

Synthesis and Characterization of Poly(arylene ether)s Containing Phosphorus, Sulfur and Heterocyclic Pendant Moieties

by

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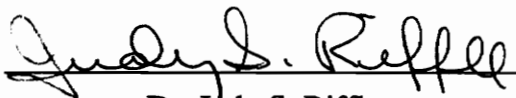
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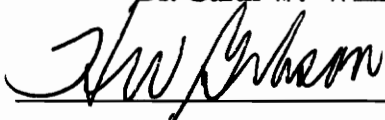
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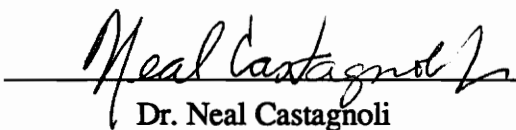
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(Abstract)

Poly(arylene ether)s containing phosphorus, sulfur, and heterocyclic pendant moieties were synthesized and their properties investigated. The preparation of monomers containing phosphorus as well as monomers derived from phenolphthalein were synthesized in high purity. These monomers were then successfully polymerized by a nucleophilic displacement reaction to prepare poly(arylene ether)s of both high and controlled molecular weight. The novel poly(arylene ether)s based on phenolphthalein had glass transition temperatures ranging from 265 to 312 °C. Furthermore, the modulus of these macromolecules was significantly higher than that of typical poly(arylene ether)s (e.g. bisphenol A based systems), probably as a result of enhanced intermolecular forces.

Phenolphthalein in poly(arylene ether)s has been shown not only to improve the thermal and mechanical properties, but also it provides a pendant functional group for chemical modification of the polymer. As a result, a base polymer can be customized to a variety of new materials using derivatization techniques. The possibility of metal complexing in phenolphthalein poly(arylene ether)s was also investigated.

A variety of reactive and non-reactive end-capped poly(arylene ether)s of controlled molecular weight were synthesized for use in reactive toughening modified epoxy and cyanate ester networks and these results are briefly summarized.

Model studies using HPLC were also conducted to determine reaction kinetics in nucleophilic poly(arylene ether) formation. The results demonstrate that potassium carbonate mediated step polymerizations likely proceed with etherification of one of the phenolic groups, prior to difunctional coupling, which can achieve high molecular weight. The formation of cyclooligomers in the step-growth polymerization of poly(arylene ether)s was also studied.

**This dissertation is dedicated
to my loving parents**

**Donna Mae
and
Dr. Duane Bruce Priddy, Sr.**

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Definition of Acronyms

Acronym	Definition
BFPPO	Bis (4-fluorophenyl) phenyl phosphine oxide
BIS A	Bisphenol A (4,4'-Isopropylidinediphenol)
BP	4,4'-Biphenol
BzBP	4-Benzoylbiphenyl
4-CDPS	4-Chlorodiphenylsulfone
DCDPS	4,4'-Dichlorodiphenylsulfone
DDS	4,4'-Diaminodiphenylsulfone
DFB	4,4'-Difluorodiphenylsulfone
DGEBA	Diglycidyl ether of Bisphenol A
DGEPP	Diglycidyl ether of Phenolphthalein
DMAc	N,N-Dimethylacetamide
DMPU	N,N'-Dimethylpropylene Urea
DMSO	Dimethylsulfoxide
DSC	Differential Scanning Calorimetry
FL	9,9-Bis(4-hydroxyphenyl)fluorene
GPC	Gel Permeation Chromatography
η	Intrinsic Viscosity
HMPA	Hexamethylphosphoramide
HPLC	High Performance Liquid Chromatography
HQ	1,4-Hydroquinone
IR	Infrared Spectroscopy

ISTD	Internal Standard
<i>m</i> -AP	<i>meta</i> -Aminophenol
NMP	N-Methylpyrrolidinone
NMR	Nuclear Magnetic Resonance Spectroscopy
<i>p</i> -TSA	<i>para</i> -Toluenesulfonic acid
PA	Phenolphthalein Anilide
PAE	Poly(arylene ether)
PEK	Poly(arylene ether ketone)
PEPO	Poly(arylene ether phosphine oxide)
PES	Poly(arylene ether sulfone)
PI	Phenolphthalimidine
<i>p</i> NPH	<i>para</i> -Nitrophenylhydrazine
PP	Phenolphthalein
PTC	Phase Transfer Catalyst
RB	Round Bottom
S _N AR	Nucleophilic Aromatic Substitution Mechanism
<i>t</i> -BOK	Potassium <i>tert</i> -butoxide
<i>t</i> -Bu	<i>tert</i> -Butyl
TEM	Transmission Electron Microscopy
T _g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
TMS	Tetramethylsilane
UV/vis	Ultraviolet/visible Spectroscopy

1.0 INTRODUCTION

Poly(arylene ether)s are a significant area of the field of engineering thermoplastics. This specific area of macromolecules has been investigated for over thirty years, with much of the pioneering research being done on poly(arylene ether) ketones and sulfones. These materials have excellent thermal, oxidative, and hydrolytic stability. In addition, excellent dimensional stability above 100 °C and below 0 °C allows these materials to be used in many applications including automotive, electrical, aerospace, and toughening resins for carbon fiber composites.

This research focuses on incorporating both phosphorus, sulfur, and phenolphthalein into the poly(arylene ether) backbone. Phenolphthalein and its amide derivatives are excellent bisphenols for the preparation of high T_g poly(arylene ether)s. Due to its unique structure, the pendant heterocyclic lactone on phenolphthalein has a significant contribution to the rigidity of the polymer backbone, as well as interchain cohesive forces. This results in some of the highest thermal and mechanical properties reported for poly(arylene ether)s. The lactone carbonyl also provides a functional group for chemical modification of the polymer. Chemical modification allows, in principle, for one polymer to be converted to many new materials. In addition, the incorporation of phosphorus and sulfur into the backbone was expected to increase thermal properties, while retaining the desirable properties as discussed above.

Section 2.0 will provide an overview of the chemistry and important factors in synthesizing poly(arylene ether)s. This will be followed by an overview of the many different types of poly(arylene ether)s, and a review of phenolphthalein and phosphorus-containing polymers.

The mechanism of poly(arylene ether) formation was investigated. The role of a weak base, K_2CO_3 , versus using a strong base, KOH was studied as well as the kinetics of the reactions. An unexpectedly high yield of cyclooligomers (~17 wt. %) was also observed using the typical polymerization techniques. Phenolphthalein ring-opens to a purple quinone during polycondensation under basic conditions, and the mechanism of this reaction was investigated.

In summary, phenolphthalein appears to offer many advantages as a functional monomer which may be incorporated into the poly(arylene ether) backbone. First, both thermal and mechanical properties were increased significantly as compared to the more typical bisphenol A based materials. Next, the heterocyclic lactone on phenolphthalein provides a unique functional site for chemical modification of the polymer backbone. Due to ring-opening and crosslinking of this lactone at high temperatures, poly(arylene ether)s containing phenolphthalein had higher char yields. Lastly, due to the high electron density of the lactone, there is indication that the phenolphthalein moiety may complex with metals to afford novel polymer-metal hybrids.

2.0 BACKGROUND

2.1 Poly(arylene ether)s

2.1.1 Poly(arylene ether) Synthesis

The preparation of poly(arylene ether)s (Figure 2.1.1.1) can be accomplished by a number of different synthetic strategies. These include nucleophilic substitution,¹⁻⁸ electrophilic substitution,⁹⁻¹² oxidative coupling,¹³⁻²⁰ metal (Pd, Ni, Cu) coupling,²¹⁻⁴³ silyl ether displacement,⁴⁴ ring opening of aryl cyclics,^{45,46} and decarboxylation of polycarbonates.⁴⁷⁻⁴⁹ Each of these synthetic strategies will be discussed briefly with a special emphasis on the nucleophilic aromatic substitution (S_NAR) mechanism as it is the synthetic method utilized in this research.

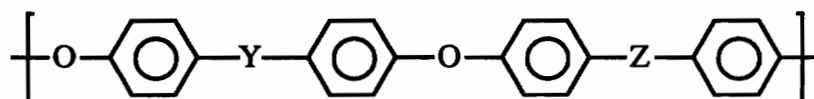


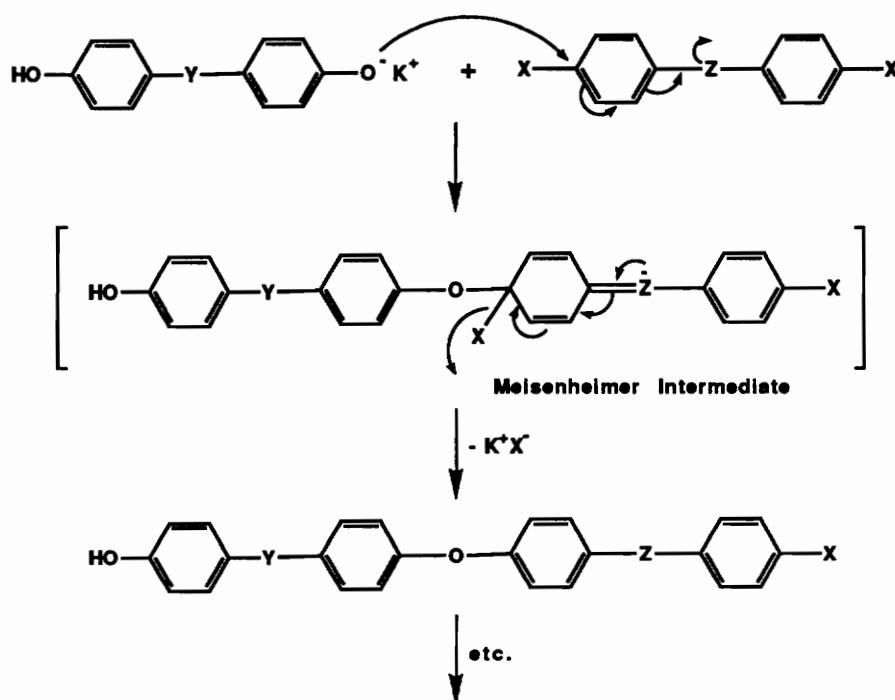
Figure 2.1.1.1 Generic structure of a poly(arylene ether).

