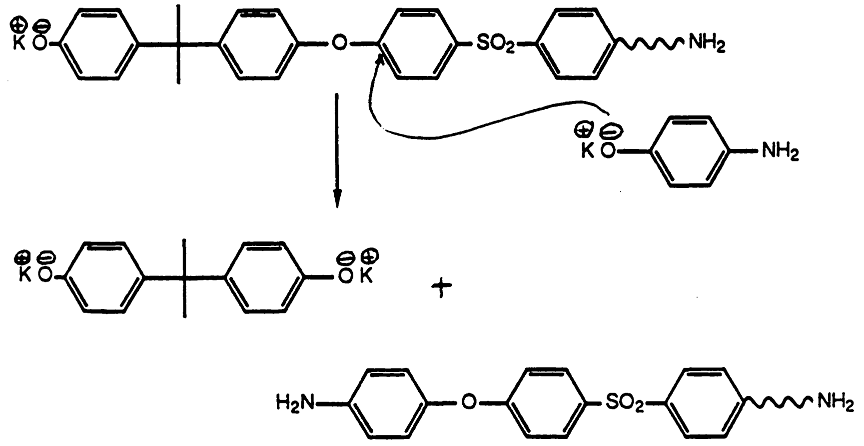
The utilization of a high boiling, dipolar aprotic solvent and K_2CO_3 at elevated temperatures satisfies the reaction requirements for this type of a step-growth polymerization. The success of this polymerization lies in the ability of the solvent to homogenize both the phenate and the growing polymer chain under anhydrous conditions. DMAC has a similar cation solvating power to DMSO and it is not significantly affected by excess anhydrous K_2CO_3. The only apparent limitation in this scheme is its modest boiling point of 155°C.

Further work in our laboratories has resulted in the use of N-methyl pyrolidone, NMP, as the reaction solvent of choice for these type step growth polymerizations [310]. It has a boiling point of 202°C and can be used for extended periods of time near its boiling point [297]. It satisfies all the requirements for a solvent in these type step-growth polymerizations, even though there is a "darkening" of NMP during the polymerizations.

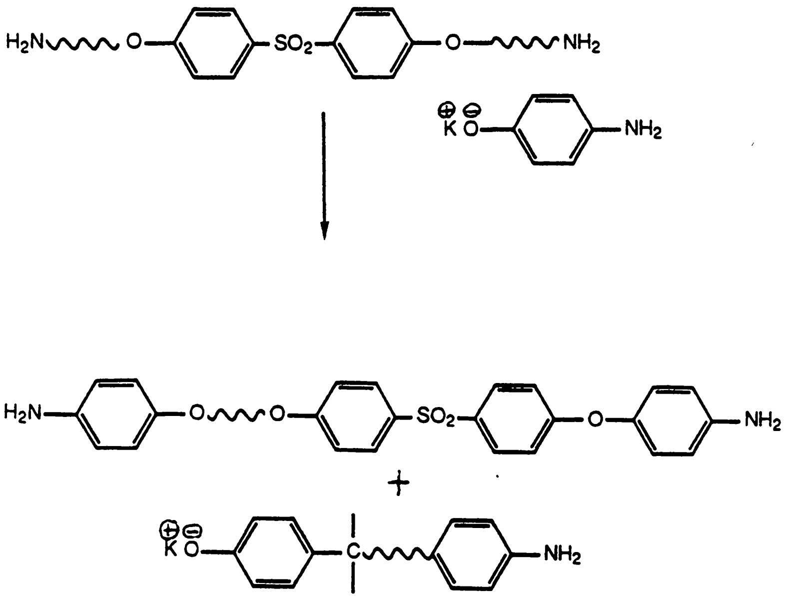
4.1 *Analysis of Diamine Terminated Arylene Ether Sulfone Syntheses*

Early workers utilized the classical DMSO/NaOH route with DCDPS and p-aminophenol to prepare sulfone ether diamine or SED [298]. This work was extended to a system of DCDPS, bisphenol A and p-aminophenol to obtain oligomeric diamines in accordance with theoretical calculations made with the Carothers equation. A logical consequence of the development of an alternate DMAC/K_2CO_3 route was to prepare the SED with this procedure [311]. There was no indication that the synthesis of higher molecular weight species was undertaken in this study.

In this study, we were also successful in synthesizing the same SED using the NMP/K_2CO_3 route. It did not, however, prove possible to prepare oligomeric materials using bisphenol A as the diphenolic monomer. Reaction times up to 24 hours were used in these attempted syntheses. At the conclusion of these reactions, a green colored solution typically indicates the absence of active phenate endgroups and hence amino (or chloro-) functional termination. This color, although obtained in SED syntheses, was never achieved in NMP/K_2CO_3 systems employing both bisphenol A and p-aminophenol. Work-up of these reactions yielded tan colored powders which corresponded in appearance to oligomeric materials. End group analysis of these materials, which will be discussed in more detail in a following section, gave $<M_N>$ 20,000 g/mole. These values were clearly incorrect, since a polysulfone of $>20{,}000$ g/mole molecular weight should be somewhat fibrous in appearance. This led us to believe that incomplete amine termination was occurring and the assumption of 2 amine endgroups per polymer chain in the titration procedure was artificially inflating the true molecular weight. It was postulated that ether-ether interchange reactions shown in equations 36 and 37 may occur.



(36)



(37)

These reactions would still lead to some diamine terminated oligomers; however, they may be of a lower molecular weight than calculated. These lower molecular weight species contain more amine groups per mole and would serve to deplete the calculated amount of p-aminophenol prior to quantitative chain termination. Some oligomer chains would necessarily become either chloro- or phenolic hydroxyl terminated as a result. The presence of these hydroxyl groups would account for the absence of the characteristic green reaction color near the conclusion of the reaction. In addition, oligomeric bisphenol A-based sulfones having $<M_N>$ < 5000 g/mole were slightly soluble in methanol and had to be coagulated in isopropanol. Even though targeted $<M_N>$'s for these studies were 7500-10,000 g/mole range, if interchange reactions had taken place to form lower, < 5000 g/mole, molecular weight oligomers, they could preferentially be lost in the precipitation step.

A second potential cause for incomplete end-group functionalization is the reactivity of p-aminophenol as compared to that of bisphenol A. The electron donating character of the amine group increases the basicity of the metal phenate salt for nucleophilic aromatic substitution towards the aryl halide. With the use of a weak base, such as K_2CO_3, the rate of potassium metal phenate formation will be slower for the p-aminophenol as opposed to bisphenol A. In the early studies [298] using NaOH as the base, it was found that the rate of addition of DCDPS had an effect on the molecular weight distribution of the resulting oligomer.

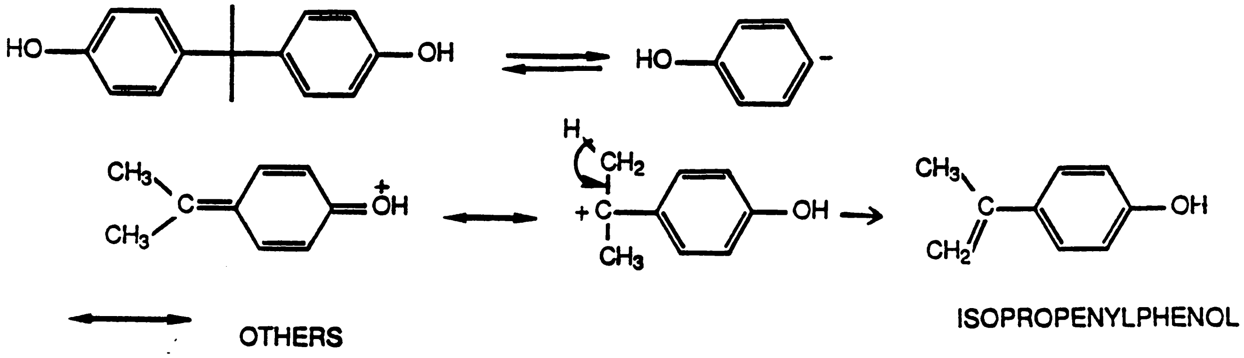
Since metal phenate formation was complete in that case, the p-aminophenol most likely reacted preferentially with the DCDPS as compared with bisphenol A. Although there was a greater probability of producing low molecular weight diamines, the DCDPS was still present in a large enough excess to prevent depletion of the endblocker. Diamine terminated materials were produced whether the DCDPS was added all at once, or portionwise. If the p-aminophenol had been consumed in the early stages of the reaction, it could not be expected to undergo ether-ether interchange reactions. In the K_2CO_3/NMP route, the metal salt of p-aminophenol was formed throughout the course of the reaction, it would be expected to participate in reactions of the type illustrated in (36) and (37). Hence, the unusually high titrated values of $<M_N>$ for oligomers prepared by this method seem explainable for the reasons discussed here. A further piece of evidence in the non-quantitative termination of these oligomers will be presented in an upcoming section.

It was thought that if the endblocker and bisphenol used in the reaction had comparable reactivities towards the activated aromatic halide, the K_2CO_3/NMP route could effectively be used to synthesize diamine terminated oligomers. In addition, if the amine and phenolic functionalities could be separated so as not to exert an electronic influence on one another, the rates of metal phenate formation for the bisphenol and the endblocker should be comparable.

4.1.1 *Endblocker Synthesis*

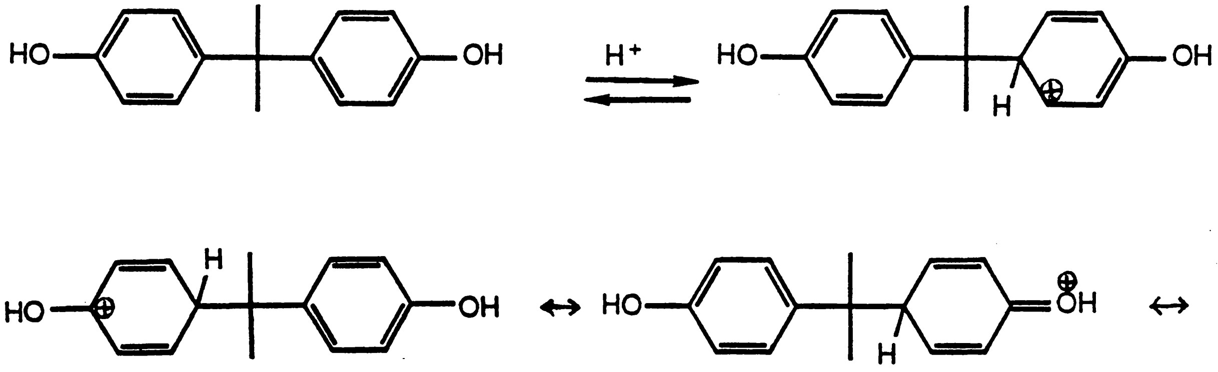
One such compound which initially seemed to meet these requirements was 2-p-aminophenyl-2-p-hydroxyphenylpropane. This compound had previously been prepared from bisphenol A, and aniline hydrochloride [311,312] or from aniline, hydrochloric acid and isopropenylphenol [313]. This compound could isolate the two polar functional groups electronically as compared to p-aminophenol since in bisphenol A the phenolic groups have little, if any, electronic effect on each other.

This compound will be referred to as the mono-amino derivative of bisphenol A, or MBA. The synthetic procedure used in its preparation has already been outlined in the experimental section. It was observed that the dissociation of HCl from aniline occurs at temperatures above 170°C. In this reaction scheme, aniline can be thought of as being in equilibrium with the HCl salt. Therefore, aniline serves both as solvent and reactant in a strongly acidic medium. It is known that a ceiling temperature exists for polymerizations employing bisphenol A [314] due in part to reactions like the following:

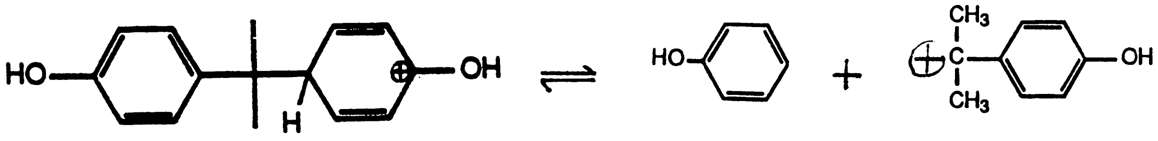


It can be seen why isopropenyl phenol was used as a starting material in MBA synthesis.

In a strongly acidic medium, this reaction is aided by ring protonation:

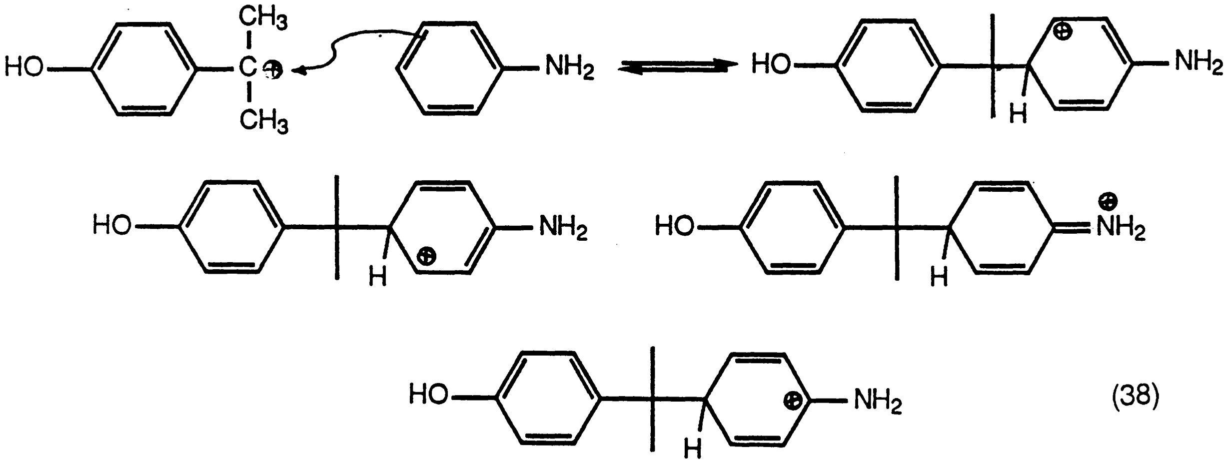


and the resulting cation is resonance stabilized. The driving force for the next step is the restoration of the cyclic π system, entropic considerations and the formation of a resonance stabilized tertiary benzylic carbocation.



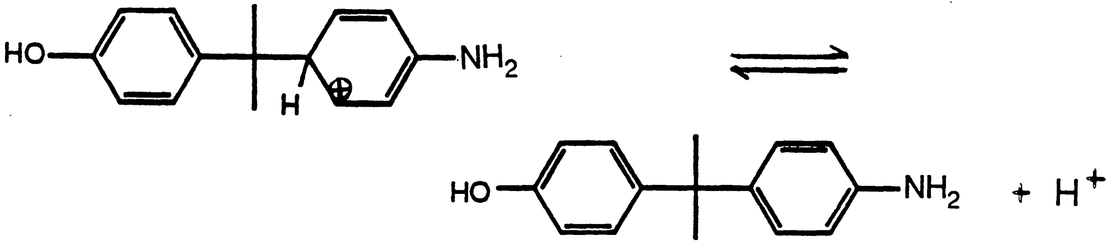
In general, electrophilic aromatic substitution reactions can be applied to aromatic amines. The para position in aniline is particularly responsive to such reactions. Furthermore, alkyl- and dialkylamino groups are such strong activating substituents that mild reaction conditions may be used [321].

The carbocation formed in the decomposition of bisphenol A is a suitable electrophile for substitution reactions with aniline.



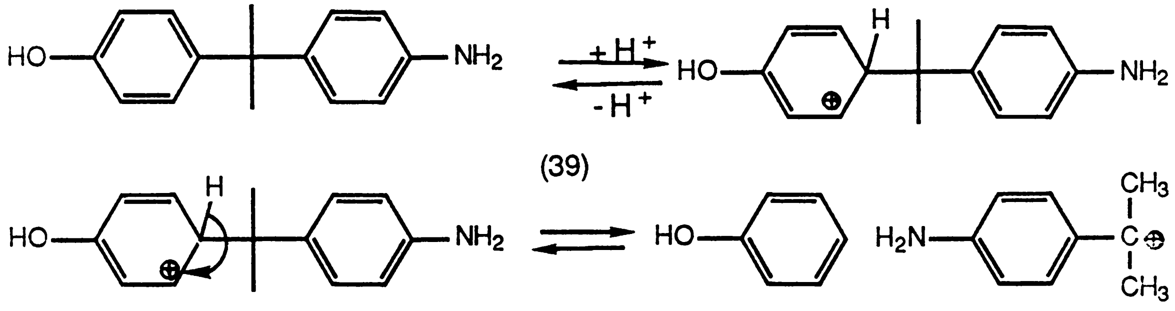
(38)

The product is again stabilized by resonance. Once again, the drive towards rearomatization yields the product, MBA, and H^+ is regenerated.