2.1.1.1 Nucleophilic Aromatic Substitution (S_NAR)

The nucleophilic route to poly(arylene ether)s was first reported by Farnham and Johnson in 1963.⁵⁰ Nucleophilic substitutions on aromatic electrophiles takes place by four mechanisms: S_N1 , S_NAR , Aryne, and $S_{RN}1$.⁵¹⁻⁵⁶ Metal catalysts can also be used to assist in aromatic nucleophilic substitutions and will be discussed in Section 2.1.1.5.⁵⁴⁻⁵⁶ The reaction mechanism depends on four factors: the aromatic electrophile, the nucleophile, the leaving group, and the reaction conditions.^{3,5,56-58} These factors will be discussed in depth in Section 2.1.2. The halogens are the leaving groups that are most

common. Nucleophiles include a variety of electron rich species including carbanions, fluoride, amines, sulfides, alkoxides, and the focus of this work, phenoxides. It is the purpose of this research to investigate factors involving only one of the mechanisms, the S_NAR .

The S_NAR mechanism takes place in a two-step addition-elimination process. The first step is the attack of the nucleophile which is the rate determining step. This results in the formation of the Meisenheimer complex which lowers the activation energy.^{9,56,57,59-61} As a result, subsequent elimination of the leaving group takes place yielding the substitution product. This Meisenheimer intermediate is a key factor in the polycondensation process of a bisarylhalide with a bisphenol. Scheme 2.1.1.1.1 shows the formation of the Meisenheimer intermediate.



Scheme 2.1.1.1.1 Generalized polycondensation mechanism *via* the S_NAR process involving the Meisenheimer intermediate.

Ether bond formation results from the displacement of halogen by phenoxide as seen in Scheme 2.1.1.1.1. Many bisphenols can be chosen to enhance the rigidity of the polymeric system as will be shown in Section 2.1.3. The activating group Z is usually a sulfone, ketone, or phosphine oxide which are each strongly electron withdrawing. This group plays an essential role in the process as it performs two major functions. By withdrawing electrons from the adjacent aromatic ring, the electron density is lowered on the carbon adjacent to the halogen. Secondly, the activating group stabilizes the anionic Meisenheimer intermediate which further facilitates the reaction with the phenate. Many new activating groups have recently been utilized and will be discussed in Section 2.1.2.^{61,62}

Aryl fluorides are the most reactive in an S_NAR reaction.⁶³ Fluorine is the smallest and most electronegative of the halogens. As a result, the small size enables the phenate to have easy access to the adjacent carbon. Fluorine's strong electronegativity results in the adjacent carbon having a more electrophilic character and thus is more susceptible to nucleophilic attack. As a result, the attack of the nucleophile is the rate determining step.

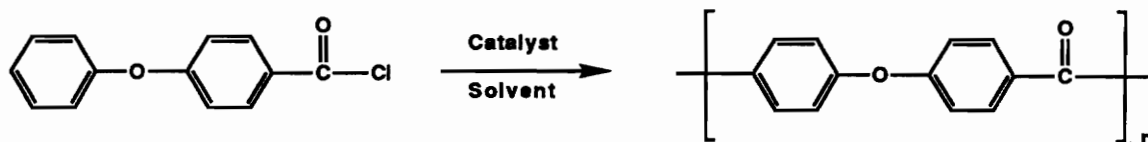
The nucleophilic reaction of an activated dihalide with a phenoxide anion is currently the preferred synthetic method for the preparation of ketone, sulfone, and phosphine oxide containing poly(arylene ether)s. This is due to the resulting polymers being linear with well defined chemical structures. Another advantage is that side reactions are minimal using this process.³⁴

Factors involved in the S_NAR polycondensation mechanism will be discussed in detail in Section 2.1.2 since it is the focus of this research.

2.1.1.2 Electrophilic Polyacylation

In 1962, Bonner became the first to report the synthesis of a completely aromatic poly(arylene ether ketone) (PEK).⁶⁴ This polymer was made by polyacylation of phenyl

ether with a bis-acid chloride under Friedel-Crafts conditions. These initial polymers were of low molecular weight due to the insolubility of the forming polymer in the solvent systems used (e.g. nitrobenzene, methylene chloride). This insolubility was attributed to the crystallinity of the polymers, as well as their high melting points.⁶⁵ In 1969, Marks discovered that liquid HF is an excellent solvent for these polymers, and the BF₃/HF complex results in a catalyst that allows the polymerization of PEK to high molecular weight.⁶⁶ The synthesis of PEK by the electrophilic route is shown in Scheme 2.1.1.2.1.¹⁰

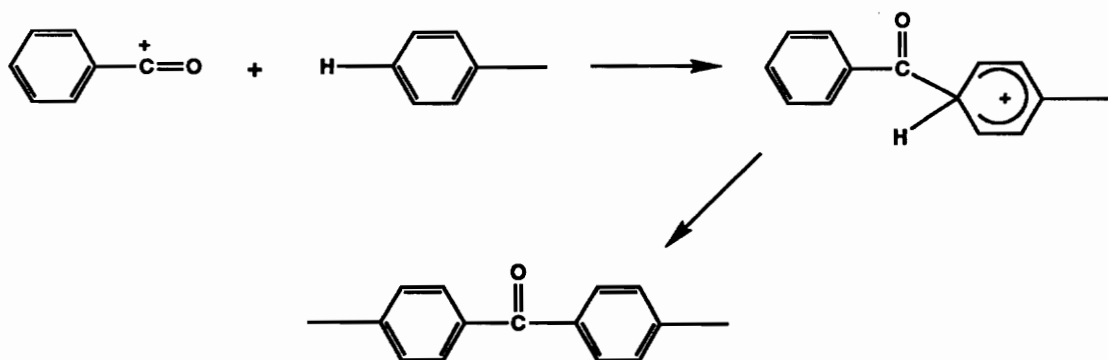


Scheme 2.1.1.2.1 The formation of poly(arylene ether ketone)s by electrophilic polyacylation.¹⁰

Table 2.1.1.2.1 Reaction conditions for the formation of poly(arylene ether ketone)s by electrophilic polyacylation.¹⁰

Solvent	Catalyst	Reference
HF	BF ₃	67
CF ₃ SO ₃ H	CF ₃ SO ₃ H	68
CH ₂ Cl ₂	> 2 mol AlCl ₃ / Lewis Base (e.g. DMF, LiCl, etc..)	69

Rose suggests that the mechanism of this polymerization is by the electrophilic attack of the acylium ion on the reactive phenyl groups as shown in Scheme 2.1.1.2.2.¹⁰

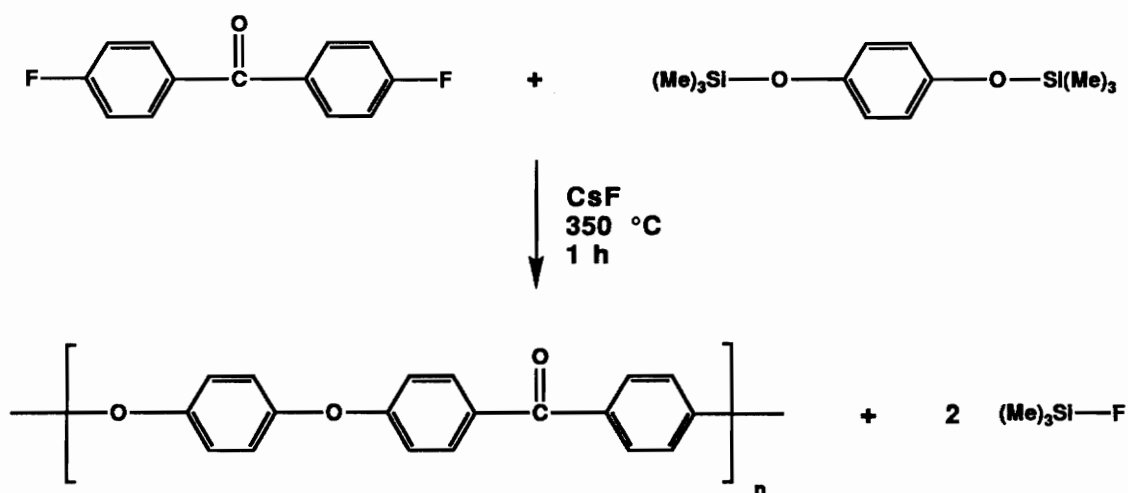


Scheme 2.1.1.2.2 Mechanism for the electrophilic acylation polymerization of PEK.¹⁰

2.1.1.3 Silyl Ether Displacement

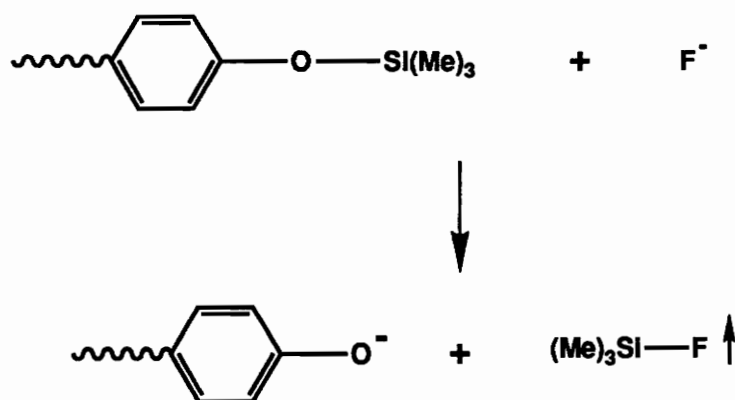
In 1984, Bier and Kricheldorf were the first to use bis-trimethylsilyl derivatives in the preparation of poly(arylene ether)s.⁷⁰ The catalyst that was utilized in this synthesis was cesium fluoride as shown in Scheme 2.1.1.3.1.^{44,70-76}

The silyl ether displacement method has three advantages as compared to the polycondensation of bisphenols in solution (DMAc/K₂CO₃). First, a solvent is not required. Second, the highly volatile fluorotrimethylsilane is the only by-product, therefore separation from inorganic salts is not required. Third, the silyl method does not liberate water under alkaline conditions, therefore it avoids saponification of functional groups, such as ester, imide, or fluoroaromatic groups.⁷⁶



Scheme 2.1.1.3.1 Synthesis of PEK *via* silylated bisphenols.^{10,44,70}

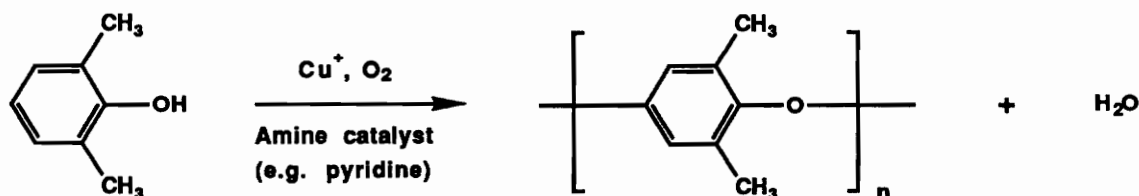
The mechanism of the interaction of CsF with the silylated bisphenol is a two step mechanism: 1) the CsF dissociates to generate F^- , which subsequently couples with $\text{Si}(\text{Me})_3$ to form trimethylsilyl fluoride and phenate; then 2) the phenate undergoes nucleophilic aromatic substitution on the activated halide to form polymer.^{76,77}



Scheme 2.1.1.3.2 Mechanism of silyl ether displacement with CsF.^{76,77}

2.1.1.4 Oxidative Coupling

In 1959, Hay *et al.* reported the synthesis of poly(phenylene ether)s *via* oxidative coupling.¹³ The polymerization was achieved by passing oxygen through a solution of 2,6-dimethylphenol in an organic solvent containing an amine and copper (I) as catalyst. This synthesis is shown in Scheme 2.1.1.4.1.¹³⁻²⁰



Scheme 2.1.1.4.1 Polymerization of poly(phenylene ether) by oxidative coupling.¹³⁻²⁰

2.1.1.5 Metal Coupling

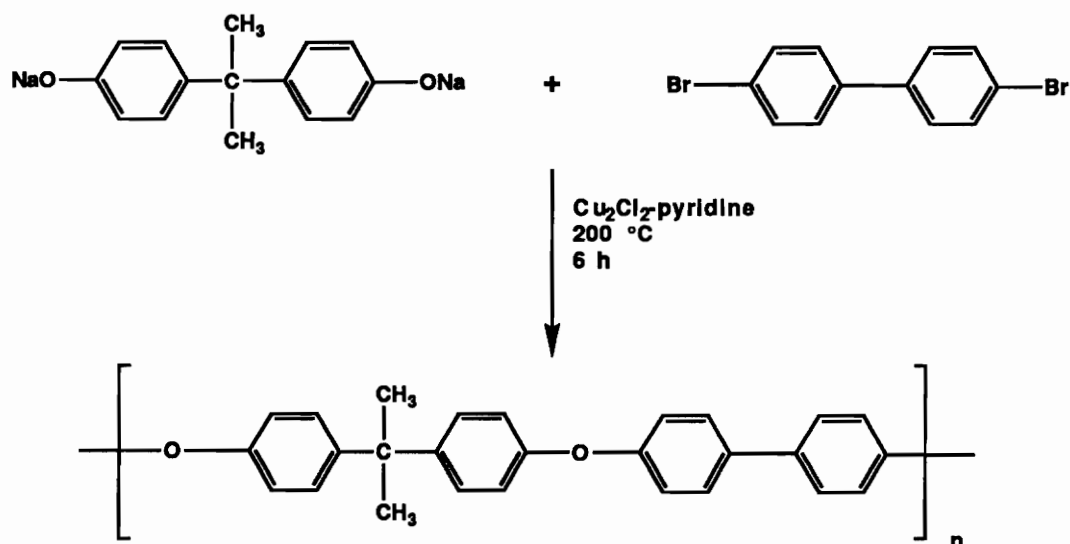
The synthesis of polymers using a transition metal in a catalyzed cross-coupling reaction is of growing interest.^{29-31,33-43} Cross-coupling reactions allow the formation of sp²-sp², sp-sp², and sp²-sp³ carbon-carbon bonds under mild conditions with excellent functional group tolerance.³⁹⁻⁴³ Metal coupling synthetic processes for the formation of poly(arylene ether)s can form novel structures which cannot be obtained by other known methods. Another advantage is that this route may provide a more economical alternative.³⁴ Three metal catalyzed systems (Cu, Ni, Pd) have been investigated and each will be discussed briefly.

2.1.1.5.1 Ullmann Reaction (Cu)

Ullmann was the first to show that copper powder could be used as a catalyst for making aromatic ethers.²¹ It has been shown that the cuprous ion is the active catalyst and not Cu⁰ or Cu⁺⁺.^{22,23} A study of the mechanism of the Ullmann reaction revealed that the

active species is Cu^+ which coordinates with the π system of the aromatic halide, resulting in cleavage of the carbon halogen bond.^{24,25}

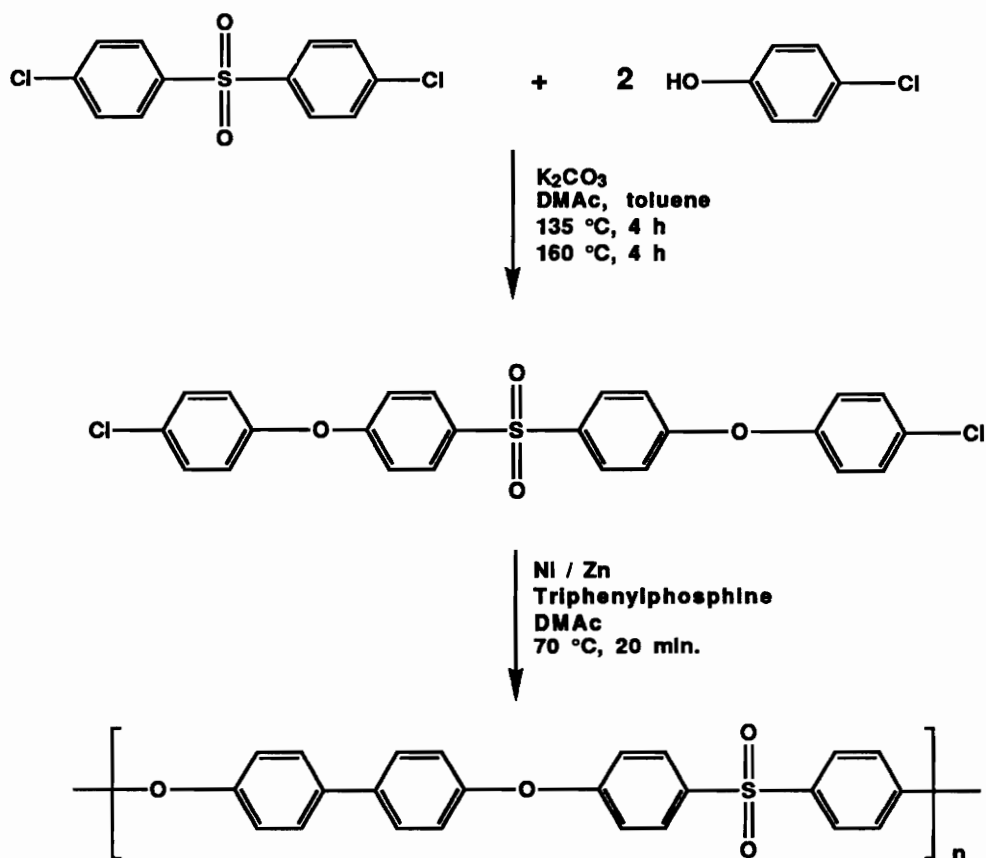
Nucleophilic aromatic substitution of non-activated aryl halides can be accomplished using the Ullmann reaction. The major difference between this process and that discussed previously in Section 2.1.1.1 is the ease of halide replacement: $\text{I}, \text{Br} > \text{Cl} \gg \text{F}$.²⁶ This is the reverse order observed for the activated dihalide for a polyether forming reaction. The Ullmann reaction requires high temperatures (e.g. 180-230 °C). The only criteria for the solvent are that it is inert and keep the resulting polymer in solution. In contrast, the activated dihalide reactions discussed in Section 2.1.1.1 require a polar aprotic solvent (e.g. DMAc, DMSO, etc.) The general reaction conditions that are necessary for an Ullman type polymerization are shown in Scheme 2.1.1.5.1.^{26,28}



Scheme 2.1.1.5.1 Synthesis of poly(arylene ether)s *via* the Ullmann condensation reaction.^{26,28}

2.1.1.5.2 Nickel Coupling (Ni)

Polymerizations that involve the formation of aromatic carbon-carbon bonds are of high interest. One synthetic method to accomplish this type of bond formation is nickel coupling.^{29,30,33,34} This synthetic process is shown in Scheme 2.1.1.5.2.1.