Further reactions can then occur (39) which are resonance stabilized as shown in (38).

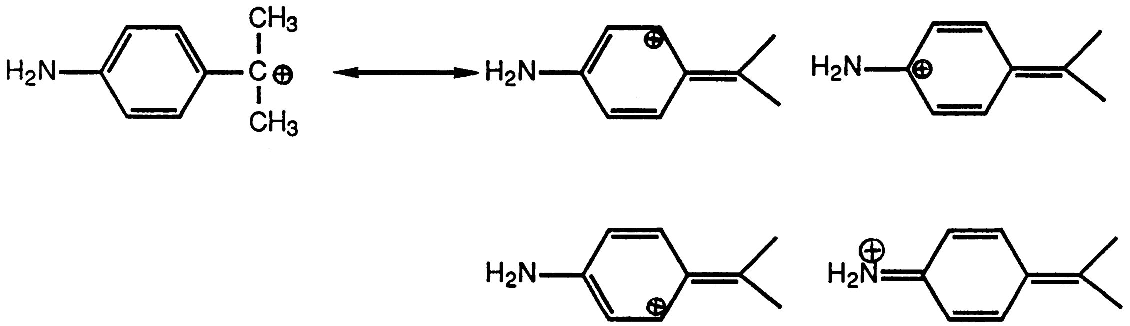
Rearomatization again yields phenol and a tertiary benzylic carbocation (40).



(39)

(40)

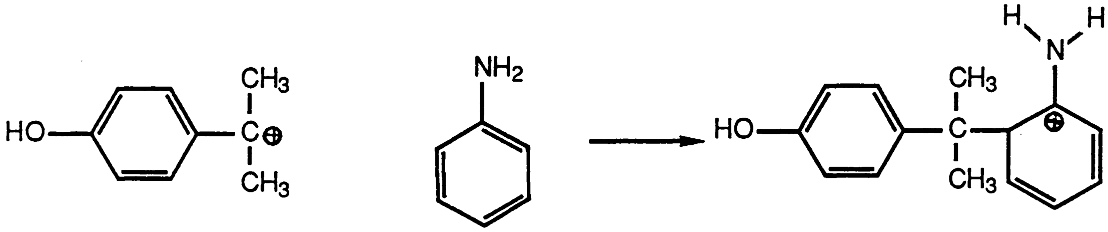
This cation may not be as reactive as species formed following the first ring protonation due to the following resonance structures:



Analagous structures can be drawn for the phenolic cation but nitrogen is more apt to sustain a positive charge due partly to its lower electronegativity than oxygen. In addition to these reasons, the removal of phenol from the system could be used to explain why the diamino-adduct was preferentially formed at very high temperatures, 1 hour at > 210°C, or at long reaction times, > 12 hours at 180°C.

The ortho position of aniline is also activated towards electrophilic aromatic substitution;

however, this attack is sterically less favorable than at the para position.



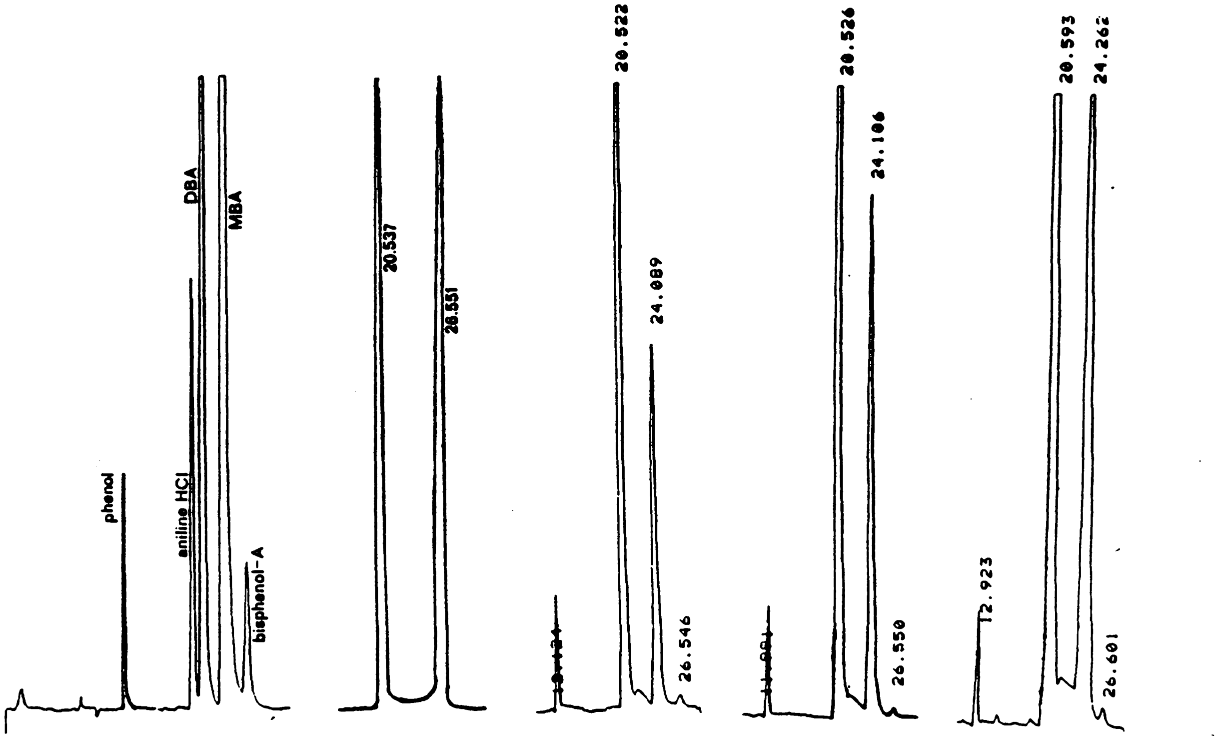
The extent of reaction between aniline hydrochloride and bisphenol A can qualitatively be followed by monitoring the evolution of phenol. Thin layer chromatography was also used to follow the disappearance of bisphenol A from the system; virtually all the bisphenol-A had been consumed after 25 minutes at 180°C.

Liquid chromatography was then used for a more careful observation of the reaction. A reversed phase method was chosen using an inert C_{18} column under isocratic conditions with a 50/50 THF/H_2O mobile phase. Solutions of both starting materials and the three main products (MBA, phenol and DBA - the diamino derivative of Bis-A) were prepared and run to determine their retention times and the proper mobile phase composition. A mixture of all 5 components was also run to investigate what effect, if any, one compound may have on the elution order of the others. The elution order did not change and the change in their retention times was negligible. Figure 7(a) illustrates the elution of all 5 components in a simple mixture. The elution times for the compounds were; phenol 12.41 min., aniline HCl 20.62 min., DBA 21.80 min., MBA 24.11 min. and bisphenol-A 26.64 min. These times were then used to identify peaks resulting from aliquots removed during the course of a reaction. Figure 7(b) is a sample taken at time t = 0 in a reaction of aniline HCl and bisphenol-A at a 4:1 molar ratio respectively. Only two large peaks are evident, corresponding to each of the starting materials. After 10 minutes of reaction at 180°C, Figure 7(c) was obtained. Phenol (12.12 min.) can be seen in the reaction mixture, as well as our desired product, MBA (24.09 min.). The aniline HCl does not appear to have decreased, probably due to its large initial concentration. Most of the bisphenol-A appears to have been consumed by this time. After 20 minutes, the MBA concentration has increased while the other peaks have remained essentially constant (Figure 7(d)). This would point to the rapid breakdown of bisphenol-A to yield the isopropenyl cation, which then undergoes reaction with aniline in a slow step to give the product, MBA. Figure 7(e), taken from the reaction at t = 40 min., again shows an increase in MBA concentration and only a small amount of bisphenol-A. The emergence of the diamino adduct at ≅21.5 min. can be seen. From t = 60 to t = 120 minutes, one can see the increase in production of the diamino substituted bisphenol-A and the corresponding decrease in MBA formation. Bisphenol-A, seen as a small blip at ≅26.6 min. finally disappears completely after reaction times of 120 minutes.

Using this information, maximum yields of MBA could be obtained by running the reaction for ≅40 minutes. This time appeared to maximize the production of MBA before appreciable formation of DBA occurred. Isolation and purification of the desired product was carried out as outlined earlier. FT-IR, NMR and a melting point was further used to characterize the product. The FT-IR spectrum did indeed show N-H stretching bands at 3410 and 3375 cm^{-1} which overlapped a much broader -O-H stretching region (Figure 8).

Proton NMR confirmed the desired product by providing integration corresponding to 6 aliphatic, 8 aromatic, 2 nitrogen and 1 phenolic proton. A further test was performed using a Fisher Automatic Titrimeter. A non-aqueous titration in chlorobenzene-glacial acetic acid yielded an amine equivalent weight of 228.5 ± 1.0 g/mole. Analogous titration of the phenolic hydroxyl group gave a molecular weight of 227.8 ± 1.0 g/mole. These values, in combination with ^{1}H NMR results and a narrow melting point using DSC, were positive indications that the MBA was indeed polymer grade monomer.

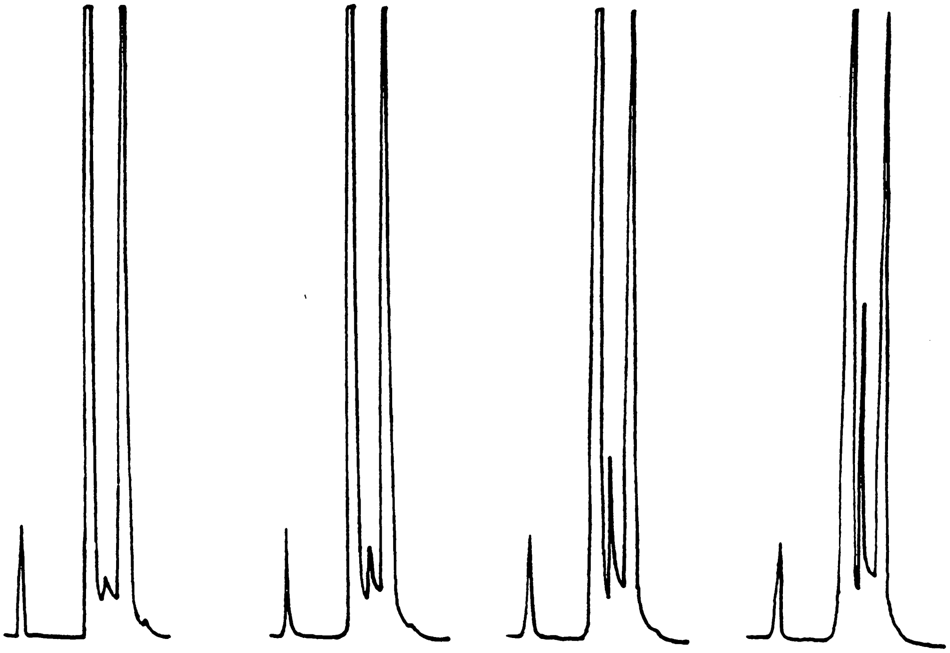
A series of reactions were run in which the ratio of aniline HCl to bisphenol-A was varied. This was attempted in order to obtain the greatest yield of MBA. Table 4 shows the results of these reactions. Maximum yields of MBA were realized at a 4:1 molar ratio of aniline HCl to bisphenol-A. The yields dropped off sharply at a 2:1 molar ratio. At high molar ratios, larger



(a) (b) (c) (d) (e)

t = 0 min. t = 10 min. t = 30 min. t = 40 min.

Figure 7. HPLC Results of MBA Synthesis as a Function of Time



(f) t = 60 min.

(g) t = 75 min.

(h) t = 90 min.

(i) t = 120 min.

FIGURE 7 HPLC Results of MBA Synthesis as a Function of Time (cont.)

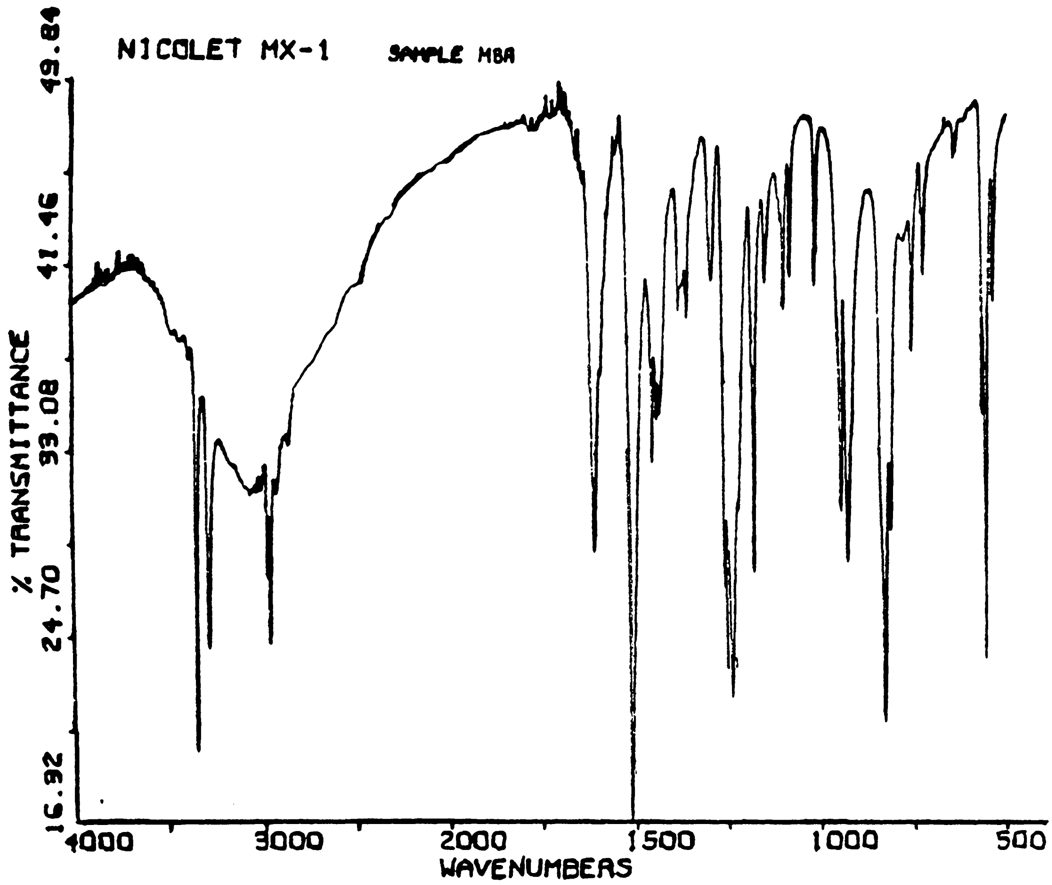


Figure 8. FT-IR Spectrum of MBA

amounts of DBA were obtained. A primary reason for these observations is that 2 molecules of phenol can be lost for each bisphenol-A molecule. This means that there are 2 reactive sites/bisphenol-A molecule and only 1 per aniline molecule. Hence the 2:1 aniline HCl to bisphenol-A ratio actually contains a stoichiometric amount of functional endgroups and very little excess aniline is available as solvent. At higher molar ratios, such as 10:1, the large excess of aniline can more easily react with MBA to form DBA. Also, during work-up, the large organic layer may trap some MBA and prevent its recovery in the normal manner. At this point, we were confident of our preparation of polymer grade MBA for use in the functionalization of arylene ether sulfone oligomers.

4.2 *SYNTHESIS OF α-ω-DIAMINE TERMINATED ARYLENE ETHER SULFONE OLIGOMERS*

Once the preparation of MBA had been realized, its use in a K_2CO_3/NMP reaction scheme with DCDPS was attempted. In a 2:1 molar ratio of MBA to DCDPS, a sulfone ether diamine was prepared in high yield. Since MBA did indeed work in the preparation of a SED by this weak base route, an attempt to use it as an endblocking reagent for a bisphenol-A based poly(arylene ether sulfone) oligomer was tried.