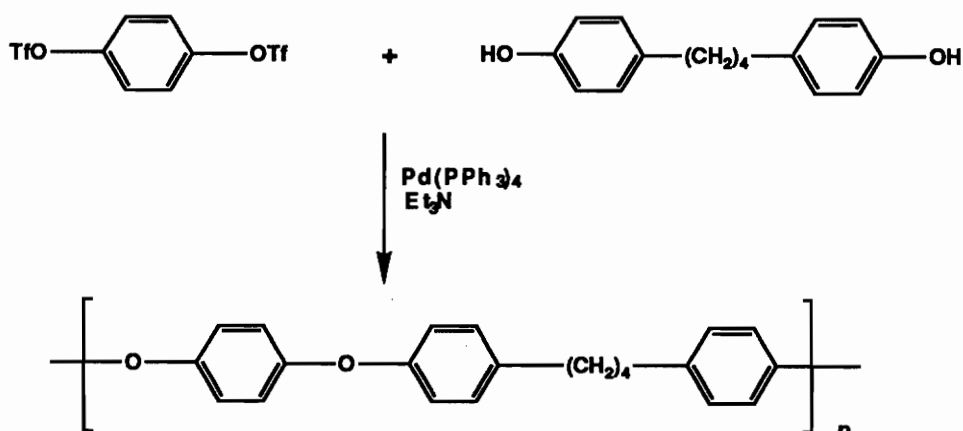
Scheme 2.1.1.5.2.1 Synthesis of poly(arylene ether)s *via* nickel coupling.^{31,34}

The nickel-catalyzed homocoupling of aryl halides is of significant interest because the reaction proceeds under very mild conditions as compared to classical Ullmann conditions. Another benefit is that functional groups such as aldehydes, ketones or esters do not interfere with the coupling process.³⁴ Conditions have been determined in which

high molecular weight polymers have been prepared by this process using excess zinc with the nickel.³¹

2.1.1.5.3 Palladium Coupling (Pd)

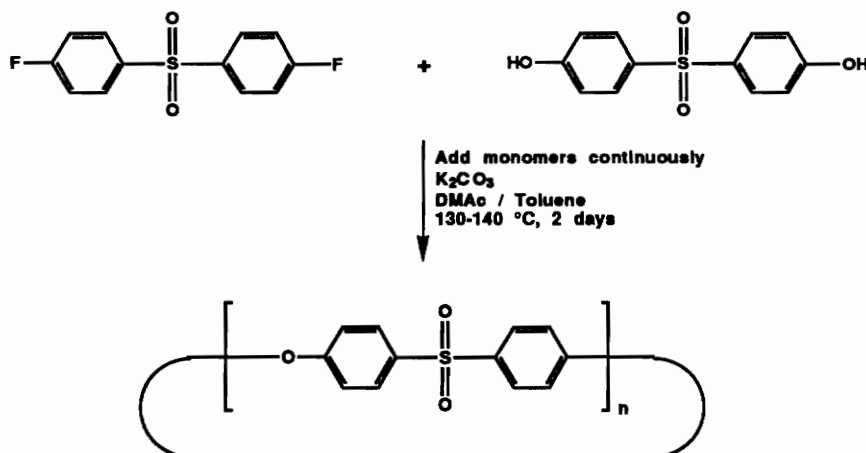
Reactions involving palladium (0) are cataloged according to the metal involved in the transmetalation to palladium. These cross-coupling reactions include organostannanes,³⁸ organoborane,³⁶ organozinc,³⁵ and organomagnesium,³⁷ but will not be discussed due to the scope of this work. Palladium (0) can be used to catalyze a polycondensation of a bistriflate and a bisphenol. Scheme 2.1.1.5.3.1 gives an example of how poly(arylene ether)s are made with this synthetic method.⁴³



Scheme 2.1.1.5.3.1 Synthesis of poly(arylene ether)s with a palladium (0) cross-coupling reaction.⁴³

2.1.1.6 Ring-Opening of Aryl Cyclics

Thermoplastic resins have been used as tougheners in composite materials. A major limitation in using thermoplastics is their high melt viscosity compared to the thermosetting resin that it is blended with. To solve this problem, ring-opening polymerization can be used. With this chemistry, low molecular weight, low viscosity precursors can be ring-opened to form high molecular weight polymers. This synthetic process has also been used to form poly(carbonate)s,⁷⁸ poly(arylene ether ketone)s,⁴⁵ and poly(arylene ether sulfone)s.^{46,79,80} An example of the chemistry utilized for the synthesis of aryl ether sulfone cyclooligomers is shown in Scheme 2.1.1.6.1.^{46,80}



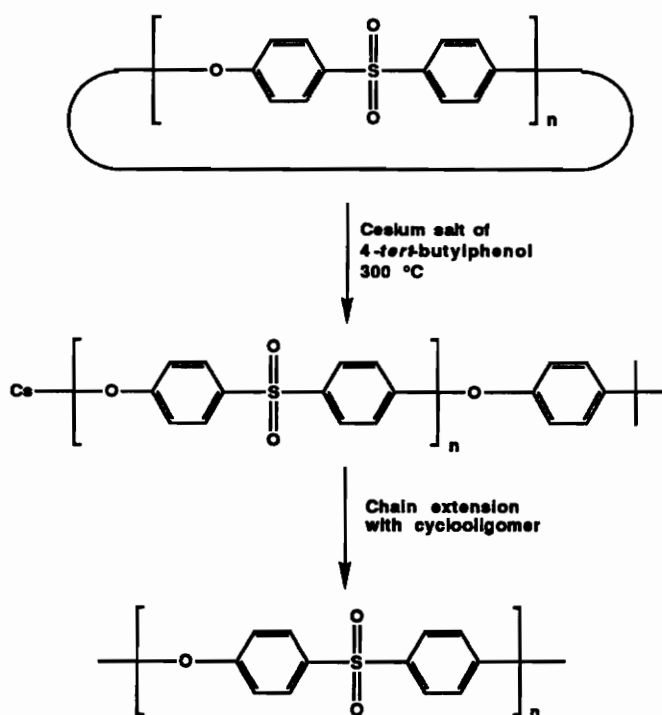
Scheme 2.1.1.6.1 Synthesis of arylene ether sulfone cyclooligomers.^{46,80}

The cyclooligomers shown in Scheme 2.1.1.6.1 have been determined by HPLC to be a mixture of even and odd numbered cyclooligomers with n being 3 - 12.⁴⁶ The cyclic tetramer is the predominant product. Individual cyclooligomers have extremely high melting points (~ 450 °C), but the mixture is amorphous and begins to flow at ~ 230 °C.^{46,80}

Many factors are crucial in the reaction conditions used to make cyclooligomers instead of linear polymer: 1) extremely low concentrations of reactive species in solution

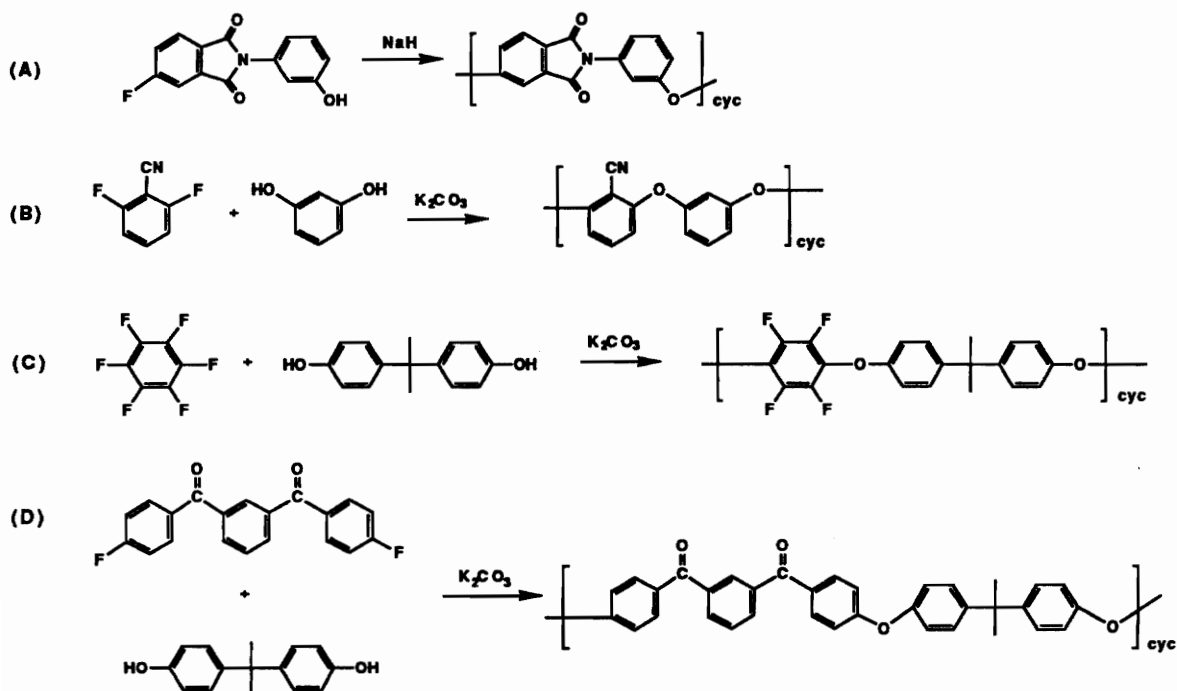
(can be accomplished by slow addition); 2) correct stoichiometry (1:1); 3) conditions in which the reaction is as fast as possible (high temperatures, fluoride leaving group, strong base); and 4) monomers that have flexible units (e.g. ether links) favor cyclo-formation.⁴⁶

To polymerize the cyclooligomers, catalysts such as the cesium salt of 4-*tert*-butylphenol can reversibly cleave the carbon-oxygen bonds in the melt. The inherent viscosities reported in DMAc at 25 °C are 0.06 dL/g for the cyclooligomers and 0.50 dL/g for the resulting linear polymer.⁴⁶ This ring-opening polymerization is shown in Scheme 2.1.1.6.2.⁸⁰



Scheme 2.1.1.6.2 Synthesis of poly(arylene ether sulfone)s *via* ring-opening of cyclooligomers.⁸⁰

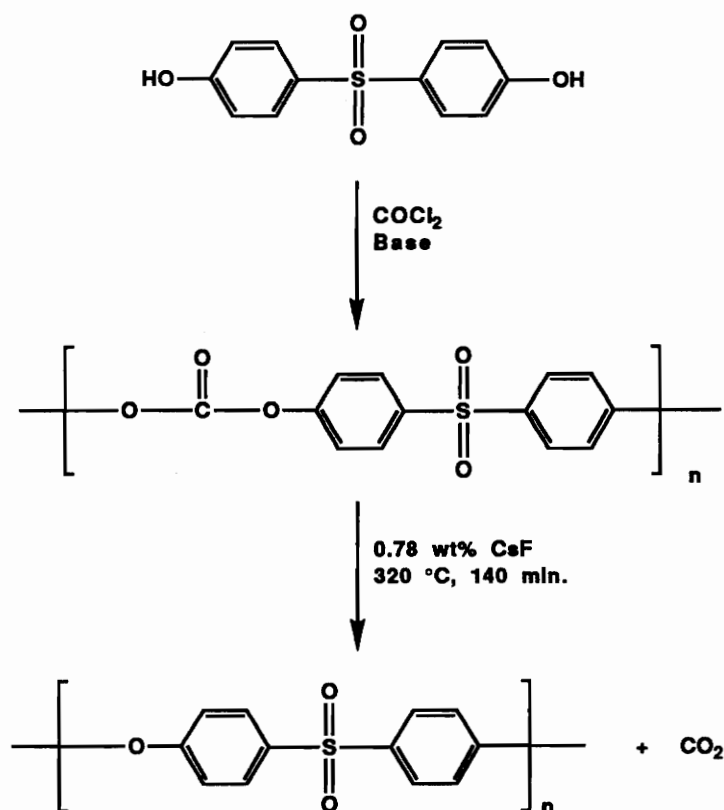
Other cyclooligomeric systems have been investigated recently by Mullins *et al.* in hopes of finding cyclooligomers that could be ring-opened polymers for composite applications.⁸⁰ These new advances are shown in Scheme 2.1.1.6.3.



Scheme 2.1.1.6.3 Other examples of poly(arylene ether)s made *via* ring-opening of cyclooligomers.⁸⁰

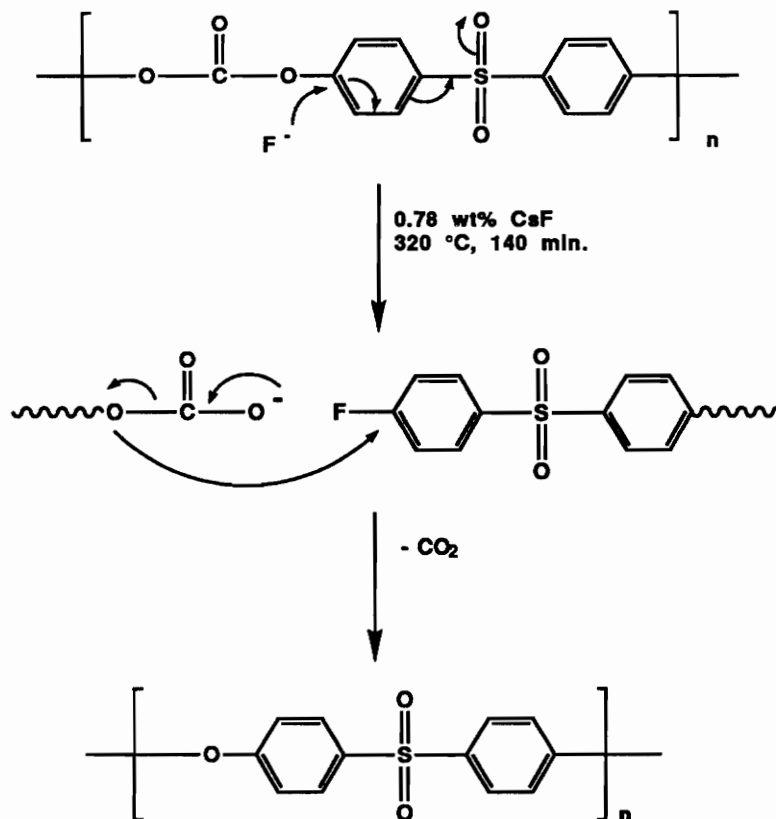
2.1.1.7 Decarboxylation of Polycarbonates

Poly(arylene ether)s can be synthesized by decarboxylation of polycarbonates. Industrially, this method is of interest due to inexpensive raw materials and ease of product isolation as compared to other methods. This decarboxylation route to poly(arylene ether sulfone)s is shown in Scheme 2.1.1.7.1.⁴⁷⁻⁴⁹



Scheme 2.1.1.7.1 Synthesis of poly(arylene ether sulfone)s *via* decarboxylation of poly(sulfone carbonate).⁴⁷⁻⁴⁹

This novel procedure involves a series of reactions: 1) the cleavage of a carbonate group by the catalyst, 2) the decarboxylation of the resulting carboxylate anion to form the phenolate, and 3) the recombination of the reactive ends. The resulting poly(arylene ether)s from this process suffers no overall molecular weight degradation, even though the chain is broken at each carbonate link.⁴⁸ The mechanistic aspects of this process are shown in Scheme 2.1.1.7.2.



Scheme 2.1.1.7.2 Mechanism of decarboxylation to form poly(arylene ether sulfone) from poly(sulfone carbonate).

2.1.2 Factors Influencing Poly(arylene ether) formation by S_NAR

2.1.2.1 Solvent

Nucleophilic aromatic substitution (S_NAR) has already been discussed in Section 2.1.1.1. Since this research involved making poly(arylene ether)s by the S_NAR reaction mechanism, it is the purpose of this section to give a brief overview as to the effect that solvent has on the polycondensation process.

One of the most important criteria for a S_NAR reaction to occur is the choice of solvent.⁸¹ The requirements for the solvent are that it must not react with the monomers or base, and it must keep the reagents and resulting polymer in solution. The most important criteria for a solvent is its dissociating power on the nucleophile. This dissociating power is directly proportional to the rate of reaction, since the attack of the nucleophile is the rate determining step. Miller has reported that the increased rate of the S_NAR reaction is, in part, due to good cation solvation, resulting in a more nucleophilic phenoxide anion.⁸²

The solvents that are preferred are the dipolar aprotic solvents. Typical solvents in this category include dimethylsulfoxide (DMSO), *N,N*-dimethylacetamide (DMAc), *N*-methylpyrrolidone (NMP), and *N,N*-dimethylformamide (DMF) as shown in Figure 2.1.2.1.1. Hexamethylphosphoramide (HMPA) is also a good solvent, but is not too common now due to its carcinogenic nature. These solvents solvate cations easily, thus dissociating the phenolate salts resulting in faster nucleophilic reactions. The most widely used solvent has been DMSO. Negative aspects in using this solvent include degradation at high temperatures and removal of solvent from product.

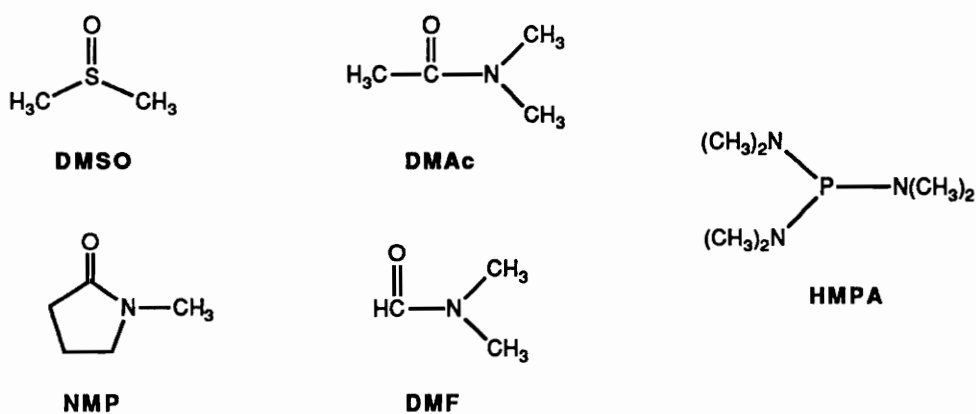


Figure 2.1.2.1.1 Examples of dipolar aprotic solvents used in the S_NAR synthesis of poly(arylene ether)s.

Recent studies to determine a stronger solvating dipolar aprotic solvent have been conducted by Labadie *et al.*⁸³ They found that the cyclic urea, N,N'-dimethylpropylene urea (DMPU) (Figure 2.1.2.1.2) has given higher molecular weights under less stringent conditions as compared to the more common solvents (Figure 2.1.2.1.1).