The initial attempt was the preparation of a $<M_N> = 5000$ g/mole primary aromatic amine terminated poly(arylene ether sulfone) oligomer, abbreviated hereafter as NH_2PSF. Proper molar ratios of monomers were calculated according to the Carothers equation and the reaction was run as described in the experimental section. This molecular weight oligomer was used since it should contain a high enough endgroup concentration to facilitate characterization, especially with respect to FT-IR and endgroup analysis. In addition, there should not be appreciable solubility of this material in methanol as we assumed from work with phenolic hydroxyl terminated sulfone oligomers of similar molecular weights.

After the oligomer had been synthesized, a small portion of the tan, powdery material was dissolved in $CHCl_3$ and cast into a thin film on a salt plate. An FT-IR spectrum was obtained which can be seen in Figure 9. This spectrum compares identically with the spectrum of a high

Table 4

Results of MBA Syntheses at 180°C for 40 Minutes

Moles Aniline HCl:Bisphenol-A	MBA % Yield	% DBA
10:1	62	31
8:1	64	28
6:1	66	21
5:1	70	17
4:1	76	14
3:1	72	16
2:1	45	11

molecular weight bis-A polysulfone below 3200 cm^{-1}. What can clearly be seen in the NH_2PSF are three peaks at 3400 cm^{-1}, 3290 cm^{-1} and 3270 cm^{-1}, due to N-H stretching vibrations. This was confirmed by obtaining identical peaks in an MBA spectrum and three slightly displaced peak absorptions in an NH_2PSF prepared by the method of Kawakami *et al.* [308]. This was taken as a positive indication that some degree of endgroup functionalization had been obtained.

The titration of a weak base, such as aniline, can be accomplished by use of a strong acid such as HBr or perchloric acid, dissolved in a weak acid with glacial acetic acid being the solvent of choice. The basic compound is also dissolved in the glacial acetic acid. Since this acid is a non-solvent for polysulfone oligomers of any molecular weight, a common procedure utilizing an inert solvent, chlorobenzene, was employed [306]. The endpoint of a titration using chlorobenzene becomes noticeably weaker as the ratio of chlorobenzene/glacial acetic acid increases. For our experiments, a 2:1 (V/V) ratio of the two "solvents" was suitable to dissolve any molecular weight bisphenol-A NH_2PSF as well as to provide a prominent endpoint.

In many weak base titrations using this procedure [305,306], the presence of water will change the apparent equivalence point. Generally, a quantity of acetic anhydride can be added to scavenge adventitious water. Excess acetic anhydride does not interfere with the titration if a proper blank is run. Unfortunately in our system, the presence of acetic anhydride results in acylation of the primary amine. It therefore became necessary to standardize the HBr/AcOH solution prior to any series of titrations. A blank was also routinely run. This procedure repeatedly titrated low molecular weight diamines with a good degree of accuracy. The following compounds were titrated with their actual molecular weights in parentheses; 4,4′-aminophenyl ether, 202 ± 4 g/mole (200.24), 4,4′-diaminodiphenylsulfone, 247 ± 2 g/mole (248.4) and the S.E.D. from p-aminophenol and DCDPS, 433 ± 3 g/mole (434.5).

Finally, the first potential MBA terminated oligomer was titrated and a $<M_N> = 5420 \pm 30$ g/mole. The close correlation of the calculated $<M_N>$ to that obtained experimentally indicated that a majority of the polymeric chains produced did indeed possess two amine endgroups.

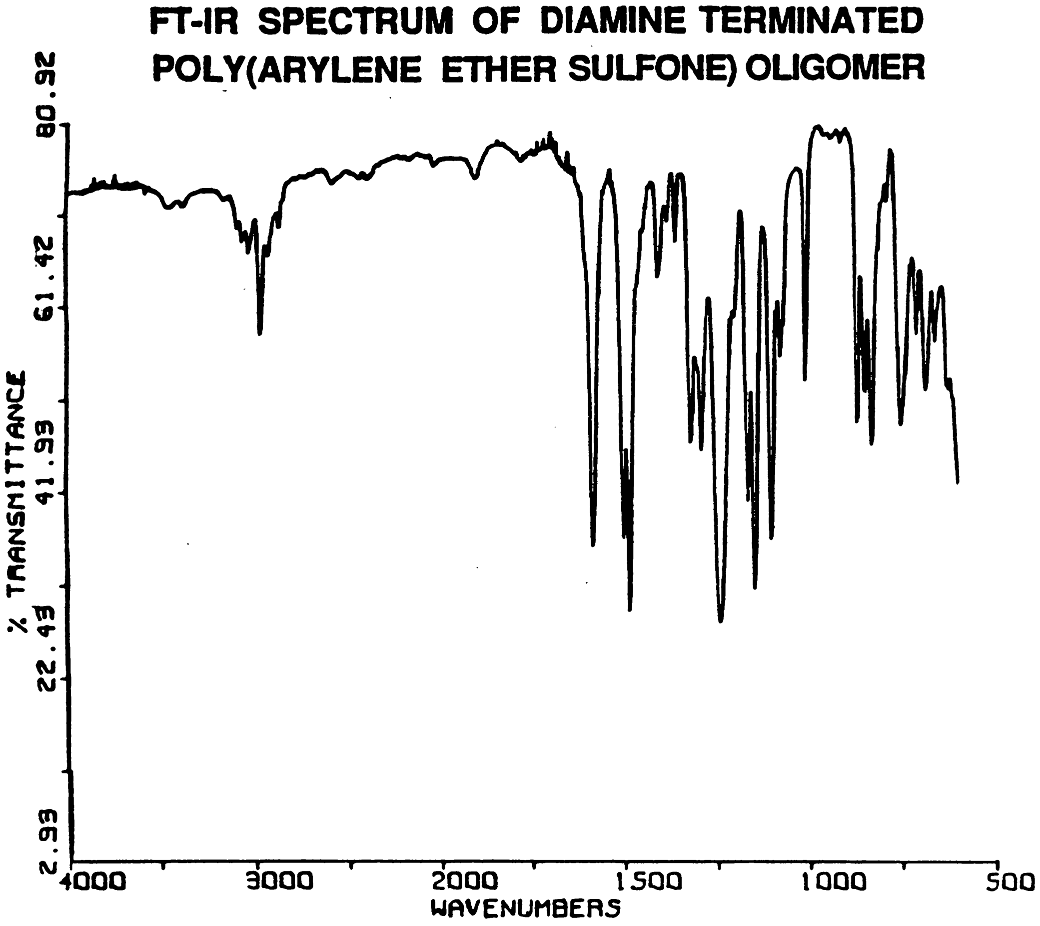


Figure 9. FT-IR Spectrum of an Amine Terminated Poly(Arylene Ether Sulfone) Oligomer

An intrinsic viscosity (I.V.) was determined next: [η] (25°C. $CHCl_3$) = 0.11 dl/g. This corresponded to the same value obtained with a 5280 g/mole phenolic hydroxyl terminated bis-A polysulfone. This 5280 g/mole oligomer had sucessfully been utilized in a block copolymer synthesis with an amine terminated poly(dimethyl siloxane), thus attesting to its highly difunctional nature. This indicates that both oligomers possess similar hydrodynamic volumes and since only ≅0.6% of the oligomers were chemically different - the endgroups - it was safe to assume they were of approximately equal molecular weights. If there had been a large discrepancy in the I.V. measurement or the titrated value, it would have indicated poor endcapping efficiency. For example, if the titrated value had been 5420 g/mole, but the I.V. was only 0.06 dl/g, it could have indicated that each chain averaged one amine endgroup but the titration assumed two endgroups per chain.

The next characterization used was gel permeation chromatography (GPC) which should more correctly be termed size exclusion chromatography. Since the aromatic amine endgroups were much less basic and also accounted for lower overall wt % of the oligomer than other amine terminated oligomers, e.g. aminopropyl terminated siloxanes, adsorption of these oligomers on the columns was not a problem. Six polystyrene standards were employed, from 1.5K to 2400K g/mole. Since molecular weights of these oligomers were not within the linear portion of the calibration curve, a cubic fit of the data best represented the true calculation for molecular weight. The shape of the GPC trace was Gaussian and the molecular weight distribution was 2.0. The monomodal shape of the raw data curve indicated that only one reaction type was occurring. Both the shape of the GPC trace and the MWD value indicated that this experiment was in close agreement with theoretical considerations. A most probable distribution of 2.0 should be obtained for this type polymerization since MWD is defined as $M_W/M_N = 1 + P$ and if $P \rightarrow 1$, the ratio will yield a value very close to 2.0.

Now that we were confident of the preparation of amine terminated sulfone oligomers using this method, we then proceeded to prepare a wide range of different molecular weight oligomers. The ratio of bisphenol to MBA was varied according to the Carothers equation and a representative survey of some of these materials can be seen in Table 5.

TABLE 5

Bisphenol A Based Amine Terminated Poly(Arylene Ether Sulfone) Oligomers

THEORETICAL $<M_n>$	ENDGROUP ANALYSIS	T_g (^oC)	MWD
4000	3700	140	1.9
5000	5300	155	2.0
7500	7100	162	2.1
9000	8800	165	2.0
10,000	9300	168	1.9
12,000	11,300	169	1.8
14,000	13,300	172	1.9
16,000	15,600	175	2.0
18,000	17,000	178	2.0
20,000	19,500	184	2.1
22,000	21,400	189	2.0
25,000	24,600	194	1.9

For the most part, the theoretical calculations were quite close to those obtained experimentally. The MWD's were all in the area of 2.0, (Figure 10) and the T_g's varied from a modest 140°C at 3700 g/mole to 194°C for a 24,600 g/mole. Oligomers with $<M_N>$'s as high as 37,000 g/mole were prepared; however, too large a sample size was needed at molecular weights $>25,000$ g/mole to achieve adequate endgroup concentrations for post reactions. Since a range of different molecular weigh phenolic hydroxyl terminated poly(arylene ether sulfone) oligomers were readily available in our laboratory, a comparison of intrinsic viscosity measurements was undertaken. The results of this study can be seen in Table 6. The only difference in these oligomes were the endgroups, -OH vs. $-NH_2$ and since these accounted for $\leq$ 1 wt % of the total polymer weights, both oligomers should be expected to exhibit similar dilute solution behavior. In all cases, the viscosity measurements were in good agreement, indicating similar hydrodynamic volumes. This was yet another positive indication that the true molecular weights of the various NH_2PSF oligomers were close to the titated values.

4.2.1 *Synthesis of Other Bisphenol-Based Amine Terminated Poly(Arylene Ether Sulfone) Oligomers*

Since a similar synthetic technique was used to prepare high molecular weight poly(arylene ether sulfones) regardless of the bisphenol monomer employed, the synthesis of amino-functional oligomers was undertaken using various bisphenols. A 50/50 molar mixture of hydroquinone and biphenol has historically been used in the preparation of statistically "random" copolymers which exhibit totally amorphous behavior. Similar calculations and procedures were used as with the bisphenol-A based oligomers and the reaction was run until the characteristic green color appeared. Upon work-up of three different molecular weight oligomers, titrated amine equivalent weights corresponded well to the visual appearance of each oligomer. They were unable to be chain extended to high molecular weight by interfacial means due to solubility problems. A chain extension using diacid chloride in NMP solution did indeed result in high molecular weight polymer. Similar results were obtained in systems employing either hydroquinone or biphenol (Table 7). Titrated values again were close to theoretical calculations and the MWD's were $\cong 2$, indicating that these monomers had similar reactivities to MBA and bisphenol-A.

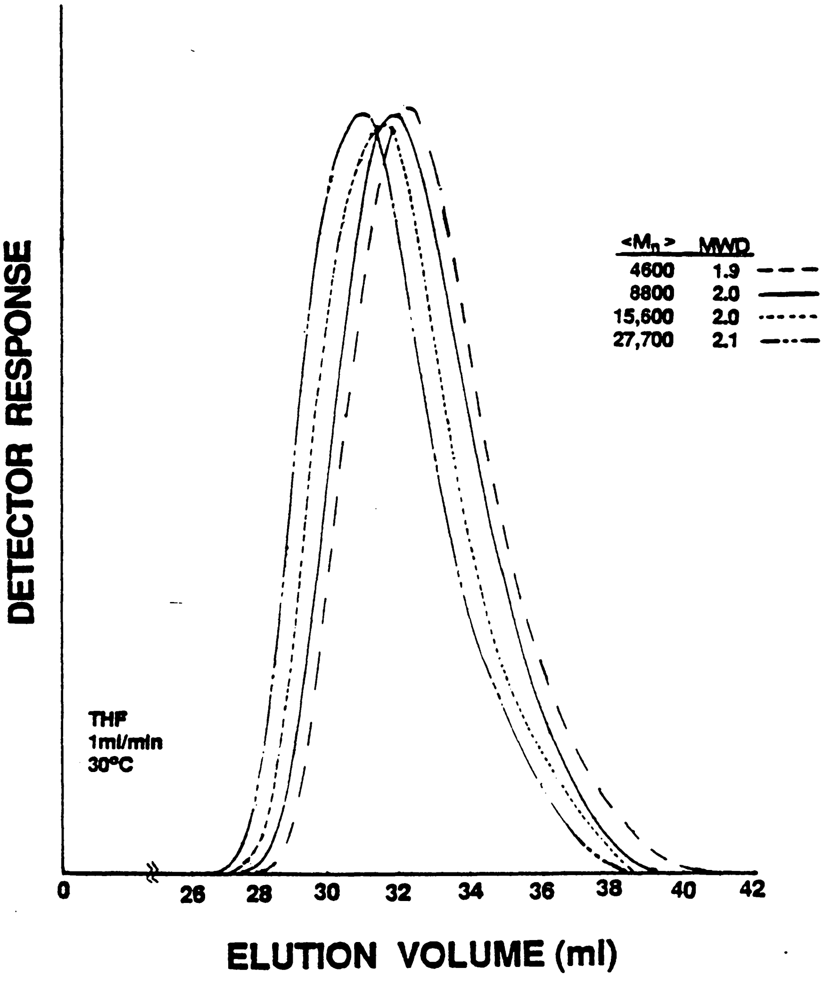


Figure 10. GPC Traces of Amine Terminated Poly(Arylene Ether Sulfone) Oligomers

TABLE 6

Comparison of Intrinsic Viscosity Measurements for Hydroxyl and Amine Terminated Sulfone Oligomers

HO- TERMINATED $\langle M_n \rangle$	$[\eta]^{25°C}_{CHCl_3}$	$-NH_2$ TERMINATED $\langle M_n \rangle$	$[\eta]^{25°C}_{CHCl_3}$
5000	0.10	5100	0.11
8200	0.13	8800	0.14
14,600	0.22	15,600	0.22
20,500	0.26	21,400	0.27

TABLE 7

Amine Terminated Poly(Arylene Ether Sulfone) Oligomers Using Hydroquinone and Biphenol

$<M_n>$ THEORY	$<M_n>$ TITRATED	$[\eta]_{NMP}^{25^\circ C}$	T_g (°C)	MWD
7500[1]	6500	0.31	191	2.2
15,000[1]	14,400	0.44	204	2.1
20,000[1]	19,200	0.73	213	2.0
5000[2]	7100	0.34	170	1.9
10,000[2]	9700	0.50	187	2.1
5000[3]	5400	0.20	196	2.0

[1] 50/50 MOLAR RATIO OF HYDROQUINONE/BIPHENOL
[2] HYDROQUINONE
[3] BIPHENOL

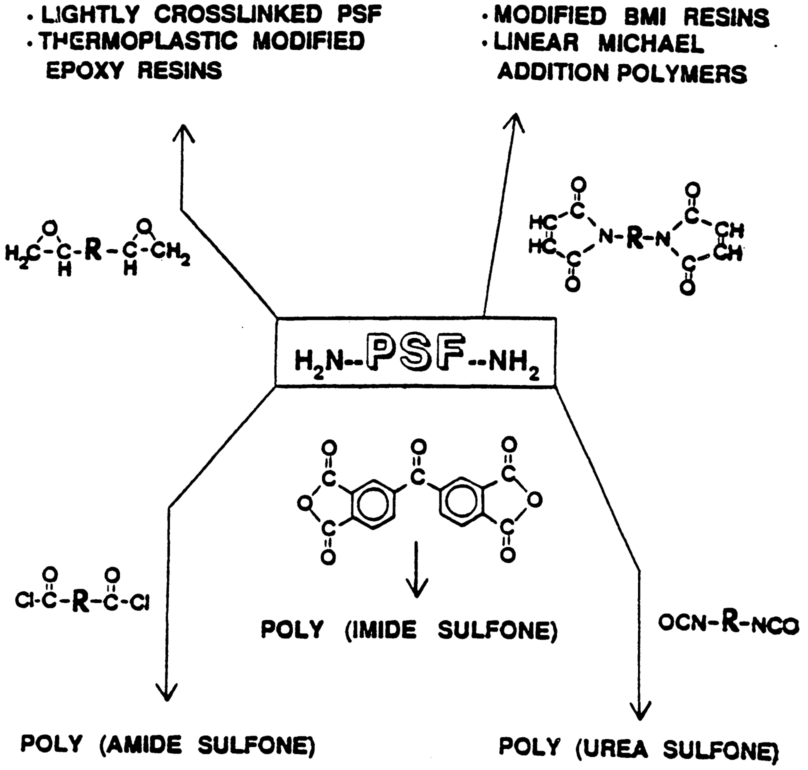
A similar reaction was tried using 4,4′-dihydroxydiphenyl sulfone (Bis-S) as the bisphenolic component. The low reactivity of the potassium phenate of Bis-S towards nucleophilic aromatic substitution with DCDPS resulted in an oligomer which did not contain quantitative endgroup functionalization. Very high titrated $<M_N>$'s were obtained but viscosity measurements and visual inspection of the oligomer's molecular weight indicated low molecular weight material. Since the assumption in the titration method is 2 amine groups per chain, if less than 2 groups are present, an artificially high value of $<M_N>$ is obtained. It is suggested that the MBA reacts preferentially to the Bis-S forming very low molecular weight oligomers which may be soluble in MeOH during the work-up procedure. Also, the Bis-S phenate is more strongly basic than the MBA phenate and may displace the MBA endgroup through an ether-ether interchange reaction, perhaps resulting in macrocyclic compounds. Both reasons would account for the loss of an efficient end-capping reaction. 4,4′-difluorodiphenyl sulfone was then tried as the activated aromatic halide due to the faster rate of halogen displacement of fluorine compared to chlorine. Difunctional amine termination could still not be achieved.

4.3 *POST REACTIONS OF AMINE TERMINATED POLY(ARYLENE ETHER SULFONE) OLIGOMERS*

4.3.1 *Introduction*

A host of polymer forming reactions are available using diamino compounds. Scheme 15 illustrates the potential post reactions for NH_2PSF oligomers. The effect of impurities on the stoichiometric balance in step-growth polymerizations has been discussed. It must be stressed that the effect of a tenth of 1% of an impurity, e.g. H_2O, will drastically upset the theoretical calculations in a typical 15 g or 3×10^{-3} molar charging of the NH_2PSF (assuming $NH_2PSF <M_N> = 5000$ g/mole). Reaction procedures for the synthesis of high molecular weight copolymers and modified thermosets were developed for each post reaction and were presented in the experimental section.

SCHEME 15



4.3.2 *Post-Reactions of Amine Terminated Poly(Arylene Ether Sulfone) Oligomers with Diacid Chlorides*

The simplest post reaction involved a simple chain extension with a diacid chloride, either the tere- or isophthaloyl chloride isomer via interfacial polymerization. It was a fast, effective manner in which to prepare high molecular weight poly(arylene ether sulfones) containing amide linkages in the backbone. It could, however, only be used with bisphenol-A NH_2PSF oligomers since solubility of the high molecular weight bisphenol-A polysulfone formed did not pose a problem. Table 8 lists the results of these interfacial chain extension polymerizations. The left side of the table has the oligomer characterization and the right side lists the chain extended polymer properties. The T_g's of the polymers level off in the 190-195°C range which is the value found for a high molecular weight bisphenol-A based poly(ether sulfone) such as UDEL P-1700. A good degree of chain extension is evidenced by the increase in intrinsic viscosity measurements.

The chain extension reaction was also followed by FT-IR. Figure 11 shows the FT-IR spectra of the NH_2PSF oligomer before and after chain extension. The N-H stretching bands at

TABLE 8

Results of Simple Chain Extension of Amine Terminated Oligomers with Diacid Chlorides

OLIGOMER			POLYMER	
$\langle M_n \rangle$ (g/mole)	T_g(°C)	$[\eta]_{25°C}^{CHCl_3}$ (dl/g)	T_g(°C)	$[\eta]_{25°C}^{CHCl_3}$
3700	140	0.12	197	1.03
5100	150	0.16	195	0.89
8800	167	0.17	191	0.87
12,300	173	0.19	196	1.21
17,000	187	0.24	189	0.79
21,000	190	0.29	195	1.39
24,600	194	0.36	193	0.82

3415 and 3375 cm^{-1} were evident in the NH_2PSF oligomer and were absent in the chain extended oligomer, most likely because they were present in such low concentrations. A distinct C=O stretch at 1650 cm^{-1} in the chain extended material was absent from the starting oligomer. Further characterization using GPC was also performed on these same two materials and is presented in (Figure 12). The shapes and elution volumes of these curves again indicated a high degree of functionality and also a high degree of conversion in the polymerization. The molecular weight obtained by GPC for the chain extended oligomer, 199,000 g/mole, indicated in this case high degree of conversion of oligomer to polymer. Comparison of this value with the intrinsic viscosity, 0.89 dl/g, gave a quantitative approximation for molecular weights obtained from this reaction.

Satisfied that this reaction proceeded to high molecular weights, we then proceeded to vary the molecular weight of the starting NH_2PSF oligomer. The polymers prepared by this method (Table 8) resulted in fibrous materials which could be solvent cast into clear, tough films. The intrinsic viscosity measurements, for the most part, indicated the achievement of high molecular weight polymers. Since these polymers are essentially high molecular weight poly(arylene ether sulfones), their T_g's level off in the area of 190-195°C, again the value associated with commercial bisphenol-A based systems.

The % polysulfone in the copolymer could be varied by controlling the $<M_N>$ of the starting oligomer and subsequently the incorporation of the polar amide segment was controlled. The polar moieties were thought to be able to change the solubility of the (essentially) high molecular weight poly(ether sulfone). These linkages were also expected to impart some measure of environmental stress crack resistance (ESCR) to the polysulfone. Polyamides exhibit good solvent resistance in load bearing applications due partly to their high inter- and intrachain forces. Unfortunately, the degree of amide incorporation due to the high molecular weight of the starting oligomer in this approach was low. Consequently, all samples underwent failure in a qualitative ESCR experiment (Table 9).

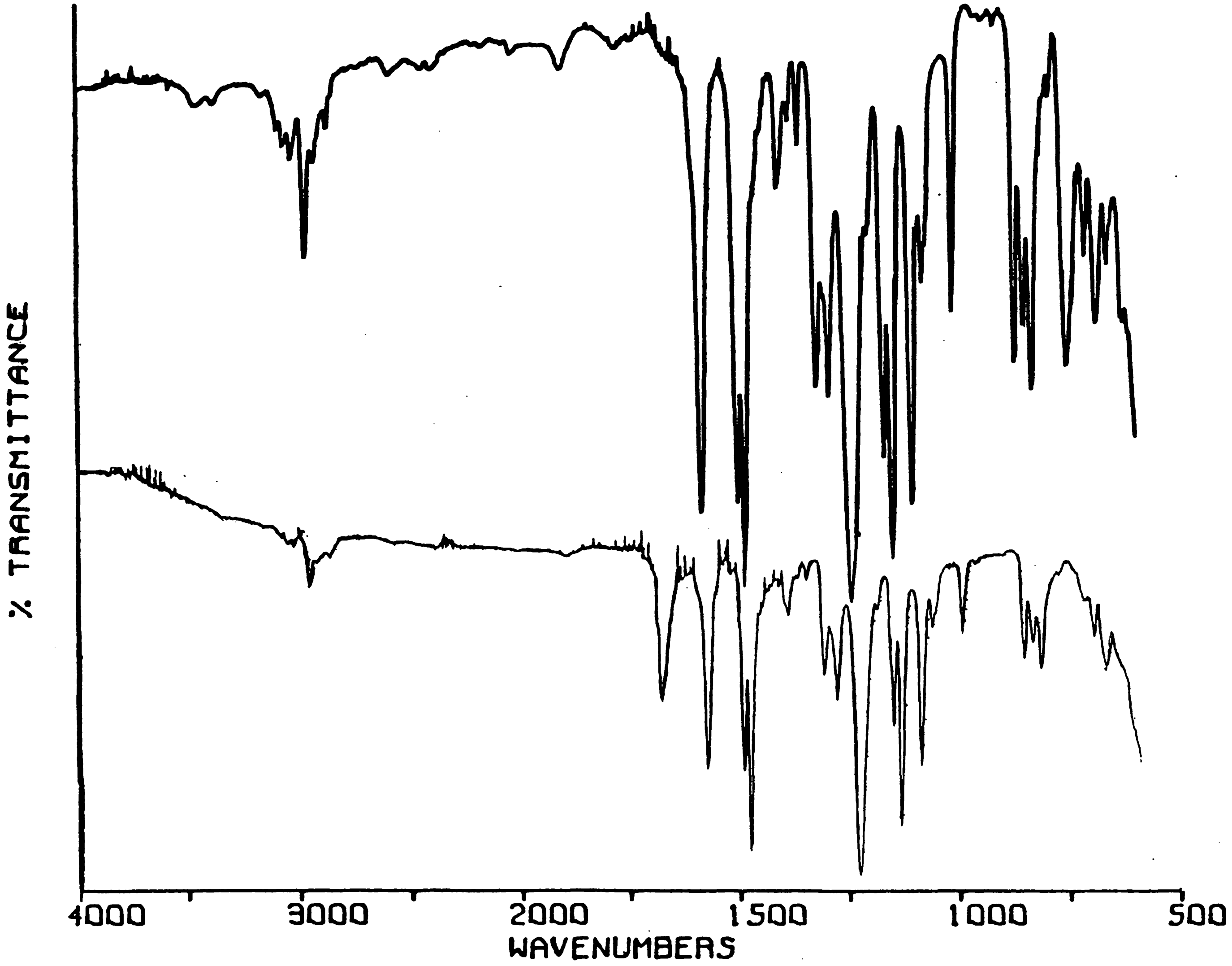


Figure 11. FT-IR Spectrum of an Amine Terminated Poly(Arylene Ether Sulfone) Oligomer and Chain Extended Polymer

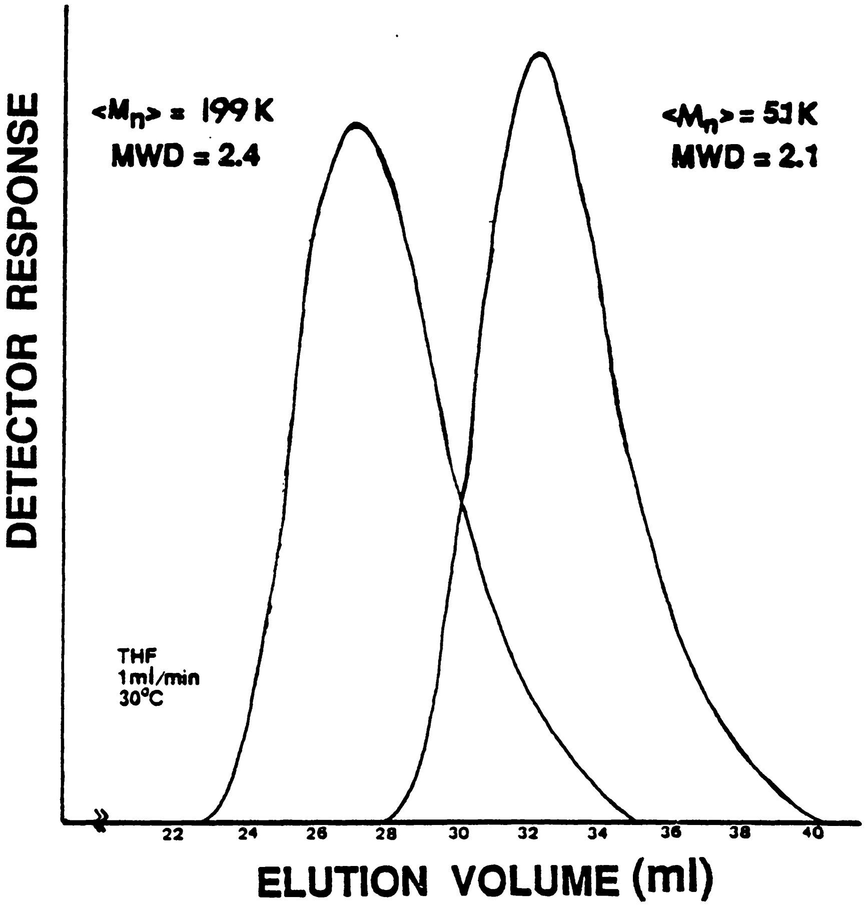


Figure 12. GPC Traces of a Quantitatively Terminated Poly(Arylene Ether Sulfone) Oligomer

TABLE 9

ENVIRONMENTAL STRESS CRACK RESISTANCE (ESCR) OF CHAIN EXTENDED SULFONE OLIGOMERS

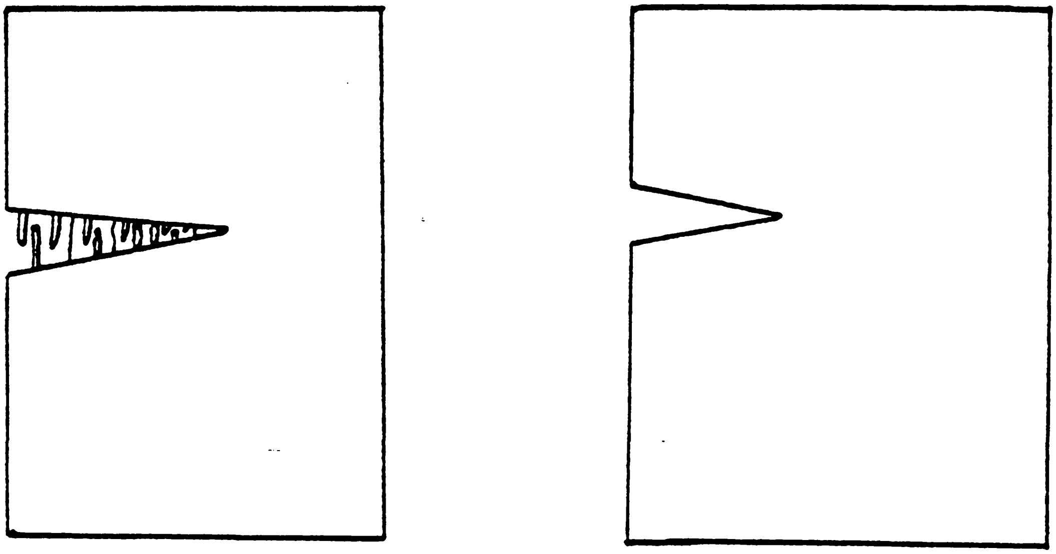
OLIGOMER $\langle M_n \rangle$ g/mole	% POLYSULFONE	E.S.C.R. (XYLENES)
3700	97.3	FAILS
5100	98.0	↓
8800	98.9	
12,300	99.2	
17,000	99.4	
21,000	99.5	
24,600	99.6	

4.3.2.1 *Considerations of Environmental Stress Crack Resistance (ESCR)*

A critical failure mechanism termed environmental stress cracking is a typical mode of failure in application end uses of polymers [331]. The presence of organic environments in contact with these materials can lead to formation of microvoids or crazes, which in turn can coalesce and lead to complete rupture of the polymer. Although crazes appear to be a series of small cracks, microscopically they contain oriented fibrillar polymer as illustrated in Figure 13. Crazes can be formed by three different methods: (1) stress, (2) solvent action and (3) stress plus solvent. Failure due to stress alone is quite common in metallic materials and is termed stress-corrosion cracking. Crazing due to solvent alone is more common in polymers, but the effect of both stress and solvent is often dramatically destructive to polymers. It must be noted that in many cases a very small applied stress, such as residual stress in molded parts may be sufficient to craze or rupture the material in certain environments. This complete failure due to the combined effects of stress and solvent is termed "environmental stress cracking". This material failure is readily encountered in many polymer systems. Structure-property data has clearly shown that amorphous polymers are far more susceptible to environmental stress failure than their crystalline, crosslinked or highly polar counterparts. Since engineering thermoplastics and their composites are replacing metallics in a variety of demanding applications, improvement in ESCR for these materials is of prime importance.