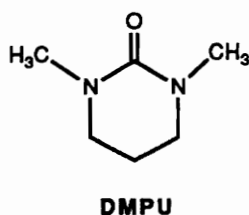


Figure 2.1.2.1.2 Structure of N,N'-dimethylpropylene urea (DMPU).

The advantages of this solvent are higher reaction rates and better polymer solubility, while not being as much of a health hazard as NMP, DMAc and HMPA. This solvent performed exceptionally well in polymerizations in which a less reactive heterocyclic-activated monomer was used, and in systems where the resulting polymer was marginally soluble in NMP or DMAc.⁸³

2.1.2.2 Effect of Water

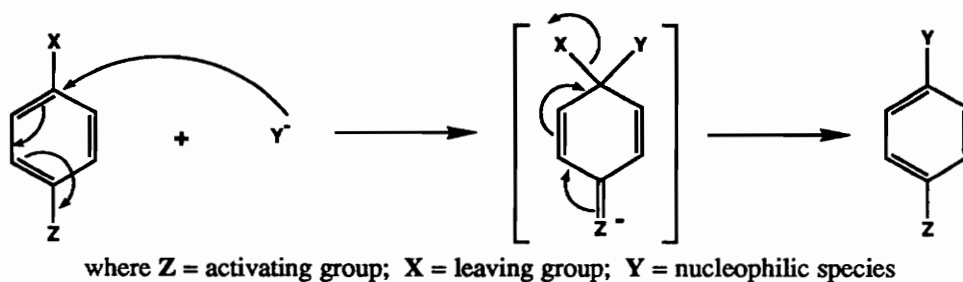
The most deleterious impurity to the S_NAR reaction is the presence of water.¹ Water can act as a nucleophile in the presence of base to hydrolyze the activated dihalide. As a result, the solvents must be carefully purified to remove water and any other impurities that may interfere with the S_NAR process.

A study by Gerbi *et al.* have suggested that the polymerization rate is sensitive to small amounts of water, and that water has a dual effect; both enhancement and retardation of polymerization.⁸⁴ The study was on the solid-liquid phase transfer catalyzed (PTC) polycondensation of hexafluorobenzene with bisphenol-A. Anhydrous K₂CO₃ was used

as the solid base and 18-crown-6 as the PTC. It was suggested that small amounts of water may act to enhance polymerization through solvation of the crown-complexed ion pair, thereby increasing its concentration in the liquid phase. Another explanation was that water may act to create a local liquid-liquid interface at the carbonate surface, thus facilitating ionization and crown complexation of the nucleophile resulting in accelerated polymerization. At higher water levels, the polymerization was retarded, most likely due to extensive solvation of the reactive nucleophile by an otherwise aprotic medium.⁸⁴ There is work that suggests that a PTC polycondensation does not go through traditional nucleophilic aromatic substitution by anionic attack, but possibly through an electron transfer reaction preceded by a charge transfer interaction.⁸⁵

2.1.2.3 Activating Group

The activating group is very important to the S_NAR process, because it is this group that determines whether a molecule will be activated towards nucleophilic aromatic substitution. Two factors are important to assess if a group fits this criteria: 1) if the potential activating group has high electron affinity, and 2) if an intermediate transition state can be formed whereby the negative charge is delocalized (stabilized) by resonance effects (e.g. Meisenheimer intermediate). The S_NAR mechanism is shown in Scheme 2.1.2.3.1.



Scheme 2.1.2.3.1 The S_NAR mechanism.

The approximate order of electron withdrawing power of some common substituents was found to be: $\text{NO} > \text{NO}_2 > \text{SO}_2\text{Me} > \text{CF}_3 > \text{CN} > \text{CHO} > \text{COR} > \text{COOH} > \text{Br} > \text{Cl} > \text{I} > \text{H} > \text{F} > \text{CMe}_3 > \text{Me} > \text{OMe} > \text{NMe}_2 > \text{OH} > \text{NH}_2$.^{53,86-88} This trend favors the groups which have the greatest electron affinity (nitro, sulfone, ketone), followed by the least reactive moieties which are electron donating (hydroxy, amine).

Advances to determine new activating groups for the polycondensation reaction have been made.^{5,56-58,61,62,88-91} The polymers made from these new groups are shown in Section 2.1.3.

2.1.2.4 Leaving Group

The leaving group is also a very important parameter to the $\text{S}_{\text{N}}\text{AR}$ reaction.^{3,5,56-58,92} The order of some common leaving groups is as follows: $\text{F} > \text{Cl} > \text{Br} \sim \text{I} > \text{OAr}$, OR , SR .^{53,63,92,93} This order is reversed from that seen for $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ due to completely different operating mechanisms. Two factors are important for a good leaving group: 1) the ability to stabilize the anionic charge formed in the Meisenheimer intermediate, and 2) ability to place a strong partial negative charge on the *ipso* carbon to which it is attached. Since the rate determining step is the attack of the nucleophile, these two factors contribute to the speed of nucleophilic attack.

Since aryl-fluorides are the most reactive of the aryl halides, studies have been made to evaluate fluorine containing monomers as possible candidates for nucleophilic displacement. This technique was studied by Carter with the use of ^{19}F NMR.⁹⁴ When an electron withdrawing group is attached to a phenyl ring, a partial positive charge results on the *ortho* and *para* positions through resonance interactions. Since NMR chemical shifts are sensitive to electron density at the particular nuclei of interest, this technique can be used to evaluate this electron density. ^{19}F NMR evaluation of nine fluorinated compounds was done and the chemical shift variation was 9 ppm. Carter determined that if an aryl-

fluoride had a ^{19}F chemical shift of -112 ppm (fluorobenzene) or less, they would be nonpolymerizable in standard dipolar aprotic solvents (NMP, DMAc, etc.).⁹⁴ However, when these "nonpolymerizable" monomers were reacted in the solvent DMPU at higher reaction temperatures, high molecular weight polymer was obtained. Use of this DMPU solvent was explained previously in Section 2.1.2.1.⁸³

2.1.2.5 Nucleophile

The reactivity of the nucleophile is another important parameter influencing the $\text{S}_{\text{N}}\text{AR}$ mechanism. Nucleophilicity often parallels basicity, although many exceptions exist. An approximate order of nucleophile strength as described by Bunnett and Zahler is: $\text{ArS}^- > \text{RO}^- > \text{R}_2\text{NH}^- > \text{ArO}^- > \text{HO}^- > \text{ArNH}_2 > \text{NH}_3 > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{H}_2\text{O} > \text{ROH}$.⁶³ The thiophenoxide anion is the most nucleophilic, most likely due to its highly polarizable nature. This research involves the use of the phenoxide anion which is second in reactivity.

Many factors influence the nucleophilicity of the phenoxide anion: 1) the solvation of the ion pair, 2) concentration of the phenoxide in solution, 3) the site of nucleophilic attack (amount of partial positive charge, steric availability), and 4) the alkali metal counterion. Lovering *et al.* have determined the order of reactivity of the alkali metal salts of phenolate ion to be $\text{Cs} > \text{K} > \text{Na}$.⁹⁵

2.1.2.6 Base

The base used to form the phenolate anion is an interesting parameter in the $\text{S}_{\text{N}}\text{AR}$ reaction and has been reviewed extensively in Section 4.2. In the early days of poly(arylene ether) synthesis by the $\text{S}_{\text{N}}\text{AR}$ route, sodium hydroxide (NaOH) was the common base utilized to form the bisphenate.^{1-3,26,50,96-103} Since then, McGrath *et al.*

was one of the first to suggest that potassium carbonate is a much better base for a variety of reasons.^{104,105} These reasons will be discussed in depth in Section 4.2.

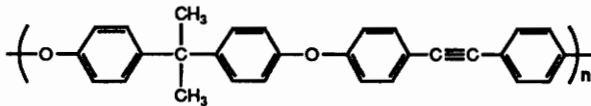
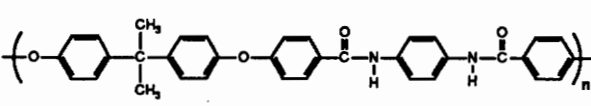
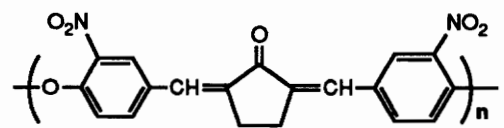
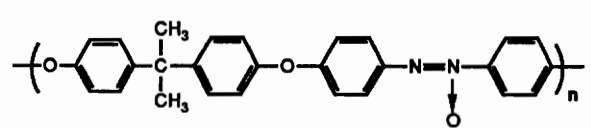
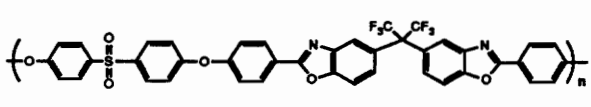
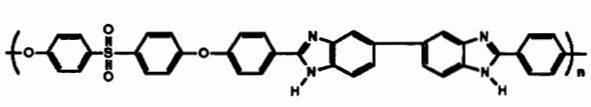
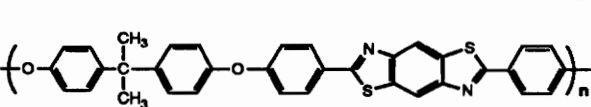
2.1.2.7 Temperature and Time