Kambour approached the problem of environmental stress failure as a plasticization effect of the organic stress cracking agent on the polymer [332]. The combination of stress and solvent lowers the T_g , resulting in flow or rupture of the polymer. He also demonstrated that the environmental stress crack failure is greatest when the solubility parameter of the environment is equal to that of the polymer. This study used the solubility parameter as the chief predictor of plasticization and subsequent crazing response. This presents an inadequate picture of the process since the solubility parameter does not usually take into account hydrogen bonding, dipole-dipole interaction or molecular size [331].

A more detailed mechanism of crazing in glassy plastics was proposed by Gent and included these four important considerations.



CRAZE

CRACK

Figure 13. Schematic Representative of a Craze and Crack

1. Stress concentration at crack tip
2. Glass-to-rubber transition at the flow tip
3. Effect of liquid or vapor environment
4. Stress-induced penetrant sorption

Although this method can be used to quantify environmental stress failure, other considerations of importance have still been excluded, for example, the kinetic approach to failure and the internal pressure build up due to diffusion of penetrant.

4.3.3 *Block Poly(Amide-Ether Sulfone) Copolymers*

The preparation of copolymers which contained higher amide content could be achieved by either lowering the $<M_N>$ of the NH_2PSF oligomer or by copolymerizing the NH_2PSF oligomer with a low molecular weight diamine such as oxydianiline (ODA). Since we did not want to lose the good properties of the polysulfone by using lower $<M_N>$ oligomers, the second option was chosen.

The incorporation of larger amounts of amide groups into a polysulfone posed a synthetic problem due to the insolubility of polyamides in interfacial polymerization solvents such as chloroform. A solution polymerization procedure was developed which could be used for chain extension of NH_2PSF oligomers or for preparation of exclusively polyamide polymers. A dipolar aprotic solvent was used with a tertiary amine to act as an HCl acceptor. A 50/50 mixture of iso- and terephthaloyl chloride was used, again to obtain a statistically "random" copolymer which would exhibit totally amorphous behavior. The molar ratio of low molecular weight diamine, ODA, to NH_2PSF was held constant at 20:1. This value was chosen so as to be able to balance both high molar quantities of amide character and high weight percents of polysulfone segments.

Following the procedure outlined in the experimental section, results of copolymers prepared using various molecular weight NH_2PSF oligomers are shown in Table 10. The copolymers prepared were fibrous in appearance and yielded yellow-brown transparent films when cast from various solvents. The % sulfone charged in these systems ranged from 39 to 85% by weight. At these high weight percents sulfone, two very important observations were made: (1) the solubilities of the copolymers did not change from those of the pure polyamide and, (2) polymers tested for E.S.C.R. using xylenes did not undergo failure with as low as 15 wt % amide groups. The copolymer prepared from the $M_N = 13{,}400$ g/mole oligomer probably failed in the E.S.C.R. experiment due to its low molecular weight as evidenced by its low intrinsic viscosity measurement.

These polyamide-polysulfone block copolymers were only soluble in dipolar aprotic solvents such as DMSO, DMF and NMP. An area of percent sulfone incorporation was delineated between 85 and 97% (from the chain extended systems) where the E.S.C.R. results went from passing to complete failure respectively. Also, between 85 and 97% sulfone content, the overall solubility of the copolymers changed from being soluble in only dipolar aprotic solvents to common solvents such as $CHCl_3$, CH_2Cl_2 and THF. Further clarification as to where this actual break in properties occurs may be determined through a lower ODA to NH_2PSF ratio or by use of a higher $<M_N>$ NH_2PSF oligomer, eg. 25,000 g/mole.

A surprising result was that none of these copolymers exhibited 2 glass transition temperatures (Figure 14). The most easily distinguishable should have been the 5100 g/mole (starting oligomer $<M_N>$) poly(amide-ether sulfone) copolymer, since the T_g of the oligomer was 150°C and the T_g of the polyamide homopolymer was 261°C. However, only 1 T_g of 225°C was noted. Either the small amount of poly(arylene ether sulfone) present was not detectable by DSC or the two different blocks were able to mix via hydrogen bonding and yield one T_g. At higher levels of sulfone content, for example with the 85% sulfone copolymer, two T_g's should again be observed. Once again, either phase mixing may account for this behavior, or, at only 15 wt % polyamide, the number of amide groups in a sequence may be lower than the critical molecular weight needed for observation of the T_g near 261°C. This last reason, along with the phase mixing argument, would help explain the closeness of T_g's for all the remaining copolymers.

The yields obtained for these polymerizations were all > 90% which is a good indication that although only 10^{-3} moles of NH_2PSF oligomer were typically used in a reaction, that it was virtually all incorporated. Comparison of FT-IR spectra from the chain extended systems to the co-poly(amide-ether sulfone) materials (Figure 15) indicates incorporation of the NH_2PSF block

TABLE 10

CHARACTERISTICS OF BLOCK POLY(AMIDE SULFONE) COPOLYMERS

OLIGOMER $<M_n>$	Inh[1] η	T_g(°C)	WT% SULFONE	ESCR[2]
5100	0.72	225	39	PASSES
7100	0.58	193	46	PASSES
17,000	0.84	193	67	PASSES
22,500	0.90	197	85	PASSES
POLYAMIDE[3]	0.91	261	0	PASSES
UDEL®	0.59	195	100	FAILS

[1] 0.2% SOLUTION IN NMP

[2] ENVIRONMENTAL STRESS CRACK RESISTANCE DETERMINED USING XYLENES AS SOLVENT

[3] 80:20 MIXTURE OF ISO- TO TEREPHTHALOYL CHLORIDE USED

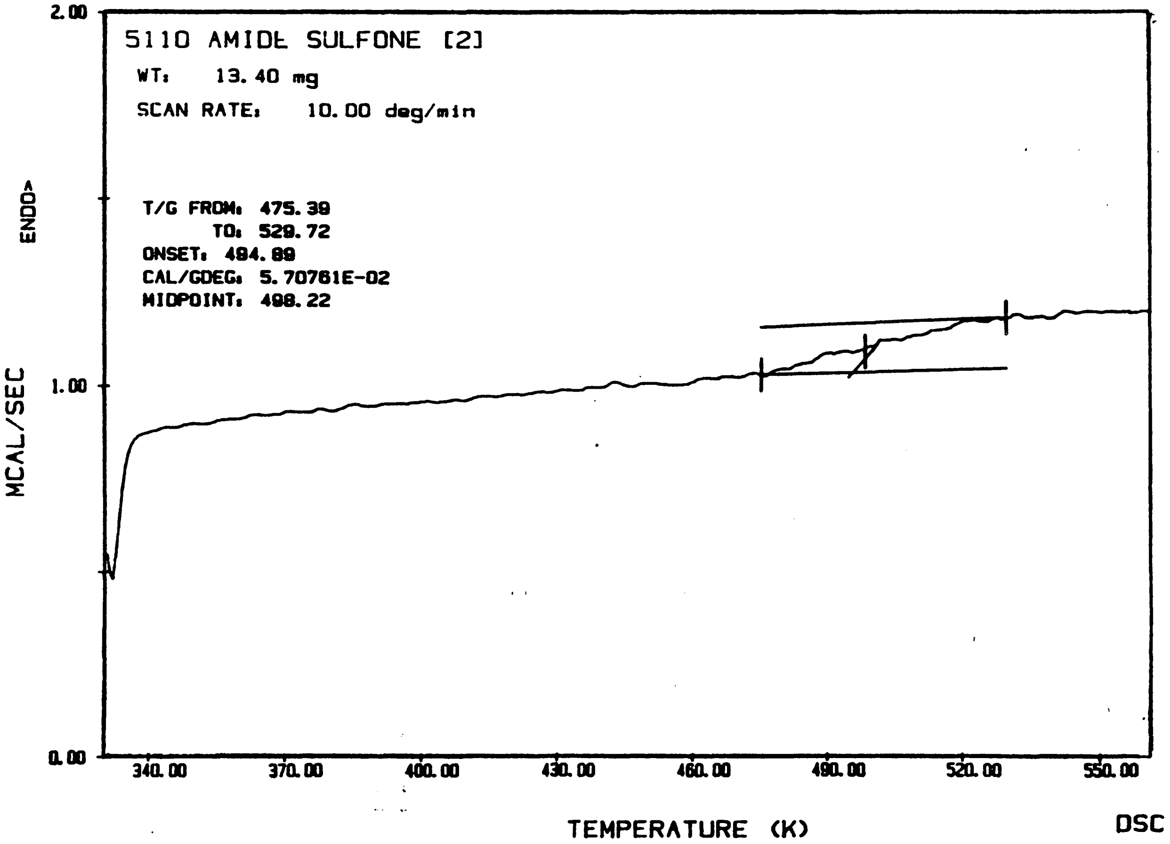


FIGURE 14 DSC Results of Poly(Amide - Ether Sulfone) Copolymers

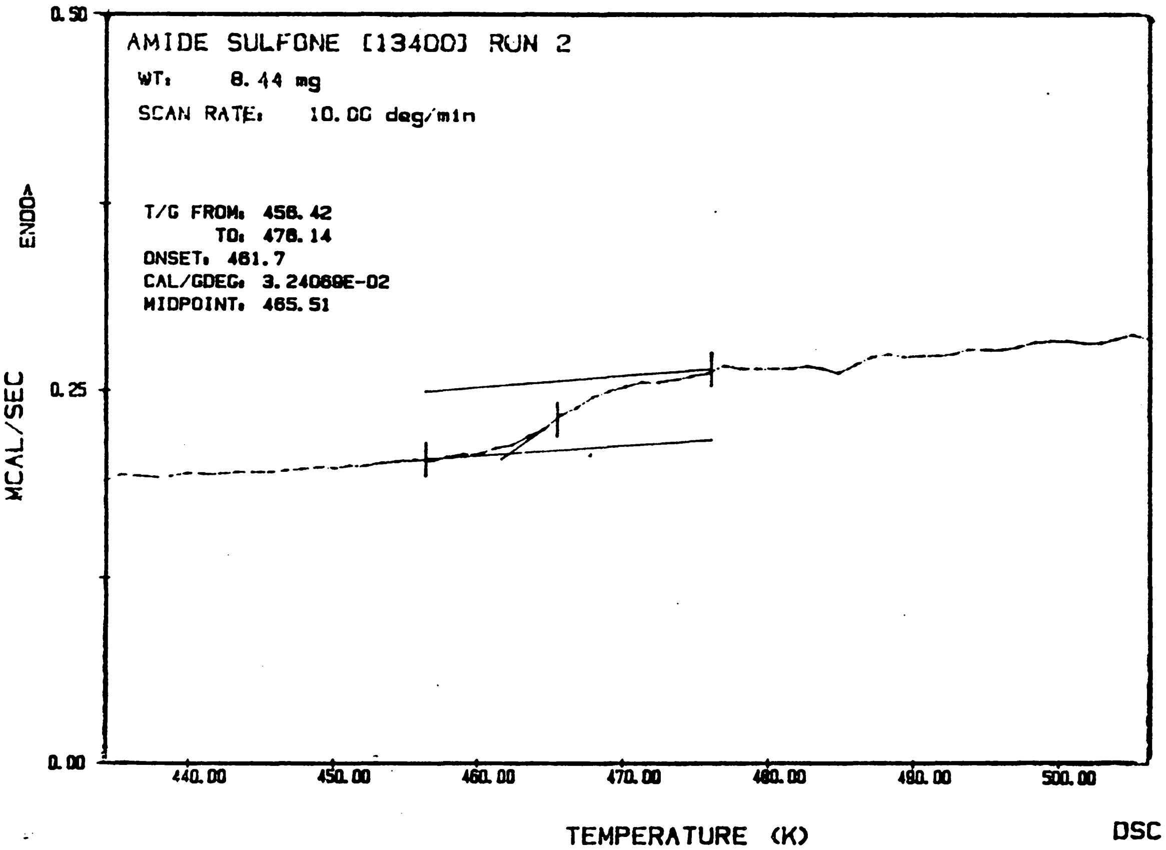


FIGURE 14 DSC Results of Poly(Amide - Ether Sulfone) Copolymers

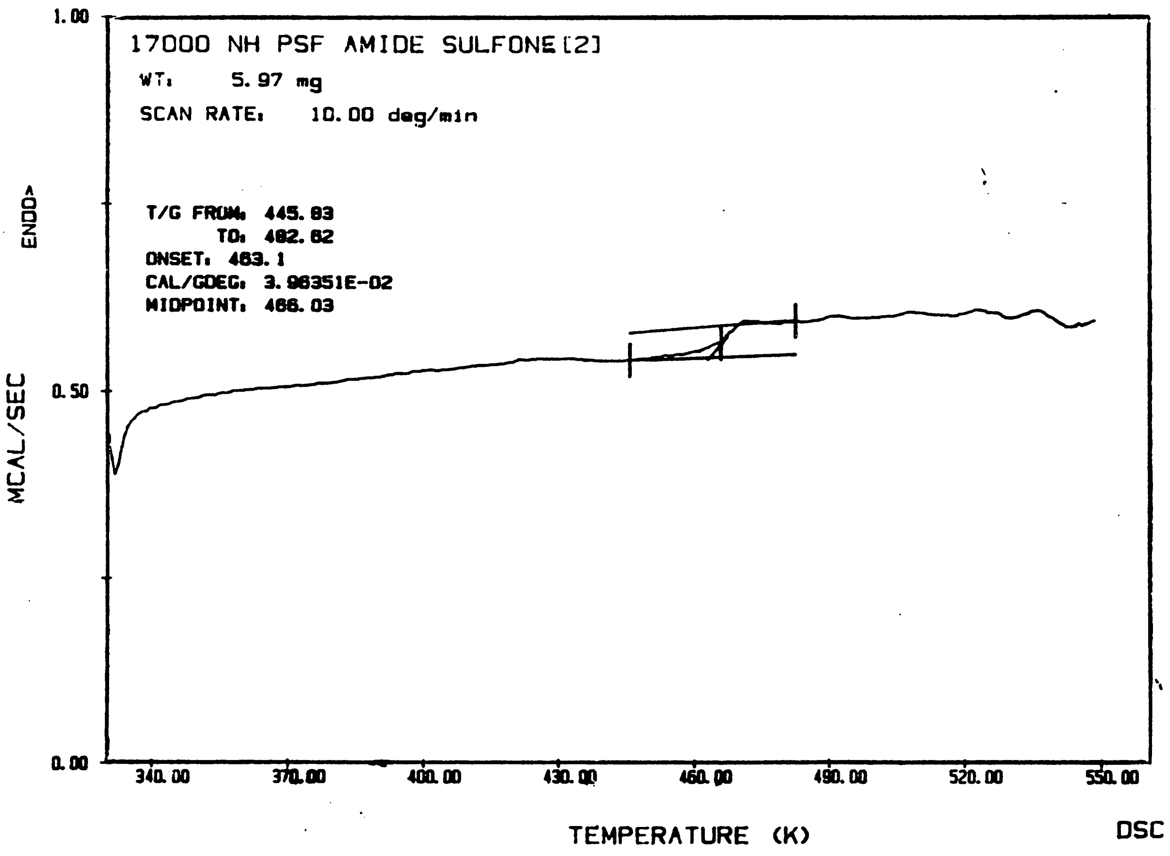


FIGURE 14 DSC Results of Poly(Amide - Ether Sulfone) Copolymers

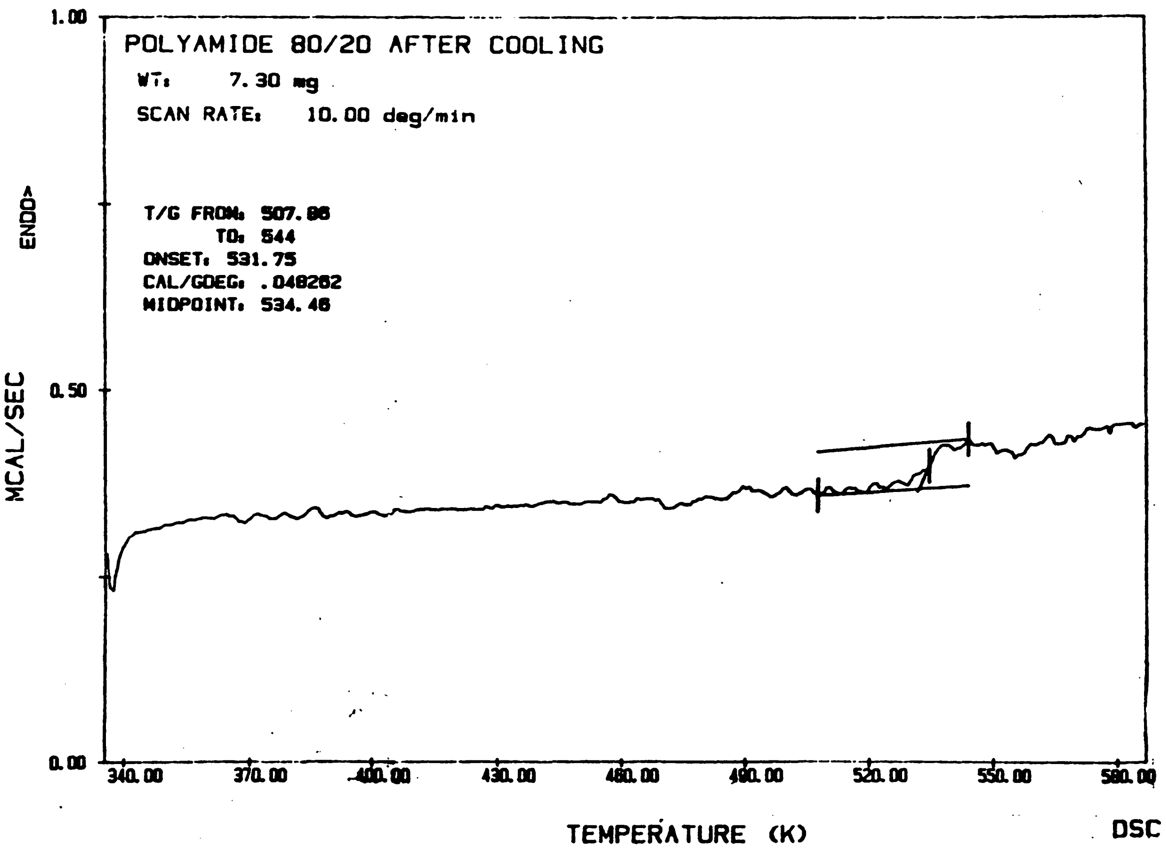


FIGURE 14 DSC Results of Poly(Amide - Ether Sulfone) Copolymers

as well as a much larger N-H (3500-3300 cm^{-1}) and carbonyl stretching bands (1690-1650 cm^{-1}), as expected.