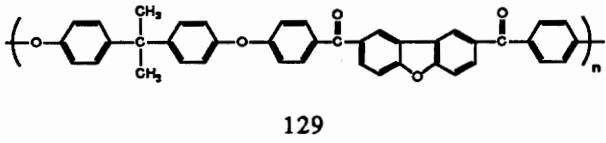
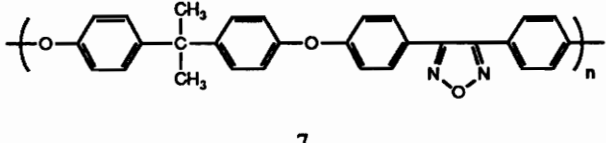
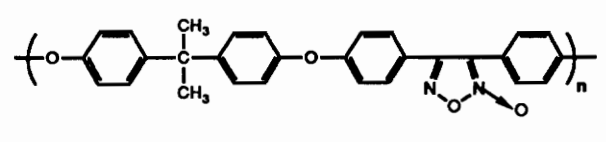
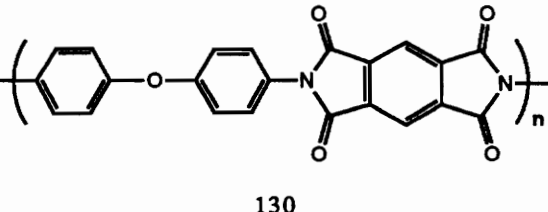
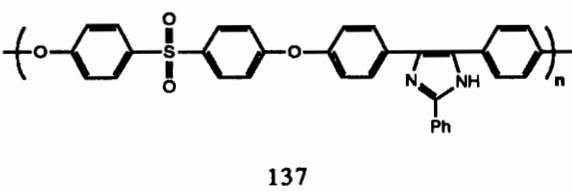
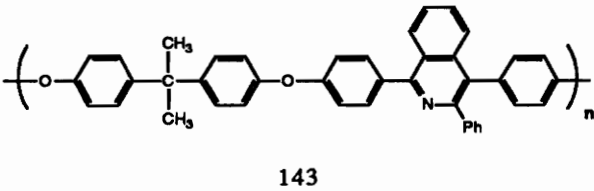
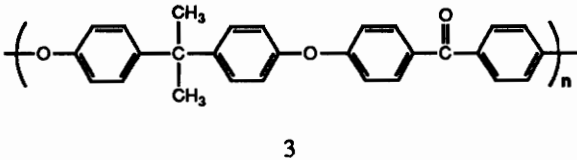
The temperature and time variables are typically dependent on all the preceding factors. In general, with highly reactive nucleophiles and/or activated dihalides, lower temperatures and times are necessary. The reverse is true for poorer nucleophiles and leaving groups.

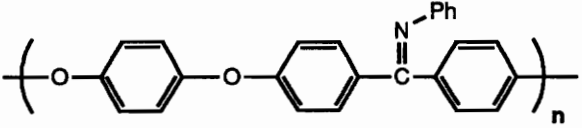
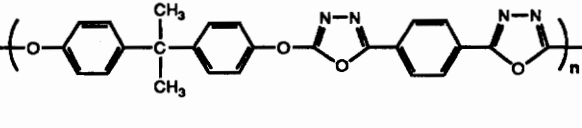
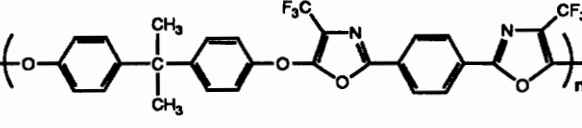
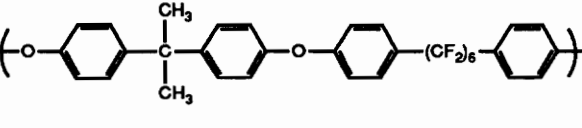
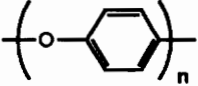
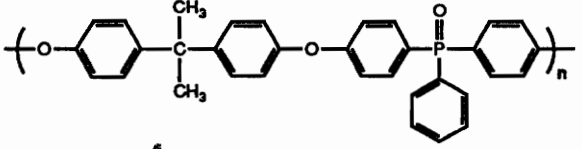
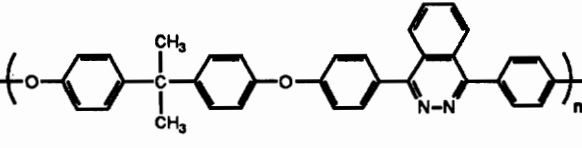
2.1.3 Survey of Poly(arylene ether) Literature

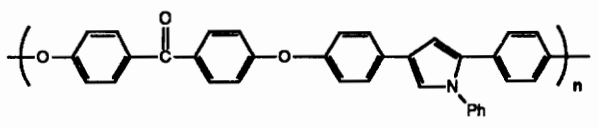
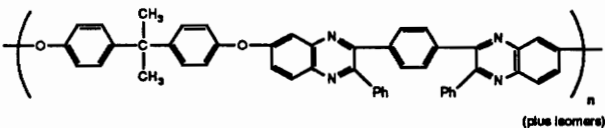
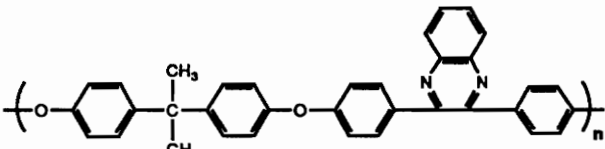
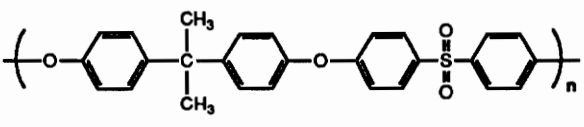
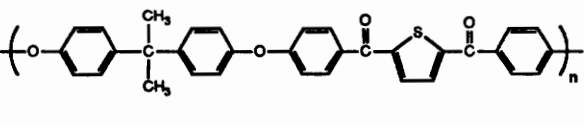
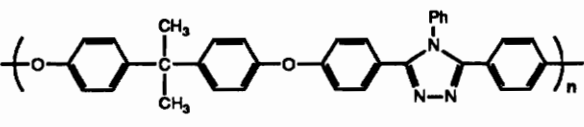
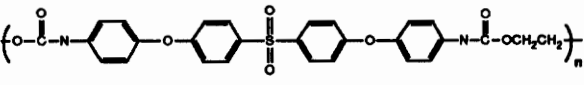
Poly(arylene ether)s generally have excellent thermal properties resulting in high glass transition (T_g) temperatures or high melting points (T_m). Poly(arylene ether)s are tough and ductile which lends to excellent mechanical properties. Lastly, the ether linkages result in excellent hydrolytic stability as compared to amide or ester linkages. There are many different classes of poly(arylene ether)s. A representation of some backbone units incorporated into poly(arylene ether)s and their T_g values are shown in Table 2.1.3.1.

Table 2.1.3.1 Examples of backbone units in poly(arylene ether)s. (NR = not reported)

Name	Specific Example (reference)	T _g (°C)	General References
Acetylene	 <p style="text-align: center;">106</p>	163	106-108
Amide	 <p style="text-align: center;">89</p>	230	89,109,110
Arylidene	 <p style="text-align: center;">111</p>	NR	111,112
Azoxy	 <p style="text-align: center;">8</p>	182	8,113
Benzoxazole	 <p style="text-align: center;">114</p>	275	61,114-123
Benzimidazole	 <p style="text-align: center;">124</p>	352	124-127
Benzothiazole	 <p style="text-align: center;">128</p>	248	128

Dibenzofuran	 <p style="text-align: center;">129</p>	205	129
Furazan	 <p style="text-align: center;">7</p>	NR	7,8
Furoxan	 <p style="text-align: center;">7</p>	NR	7,8
Imide	 <p style="text-align: center;">130</p>	not seen with DSC	115,116,118- 120,130-136
Imidazole	 <p style="text-align: center;">137</p>	277	120,137-142
Isoquinoline	 <p style="text-align: center;">143</p>	226	143
Ketone	 <p style="text-align: center;">3</p>	155	2,9-12,44,45, 48,51,52,95, 129,144-181

Ketimine	 <p style="text-align: center;">182</p>	165	182-187
Oxadiazole	 <p style="text-align: center;">188</p>	201	91,120,130, 188-192
Oxazole	 <p style="text-align: center;">193</p>	151	62,193
Perfluoro-alkylene	 <p style="text-align: center;">194</p>	93	61,62,194-196
Phenylene oxide	 <p style="text-align: center;">197</p>	82	13-20
Phosphine oxide	 <p style="text-align: center;">198</p>	198	168,198-221
Phthalazine	 <p style="text-align: center;">222</p>	235	222

Pyrazole	 <p style="text-align: center;">223</p>	206	120,223,224
Quinoxaline	 <p style="text-align: center;">225 (plus isomers)</p>  <p style="text-align: center;">90</p>	255 195	61,62,90,120, 134,135,225- 240
Sulfone	 <p style="text-align: center;">3</p>	195	1-3,5,26,27, 34,45,48,60, 77,79,84,96, 97,100,103- 105, 112, 129,132, 148- 150,160, 161,163,164, 167,173-177, 200,241-322
Thiophene	 <p style="text-align: center;">323</p>	158	323-325
Triazole	 <p style="text-align: center;">326</p>	185	120,131,189, 190,326,327
Urethane	 <p style="text-align: center;">278</p>	NR	278

This research focuses on the phosphine oxide and sulfone containing poly(arylene ether)s. Due to the scope of this review, much of what has been done with PAE's will not be discussed, but will be cited as follows.