4.3.4 *Reactions of Amine Terminated Poly(Arylene Ether Sulfone) Oligomers with Diepoxides*

4.3.4.1 *Introduction*

Reactions between diamines and diepoxides have been well documented in the literature and normally produce highly crosslinked epoxy resins [314]. Conventionally, an epoxy resin is formed by the reaction of 2 moles of diepoxide (functionality = 2) with 1 mole of a low molecular weight diamine (functionality = 4). The use of high molecular weight diamines, NH_2PSF oligomers, provides two useful end products to study in the area of epoxy chemistry.

The first approach would be to replace some of the conventional low molecular weight diamine, up to 30 wt %, with an oligomeric diamine. This has been investigated with both rubber modifiers [315,316] and various thermoplastics [317,318]. This results in an improvement of the fracture toughness for the thermoset matrix by increasing the $<M_C>$ of the system.

Alternately, an NH_2PSF oligomer may be the sole diamine employed, which results in a poly(ether sulfone) matrix containing a much lower crosslink density (or higher $<M_N>$). This approach would lead to improvements in certain thermoplastic properties, among them solvent resistance and dimensional stability. Thermoplastic modified epoxy resin systems, the first reaction described here, are currently being studied and will not be presented here [319]. The second method will be referred to as "lightly crosslinked polysulfone" systems.

4.3.4.2 *Synthesis of Lightly Crosslinked Polysulfone Matrices*

The synthesis of an epoxy resin occurs in two overlapping stages. The first is a reaction between a primary amine and an epoxide group to form a secondary amine and a secondary

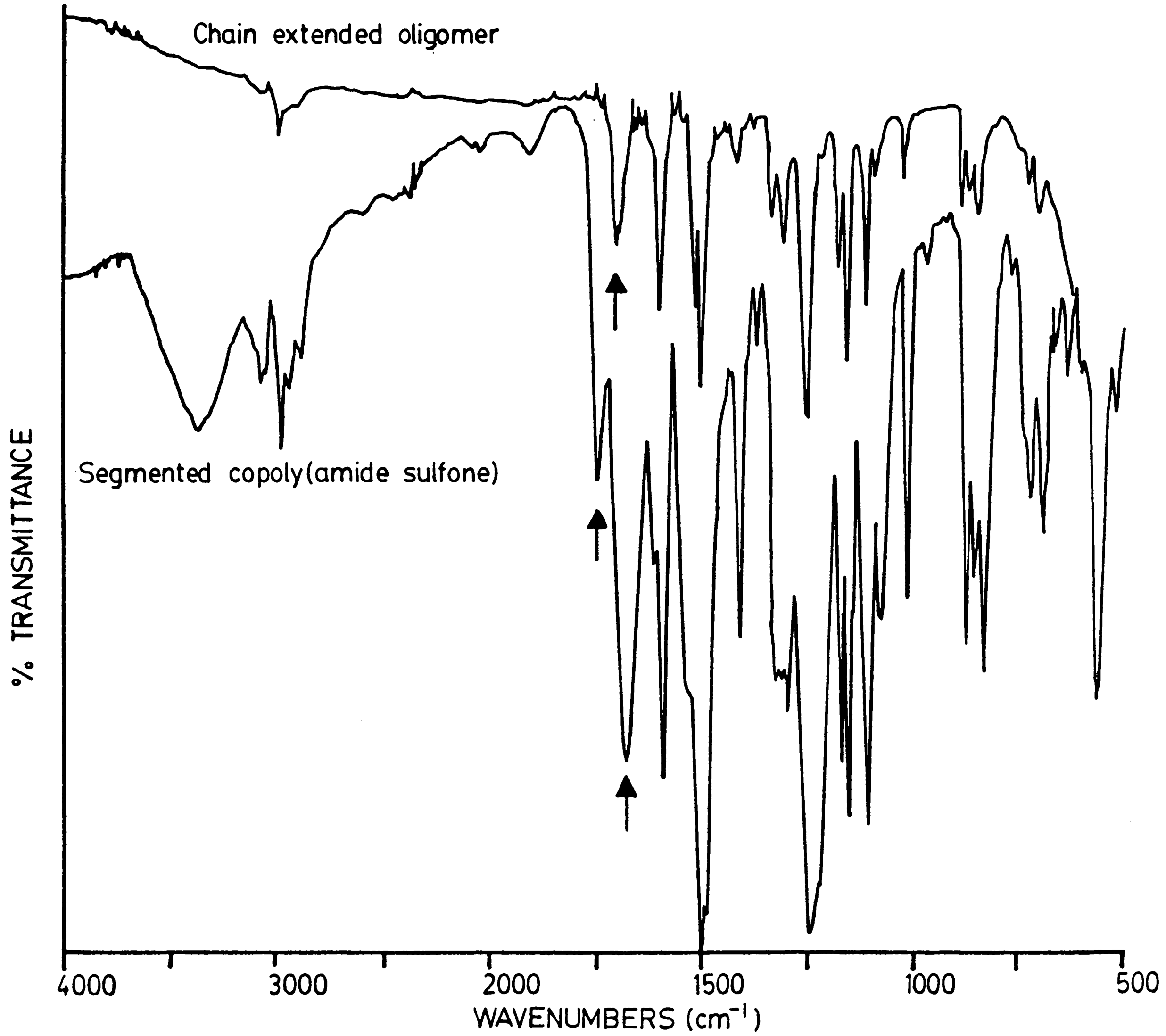
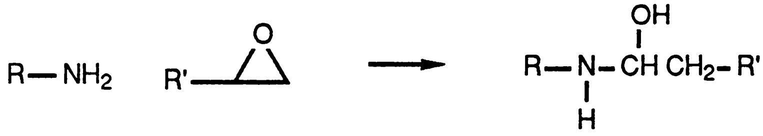
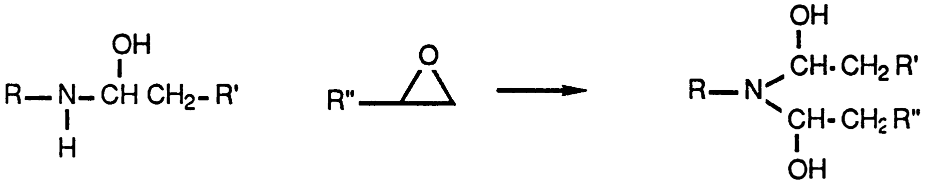


Figure 15. Comparison of FT-IR Spectra from Block Poly(Amide-Sulfone) and Simple Chain Extended Oligomers

alcohol.



The reaction is generally conducted in solution or in the melt [320]. The second step involves the reaction of secondary amines and epoxide groups to form a tertiary amine.



It is this reaction which forms the crosslink points between polymer molecules to give the resulting resin its highly crosslinked structure. This second step is done in the melt at temperatures at or near the T_g of the resulting network. A post-cure is often required for a short period of time to ensure adequate molecular motion for the remaining few percent of the functional groups to react.

The two reactants utilized in this proedure are DGEBA and an NH_2PSF. Since such small weight percents of DGEBA (M.W. = 340.42 g/mole) are used in comparison to an NH_2PSF ($<M_N>$ = 5-25,000 g/mole), a solvent was necessary for adequate mixing of the two reactants. DMF was chosen as the solvent due to its ability to adequately dissolve the reactants as well as to provide a reaction temperature similar to those used in epoxy reactions of low molecular weight compounds, 130-150°C.

A study was undertaken to follow the extent of reaction between the NH_2PSF oligomer and DGEBA at 145°C in DMF. Following the experimental procedure outlined earlier, the reaction was run using three different molecular weight NH_2PSF oligomers. The endgroup concentration in each case was held constant at 6.6 x 10^{-2}M. Aliquots were removed at various times and viscosity measurements were run to obtain the relative molecular weight increase during the reaction. Figure 16 shows the result of these three experiments. The relative viscosity increased in all cases, reaching a peak at 80-100 minutes. This corresponds to an increase in hydrodynamic volume of the polymer molecules, and, most proably an increase in molecular weight via a linear chain extension reaction of the NH_2PSF. One would expect the primary amine endgroups are reacting at a faster rate than the secondary amines, thus extending the NH_2PSF oligomer to higher molecular weights. After this time, a decrease in the $\eta_{(rel)}$ was observed. This did not result from a decrease in molecular weight, but rather, was the result of branching. As the secondary amine groups began to react, they first became branched molecules before actually becoming crosslinked molecules. Branched molecules are known to occupy a smaller hydrodynamic volume than similar molecular weight linear molecules [320]. Hence as these chain extended oligomers become more and more branched, the $\eta_{(rel)}$ continues to decrease. After 4 hours, samples of the polymers were isolated by coagulation in methanol, dried and were redissolved in DMF. The materials were still soluble at this point. At times greater than 12 hours (in the case of the 5500 g/mole NH_2PSF), coagulated samples could not be redissolved in DMF and thus had apparently gelled.

Maximum "linear" step-growth apparently occurs in the first 90 minutes and this time was chosen as the optimum time for the solution chain extension step. The reaction was then cooled to 100°C and solvent cast into thin films on glass plates or various other substrates. The solvent was removed under vacuum affording a light brown film. The films were then cured in an air circulating oven at 200°C, similar to the cure cycle for that of a conventional epoxy resin. Thermal analysis in the DSC showed a small exotherm, indicating a small amount of reaction. A post cure at 220°C for 0.5 hours was found sufficient to eliminate this behavior. The films obtained were light brown in color, transparent, creasable and *exhibited good adhesion to glass, copper and aluminum.*

A series of molecular weight NH_2PSF oligomers were then reacted with DGEBA using the same procedure. As the $<M_N>$ of the starting oligomer was varied, the resulting $<M_C>$ of the system was changed. The effect of the $<M_C>$ with respect to solubility and thermomechanical response could be studied. Table 11 illustrates the results for lightly crosslinked polysulfones prepared with a wide range of molecular weights. The T_g's of the resulting resin as well as their solubility in $CHCl_3$, THF and DMF are presented. One can again see that the T_g's do not increase past the T_g of a high molecular weight poly(arylene ether sulfone). In fact, the resin T_g's were lower than initially expected. The effect of the flexible ether linkages in the DGEBA must be responsible

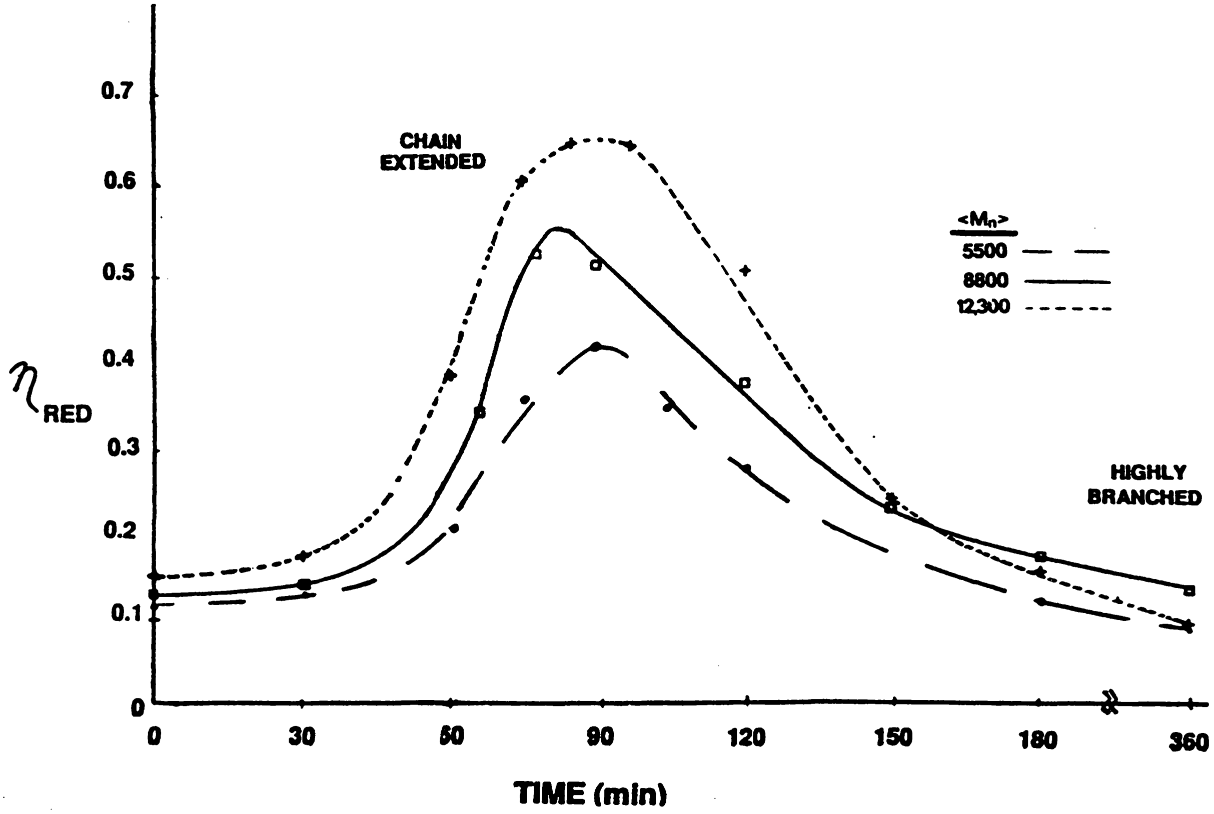


Figure 16. Effect of Time on Reduced Viscosity for Lightly Crosslinked Polysulfones

for the depression of the T_g since it appears more pronounced at the lower molecular weights of NH_2PSF, i.e. samples which contain a larger percent of the ether linkages.

The solubilities of the lightly crosslinked polysulfone could be seen to vary with the $<M_N>$ of the starting oligomer. A NH_2PSF oligomer of $<M_N>$ = 24,600 g/mole is quite close to the $<M_N>$ of a commercial UDEL polysulfone and they exhibit very similar thermal and mechanical properties. After treatment of UDEL with DGEBA, the properties were unchanged. The small number of crosslinks in the NH_2PSF did not result in a noticable increase in the T_g but the solubility of the resin in THF was altered. This effect became more pronounced as the $<M_N>$ of the starting oligomer decreaesd and the crosslink density of the resulting resin increased. The resin produced from $<M_N>$ = 8800 g/mole NH_2PSF oligomer was totally insoluble in both $CHCl_3$ and THF. At $<M_N>$ = 4600 g/mole, the crosslink density of the lightly crosslinked polysulfone was sufficiently high to be insoluble in all three solvents tested.

Next the effect of the crosslink density in a thermal mechanical test was investigated. The results can be seen in Figure 17. The test was run as described earlier using a 10 g load and a heating rate of 10°C/min from 50 to 300°C. The UDEL polysulfone underwent complete penetration by 220°C, starting just below its T_g. The crosslink density in the resin produced from an oligomer $<M_N>$ = 24,600 g/mole extended this temperature by 20°C. The resin produced from the 19,500 g/mole oligomer had a sufficient number of crosslinks to prevent complete penetration through the sample up to 300°C, even though the DSC T_g of the system was 191°C. Less sample penetration was evident as the crosslink density of the resin increased, as expected. The light crosslinking of these NH_2PSF oligomers created an extended modulus - temperature plateau by preventing flow of the polysulfone above its T_g. This resulted in an extended use temperature range for materials produced in this manner. Improved solubility resistance was also gained as a result of the lowering of the $<M_C>$ of the matrices.

The excellent adhesive properties between these lightly crosslinked polysulfones and various substrates, especially to untreated copper foil was a somewhat surprising result. Analogous crosslinking points are contained in both this system and in epoxies. Epoxies are well-known structural adhesives, but they contain an order of magnitude more secondary hydroxyl groups than

TABLE 11

Results of Lightly Crosslinked Polysulfones

* OLIGOMER		RESIN	SOLUBILITY		
<Mn> g/mol	T_g (°C)	T_g (°C)	$CHCl_3$	THF	DMF
4600	149	186	i	i	i
8800	158	182	i	i	sw
13,100	170	188	sw	sw	sw
19,500	189	191	s	sw	s
24,600	194	196	s	sw	s
UDEL®	195	CONTROL	s	s	s

* ALL OLIGOMERS ORIGINALLY SOLUBLE
i = insoluble, s = soluble, sw = swells

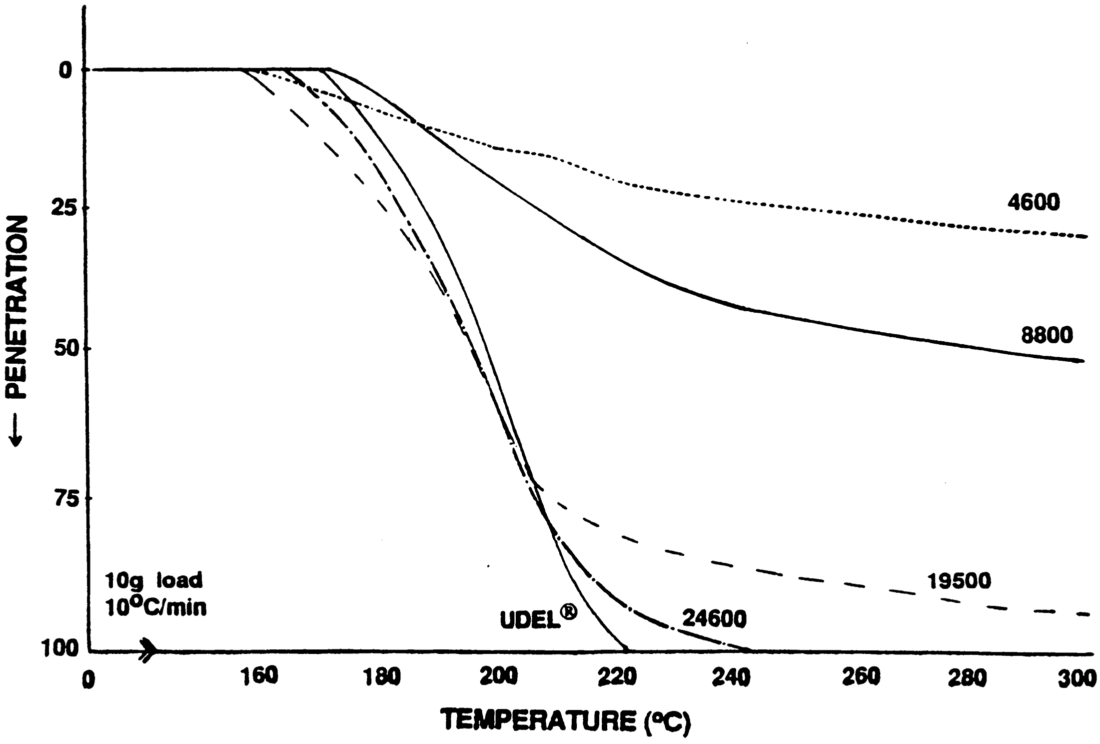


Figure 17. TMA Results of Lightly Crosslinked Polysulfones

the lightly crosslinked polysulfones. Although the interactions are not fully understood, these secondary hydroxyl groups are thought to be responsible for the adhesive properties of epoxy systems. Further investigation into the quantitative evaluation of this phenomenon would be warranted.

4.3.5 *Reactions of Amine Terminated Poly(Arylene Ether Sulfone) Oligomers with Bismaleimides*

4.3.5.1 *Introduction*

Some of the background and chemistry available with bismaleimides has been discussed in an earlier section. The two potential reactions of interest are (1) the thermal, free radical reaction of the unsaturated groups, and (2) the reaction of a suitable reagent, such as an amine, across the activated carbon-carbon double bond via a Michael reaction. Investigations utilizing both of these reactions will be discussed here.

4.3.5.2 *Synthesis of Linear Polyaspartimides*

The bismaleimide of methylene dianiline, 1,1′-(methylene-4,1-phenylene) bismaleimide or BMI, was the reagent used throughout this study. The literature contains examples of reactions between bismaleimides and aliphatic [331-333] and aromatic [332,335,54,55] diamines as well as arenethiols [334] to produce linear, high molecular weight polymers called polyaspartimides. The aromatic amines are the weakest ases of the three and hence require longer reaction times than the other two examples. The reaction is carried out in a protic solvent, such as m-cresol to stabilize the intermediate. A weak protic acid, generally glacial acetic acid, catalyzes the reaction by favoring the enolization reaction.

Literature preparations of various Michael addition polymers were repeated to insure the synthetic viability of this route. An aromatic, amine terminated NH_2PSF oligomer was then used in place of the low molecular weight diamine. Reaction times for these compounds were often twice as long as that required for a diamine such as oxydianiline or ODA. This is most likely attributable to the low concentration of reactive functional groups in solution. Table 12 shows the results of these linear polyaspartimide polymerizations using a range of NH_2PSF oligomers. Only lower molecular weight oligomers were used in an attempt to keep the endgroup concentration from becoming too low. The control utilized ODA and due to the high degree of hydrogen bonding, it was not soluble in common solvents such as $CHCl_3$ and THF. The polymer films formed were brownish in color, but were transparent and creasible. Use of an excess of BMI in order to prepare BMI terminated polymers appears to have succeeded judging by the low intrinsic viscosity measurements obtained for the $<M_N>$ = 3700, 6500 and 13,400 g/mole samples. The targeted molecular weight calculated was 30,000 g/mole in all three cases. Unfortunately, an adequate method for the quantitative determination of the polymer molecular weight via analysis of the BMI endgroup could not be developed.

The last reaction variable was the reaction solvent. A protic solvent was shown earlier to help stabilize the enol intermediate, thus preventing a branching side reaction from occurring at that carbonyl oxygen. It was believed, however, that the bulkiness of an oligomeric species might significantly reduce the rate of this side reaction so that the reaction might be carried out in an aprotic solvent such as DMF. Stoichiometric quantities of a 5100 g/mole NH_2PSF oligomer and BMI were reacted in DMF. After one hour at 140°C, a noticable increase in solution viscosity was observed. A reduced viscosity measurement showed an increase from 0.11 at the beginning of the reaction to 0.29 dl/g after one hour. A sample of the reaction was coagulated in methanol, dried and redissolved in DMF. If the branching side reaction had occurred, it did not do so to the extent of producing a crosslinked, insoluble fraction of the reaction. This was in stark contrast to a reaction of ODA and BMI at 140°C. This reaction became so viscous that it was unable to be stirred with a mechanical stirrer.

The success of this reaction in DMF led us to wonder about using a large excess of BMI. The Michael addition would still occur, but there would essentially be an end-capping of the oligomeric amine endgroups with a bismaleimide. If a large enough excess of BMI were used, virtually no chain extension of the oligomer would occur. The unreacted BMI groups could then be treated thermally to induce the free radical crosslinking reaction, yielding a crosslinked

TABLE 12

Results of Poly(Aspartimide) Syntheses

OLIGOMER $\langle M_n \rangle$ (g/mole)	$[\eta]^{25°C}_{CHCl_3}$ (dl/g)	T_g (°C)
200	0.59*	211
3700	0.27	187
4600	0.88	189
6500	0.27	183
8800	0.91	187
13,400	0.23	190

* OXYDIANILINE CONTROL MEASURED IN DMSO AT 25°C

bismaleimide resin modified with a thermoplastic oligomer. This approach will be discussed in the next section.

The reaction of an amine terminated poly(arylene ether sulfone) oligomer, in the place of a low molecular weight diamine, with a bismaleimide, appears to also be a viable post reaction for linear, high molecular weight polymer formation.

4.3.5.3 *Synthesis of Thermoplastic Modified Bismaleimide Resins*

As outlined in the previous section, the incorporation of a thermoplastic NH_2PSF oligomer into a bismaleimide resin system seemed to be an obvious extension of the poly aspartimide work. BMI resins are notoriously brittle due to their high crosslink density, but offer many good high temperature properties. Chemical incorporation of a tough, poly(arylene ether sulfone) modifier may act to increase the $<M_C>$ of the network without seriously affecting the high T_g of the resin. The synthesis, outlined previously, was relatively simple and followed along the lines of the lightly crosslinked polysulfone system. The BMI and NH_2PSF were heated in DMF for 0.5 hour at 140°C and were then solvent cast into thin films. The solvent was removed under vacuum and the films were cured in an air circulating oven at 200°C and then raised to 250°C for the thermal curing of the carbon-carbon double bonds. This reaction is known to occur [6] at temperatures $>230°C$. The resulting films were deep brown and transparent, and slightly less brittle in comparison to the pure BMI control. The results can be seen in Table 13. A single molecular weight NH_2PSF oligomer was used throughout this reaction sequence and the ratio of BMI to NH_2PSF was varied. A 1:1 molar ratio of the two reactants, (6 wt % BMI/94 wt % PSF), after curing resulted in a film which was insoluble in DMF and $CHCl_3$ even after 6 months. A larger percentage of BMI results in a higher crosslink density for the network produced. Better solvent resistance and improved dimensional stability are the expected results of this trend. The T_g of the system does not noticably increase up to a 50/50 weight ratio of the two monomers. As BMI becomes the major component in the system, the T_g begins to rise, due mostly to the influence of a greater number of crosslinks "tying in" molecular segmental motion.

TABLE 13

Results of Thermoplastic Modified Bismaleimide Resins

WT % BMI	WT % NH_2PSF	MOLAR RATIO	T_g (°C)	SOLUBILITY $CHCl_3$	SOLUBILITY DMF
0	100	* CONTROL	150	S	S
6	94	1:1	180	i	i
25	75	5:1	185	i	i
50	50	15:1	183	i	i
60	40	22:1	190	i	i
85	15	84:1	204	i	i
100	0	CONTROL	240	i	i

* POLYSULFONE $\langle M_n \rangle = 5300$ g/mol

The effect of crosslink density on the thermomechanical response can be seen in Figure 18. The BMI control can be seen to have good dimensional stability, allowing no penetration up to 300°C. The UDEL polysulfone control underwent complete penetration by 220°C. (The 5300 g/mole oligomer was not used as the control in this study since its molecular weight was too low to form a coherent film for analysis). The 6 wt % BMI (1:1 molar ratio) sample did not undergo complete penetration until 290°C. As the wt % BMI was increased, the crosslink density became greater and as a result, penetration through the sample became smaller.

The solubility tests on the thermoplastic modified BMI's showed that no polysulfone could be extracted and hence was chemically reacted into the network. A reaction run at room temperature in DMF and cured in the typical fashion resulted in a resin which was slightly soluble in $CHCl_3$. FT-IR analysis of the $CHCl_3$ indicated that the amine terminated poly(arylene ether sulfone) oligomer was not quantitatively incorporated into the BMI resin.

This promising area of thermoplastic modification of thermosetting resins is hampered by this synthetic procedure. The thin films obtained by solvent casting techniques are not thick enough to provide the necessary sample dimensions for desirable mechanical testings and hence alternate approaches must be found.

4.4 *Synthesis of Poly(Arylene Ethers) via the Ullmann Ether Synthesis*

Research studies with poly(arylene ether sulfones) have shown that these materials exhibit excellent radiation stability with retention of mechanical properties [322,333]. The primary contributor to this effect would be expected to be the aromatic character of these structures [324]. Recent work in our laboratory has further emphasized that the weakest link in these polymers under e-beam bombardment is the -SO_2-group [323]. Thus, the preparation of a poly(arylene ether), 17,

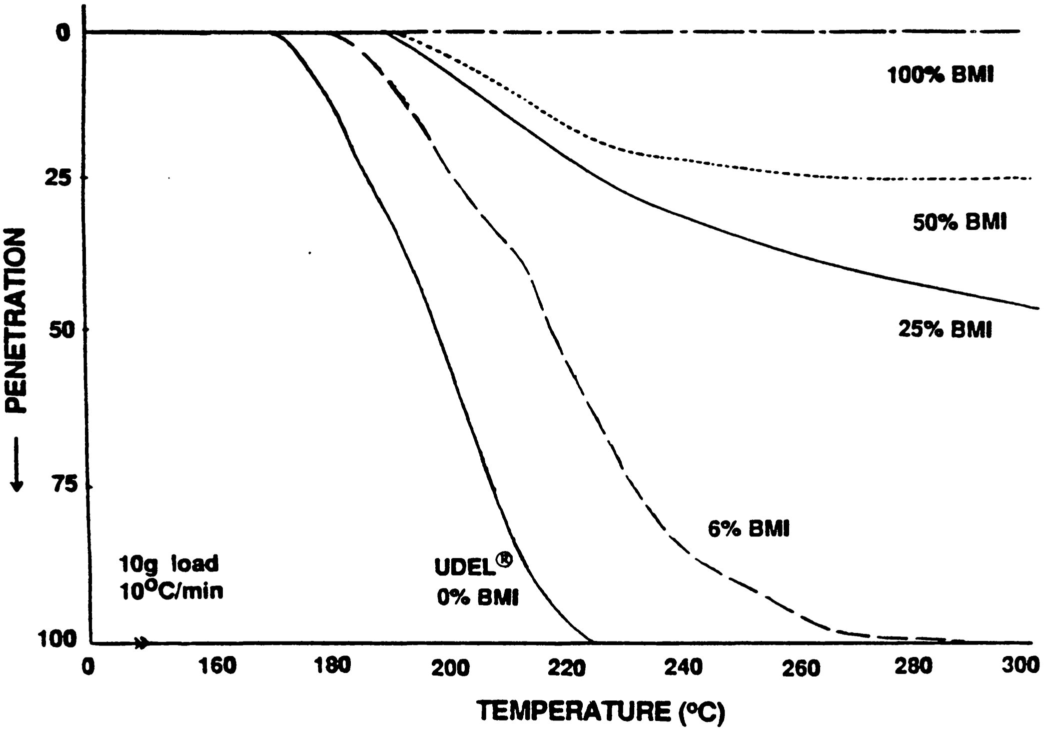
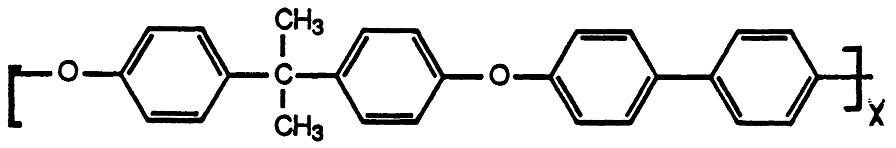
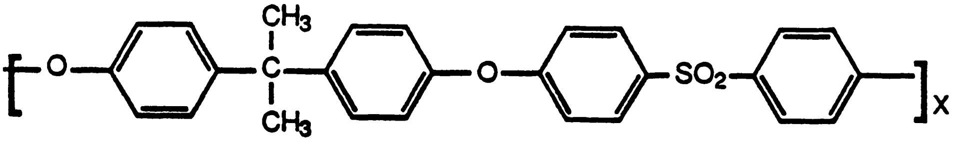


Figure 18. TMA Results of Thermoplastic Modified Bismaleimide Resins

should show a distinct advantage over that of a sulfone containing polymer, 18.



17



18

The synthesis of a non-sulfone containing polymer such as 18 is not a trivial task. The sulfone group in an aryl halide serves as an activating group for nucleophilic aromatic substitution by a suitable base. Without this electronic effect, a markedly different synthetic pathway must be utilized. Nucleophilic aromatic substitution of non-activated aryl halides can be accomplished using the Ullmann condensation reaction [325]. Ullman [230] first illustrated that copper powder is a catalyst for making aromatic ethers by this reaction; now it has been suggested that the cuprous ion is the active catalyst [258]. High molecular weight material can be prepared by proper modification of this reaction scheme.

Independent investigators have reported the preparation of totally amorphous [248,249] or semi-crystalline [236-238,233] poly(arylene ethers). Studies of the Ullmann condensation reaction [251,253,254] have determined that copper salts, and in particular Cu (I) salts, are uniquely reactive in non-activated systems for nucleophilic displacement reactions. The ease of halogen displacement is I, Br > Cl > > F which is the reverse of that observed in activated aryl halide systems. Also, the effect of the alkali metal counterion on bisphenate reactivity is negligible among common ions, e.g. $Na^+ \cong K^+$. Although the mechanism of the Ullmann ether reaction has not been fully elucidated, using proper modifications of known reaction conditions successfully leads to the synthesis of high molecular weight poly(arylene ethers).

Table 14 shows the repeat unit and physical characteristics of several poly(arylene ethers) prepared using the Ullmann condensation reaction, as well as a poly(arylene ether sulfone) (III).

By comparison, the T_g's of the true poly(arylene ethers) are substantially lower than that of a bisphenol-A polysulfone. These T_g's can be increased by wholly or partially substituting a more rigid bisphenol such as hydroquinone, resorcinol or biphenol for the moderately flexible bisphenol A unit. Alternately, 4,4′-dibromoterphenyl may be used as the aryl halide which exhibits some trend towards crystallization [248].

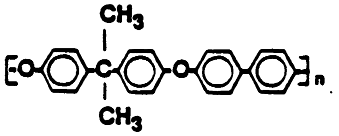
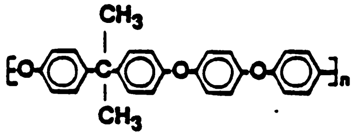
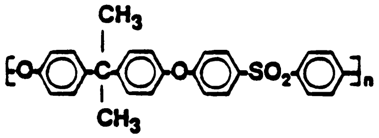
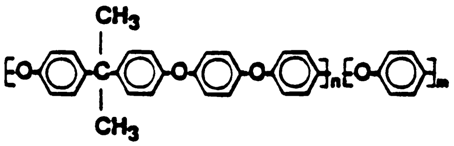
When 4-bromophenol is utilized as the monomer, a fully aromatic polyether can be prepared (IV). An inherent 1:1 stoichiometry exists but the poly(phenylene ether) prepared, PPE, possesses a high degree of crystallinity. The DSC of PPE (Figure 19) illustrates this point as distinct crystallization and melting peaks were observed. The ΔH of fusion for PPE is quite high at 7.2 cal/g which agrees well with the literature [244]. Infrared analysis performed on model compounds [238] indicated an intense absorption at 1025 cm^{-1} was observed for ortho-linked phenylene ethers, PPE prepared from a 95/5 mixture of 4- and 2-bromophenol, respectively, still exhibited this peak. An FT-IR of PPE produced in this study (Figure 20) does not show this peak, leading one to believe that little or no crosslinking occurred at the ortho position. The polymer was also soluble at > 140°C in nitrobenzene, o-dichlorobenzene and NMP. The attempts to prepare compression molded samples at 320°C and various pressures resulted in failure. The tan colored powder rapidly (< 10 min) turned deep black and decomposed. Apparently the residual copper catalyst caused decomposition at elevated temperatures [326] and must be removed to prevent this from occurring. The low T_g of this material coupled with its high crystallinity make it unsuitable for development in many areas.

An important result of the PPE synthesis was that the strong base employed, sodium hydroxide, did not effect the bromo-substituent as inferred by attainment of high molecular weight in the system. Thus the hydrolytic side reactions which must be considered with activated aromatic halide reactions [246] do not appear to be a limiting factor here. This led to the development of an improved synthetic procedure for the preparation of amorphous poly(arylene ethers) as presented in the experimental section.

The ability to prepare amorphous, high molecular weight in this work has been demonstrated using the conventional tertiary amine, pyridine [238,249] and a higher boiling compound, quinoline.

TABLE 14

Results of Poly(Arylene Ether) Synthesis Using the Ullmann Reaction

NO.	POLYMER POLYMER REPEAT UNIT
I	
II	
III	
IV	
V	

POLYMER	%WATER ADSORPTION	$[\eta]^{25°C}_{CHCl_3}$ dl/g	T_g °C[1]	T_m °C
I	0.17	1.09	166	-
II	0.13	0.62	116	-
III	0.72	0.92	195	-
IV	-	I	90	250
V	-	0.39[2]	96	-

---

[1] Thermal analysis performed using DSC.

[2] Viscosity run in trifluoromethane sulfonic acid at 25°C

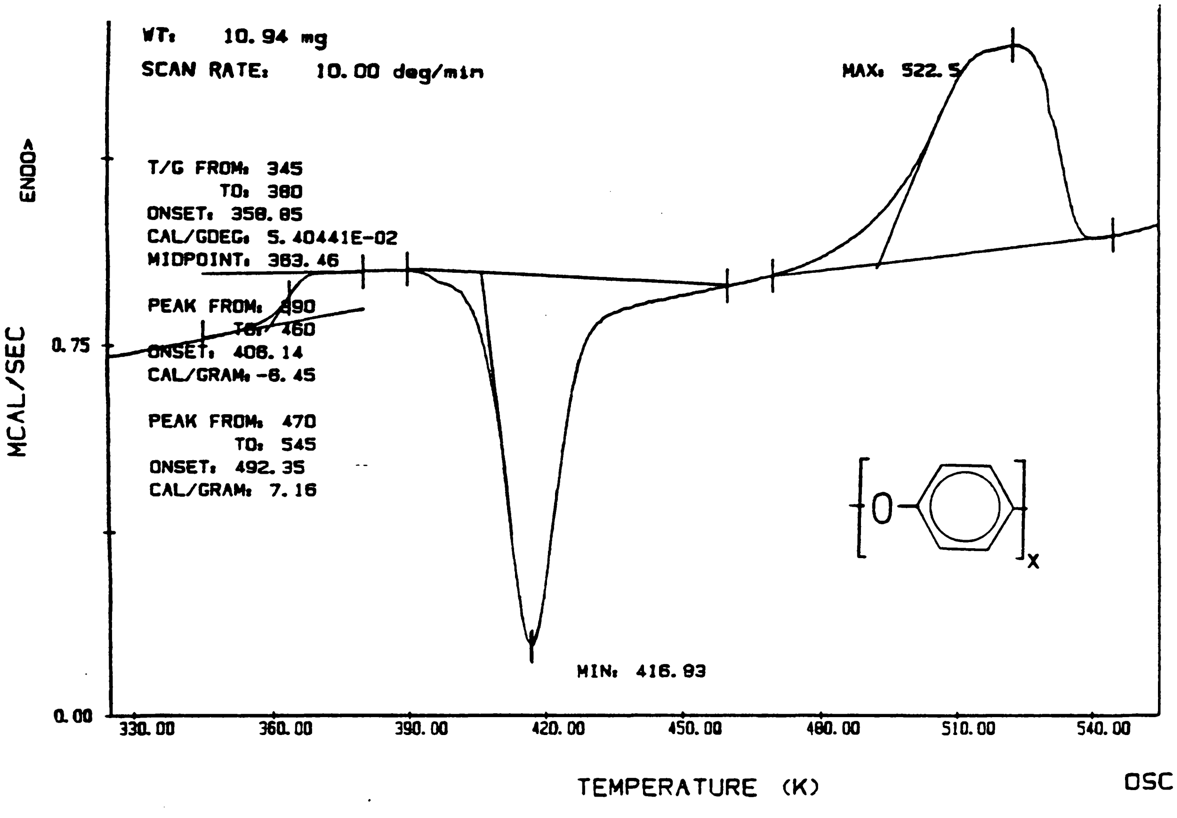


Figure 19. DSC of Poly(Phenylene Ether)

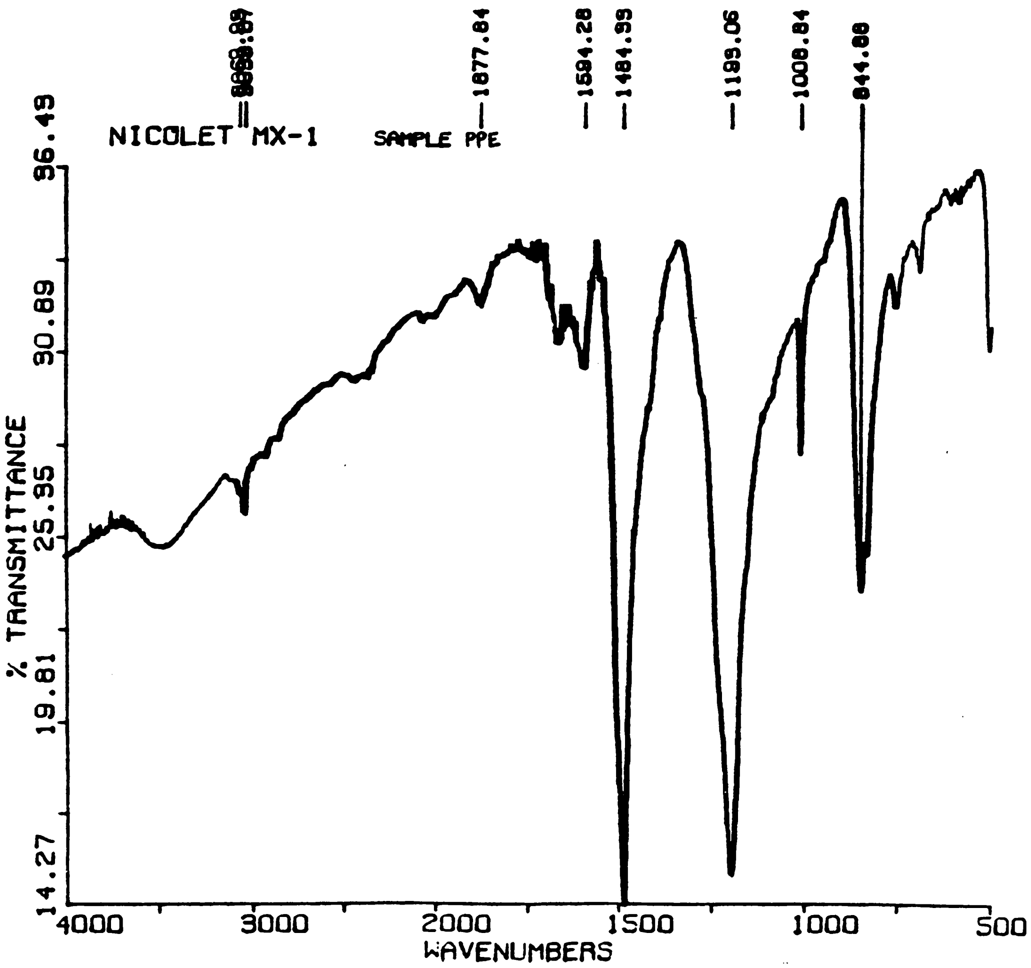


Figure 20. FT-IR of Poly(Phenylene Ether)

The use of quinoline (B.P. = 300°C) negates the problems associated with the loss of pyridine (B.P. = 115°C) at required reaction temperatures for the Ullmann ether synthesis, ≥ 200°C.

Since the T_g's of these poly(arylene ethers) are low, it would obviously be desirable to prepare copolymers either with higher T_g's or with some degree of crystalline behavior. The incorporation of a small amount of 4-bromophenol into an amorphous polymerization would not upset the stoichiometric balance since it is an A-B monomer. It is expected to copolymerize with the other monomers to give rise to small sequences resembling the PPE repeating unit. Investigators have shown [238,239] that the crystalline unit cell for PPE is ≅ 4 oxyphenylene groups. Four of these groups linked together can give rise to a semi-crystalline region in the copolymer, but will be too small to show a T_g . Hence the lower T_g of a true polyether as compared to a polysulfone may not be a factor if a degree of crystallinity can be developed.

Another approach is the copolymerization of 4-bromophenol with bisphenol-A and 4-bromophenyl ether as shown in Table 14 (V). The reaction of 1 molecule of 4-bromophenol as shown in V can be envisioned to yield the 4 oxyphenylene groups potentially necessary for crystallinity. A 10 mole percent charging of 4-bromophenol to this system resulted in a slightly fibrous but low molecular weight material as indicated by low T_g and intrinsic viscosity measurements. No crystallinity could be detected by DSC but the sample underwent decomposition above 250°C. Higher reaction temperatures may be necessary for this type copolymerization to occur in good yield and high molecular weights.

The percent water absorption for a few of these polymers has been measured and can be seen in Table 14. One can see that the non-sulfone containing polymers exhibit less water absorption than poly(ether sulfones) [249]. Since the sulfone moiety is somewhat responsible for both water absorption and e-beam degradation, the absence of this group may provide improved properties for a poly(arylene ether) versus that of a poly(arylene ether sulfone) polymer.

The Ullmann ether reaction catalyzed by copper chloride-quinoline appears to be viable method for the preparation of high molecular weight poly(arylene ethers) from non-activated aromatic halides. It is the first report of the synthesis of both amorphous and semi-crystalline polymers and opens the door to a large number of potentially useful copolymers. Particularly interesting would be the synthesis and characterization of wholly aromatic poly(arylene ether) and comparison of their molecular motion and ductility with poly(arylene ether sulfones) [328] and ketones [329,330]. By utilizing a mixture of bisphenols, e.g., 50:50 hydroquinone-biphenol, the statistically random copolymer produced usually exhibits totally amorphous behavior. Then by varying this ratio to 60:40, 70:30, etc., a semi-crystalline polymer may be obtained and the amount of crystallinity may be controlled by the monomer charge ratio. Despite significant progress, further understanding of the catalysis feature is needed for improved synthesis of poly(arylene ethers).

Chapter 5

CONCLUSIONS

The investigation of the synthesis of poly(arylene ethers) has resulted in synthetic methodology which allows structural control over the resulting polymers. True poly(arylene ethers) have been synthesized via a modification of the Ullmann condensation reaction. The synthetic viability of this reaction in polymer applications has been demonstrated for both amorphous and semi-crystalline polymer preparation. The potential to prepare wholly aromatic poly(arylene ethers) opens the door to a large number of new and interesting polymer systems.

Poly(arylene ether sulfone) have been prepared using conventional nucleophilic aromatic substitution in a dipolar aprotic solvent. Primary aromatic amine chain ends have been introduced into these systems and as a consequence, molecular weight control was achieved. Earlier investigators synthesized low molecular weight amine terminated sulfone oligomers using DMSO and a strong base such as NaOH. A number of side reactions and the lower boiling point associated with DMSO limits the versatility of this classical route.

An improved procedure has been developed in this laboratory which utilizes a weak base, K_2CO_3 and NMP (N-methylpyrrolidone) as the solvent. This procedure was extended to include the synthesis of amino-functional oligomers of controlled molecular weight using a novel endcapping reagent, 2-p-aminophenyl-2-p-hydroxyphenylpropane or MBA. This allows one to carry out the reaction of MBA, a bisphenol and an activated aryl halide in situ to synthesize a wide variety of amine terminated poly(arylene ether sulfone) oligomers.

The synthesis and characterization of amine terminated poly(arylene ether sulfone) oligomers has been investigated and their synthetic versatility as reactive intermediates has been demonstrated by the success of a number of polymeric post reactions. Block poly(amide-ether sulfone) copolymers were prepared for environmental stress crack resistance measurements with xylenes. High levels of sulfone incorporation could be tolerated due to the high degree of interchain forces attributable to the polyamide blocks.

The effect of crosslink density on thermomechanical response was investigated by varying the $<M_N>$ of the sulfone oligomer used in a thermosetting system. Crosslinked poly(arylene ether sulfone) systems and, bismaleimide resins were studied and higher crosslink densities provided better solvent resistance, as expected.

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