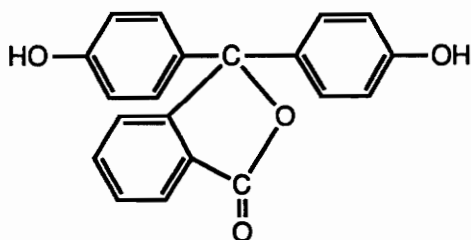
Poly(arylene ether)s have been used in copolymers,^{8,47,48,79,112,115-119,128,130-136,143,152,154,163,168-170,177,178,184,186,194,222,241,249,251,256-260,263,267-269,283,286,287,290-294,300,302,306-309,317-319,328-343} blends,^{168,172,243,264,309,317,344} and inorganic glass hybrids (ceramers).^{166,175,204,205,316}

Many functionalities have been incorporated into the poly(arylene ether)s resulting in systems that are fluorinated,^{329,345,346} sulfonated,^{261,284,285,332,335,347} nitriles,³⁴⁸ nitrated,³³³ and deuterated.^{262,270,274} Functionalities for curing of poly(arylene ether)s have been attached either as chain ends or pendant on the polymer backbone. These functionalities include acetylene,^{27,106-108,237,297,328,344,349-354} phenyl ethynyl,³⁵⁵ carboxylic acid,^{163,258} maleimide,^{154-156,162,280,286,298,312,330,356-360} and amine.^{145,149,150,154,155,160,185,200,252,254,266,271,287,288,298,304,305,322,333,357,358,360}

The physical characterization that has been carried out on PAE's includes mechanical properties,^{103,156,159,216,241,245,247-249,255,272,353} thermal properties,^{26,96,100,103,155,192,202,215,216,242,245,249,295,296} molecular weight distribution,^{159,250,321,361} NMR,^{90,91,107,108,116,143,170,193,222,253,260,262,270,274,275,280,282,284,285,326,331,332,347,349,362} dynamic mechanical analysis,^{26,262,289} gas permeability,^{261,289,299,347} radiation resistance,^{8,151,272,277,294,298,313,334} oxygen plasma resistance,^{202,203,206,216} refractive index,^{175,204,205,276,316} spectrophotometric analysis,³¹⁰ and potentiometric titration.³²⁰

2.2 Phenolphthalein in Polymers

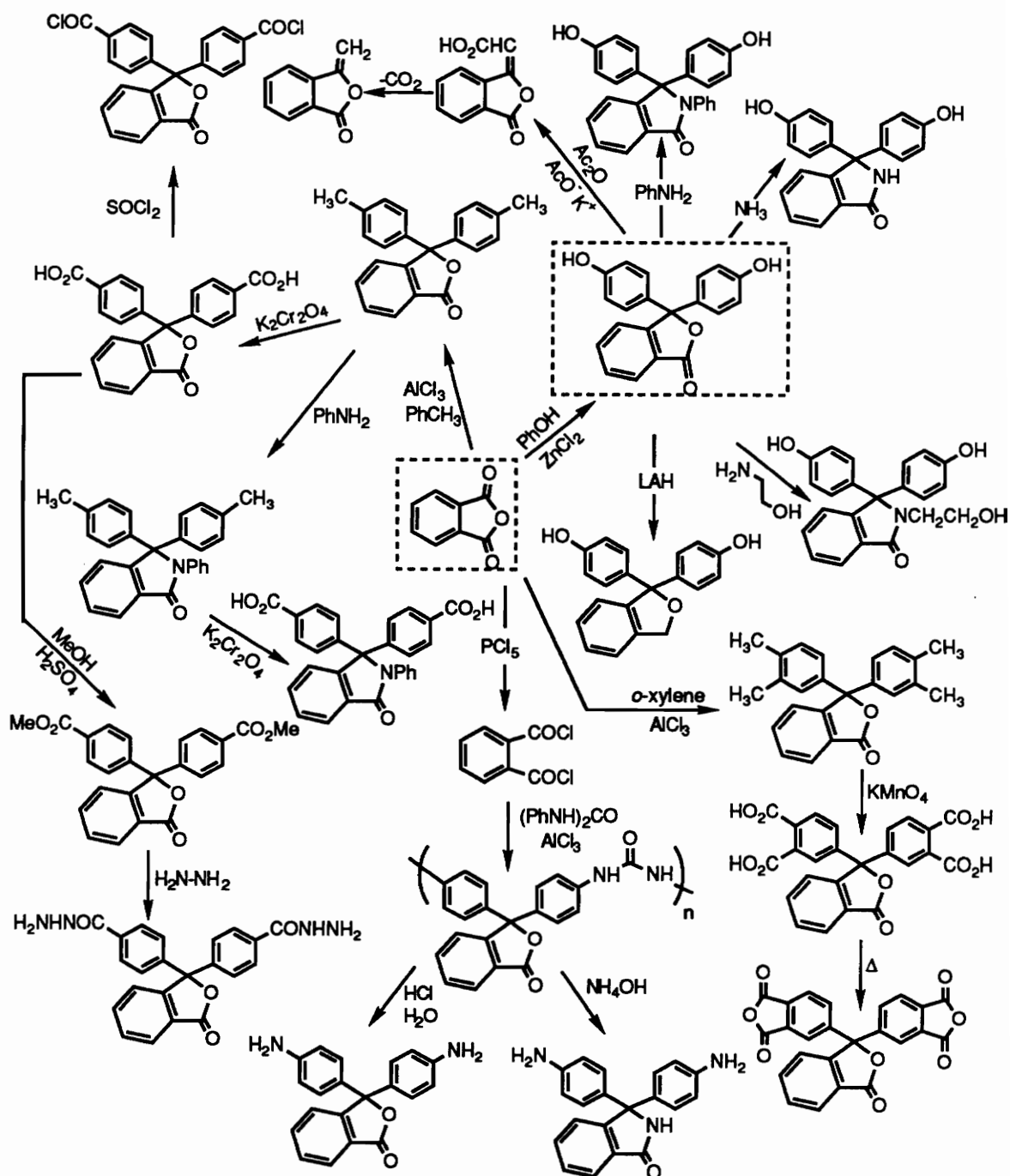
2.2.1 Chemistry of Phenolphthalein



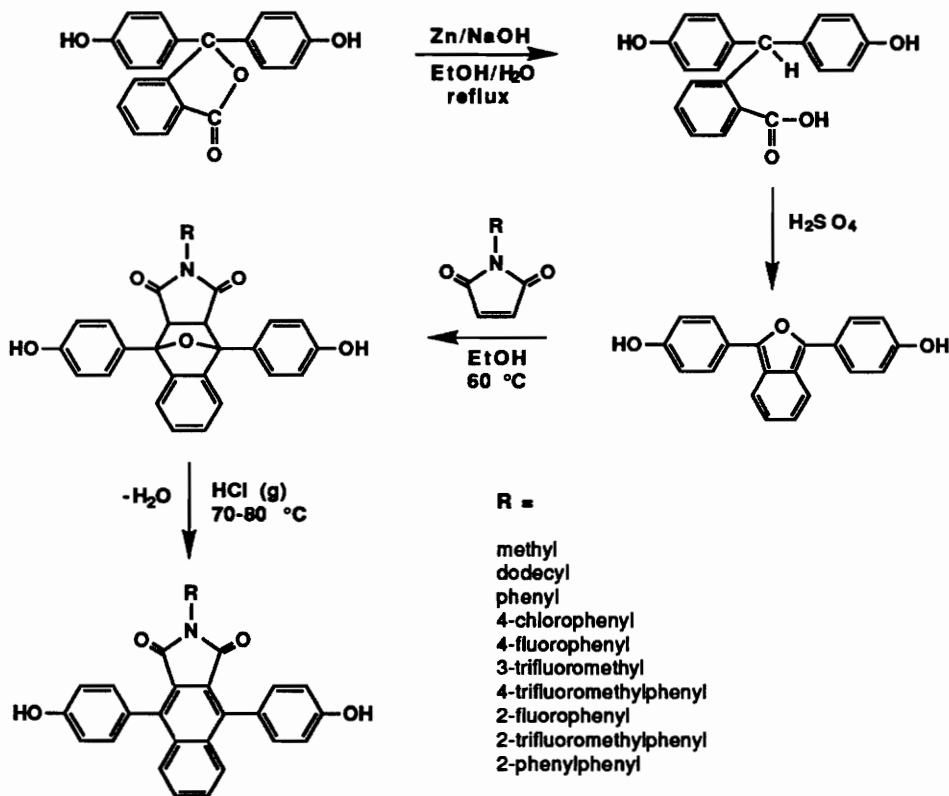
Phenolphthalein is made by condensing phthalic anhydride and phenol in the presence of a dehydrating agent.³⁶³ It is used primarily as a pH indicator and as a cathartic drug in laxatives (e.g. EX-LAX[®] and Feen-a-mint[®]).³⁶⁴ As a result, much of its utility as a rigid heterocyclic bisphenol has been overlooked. Phenolphthalein is apparently not manufactured anywhere in the United States. Production plants are said to exist in India, Africa, Japan, China, Korea, and Pakistan. World production of phenolphthalein is estimated at 0.5 million pounds a year.³⁶³

Phenolphthalein is a bisphenol that contains a heterocyclic pendant lactone. As a result, this monomer can be a versatile intermediate to a series of other derivatives. Scheme 2.2.1.1 shows the versatility of phenolphthalein.³⁶⁵

More recently, Strukelj and Hay have utilized phenolphthalein as a starting material to synthesize a novel bisphenol containing an imide functionality as shown in Scheme 2.2.1.2.³⁶⁶⁻³⁶⁸ The corresponding polyarylene ether ketones and sulfones were synthesized resulting in Tg values of 275 °C and 310 °C, respectively, when R = phenyl. The TGA (-10%) were given as 552 °C and 556 °C, respectively.³⁶⁶⁻³⁶⁸



Scheme 2.2.1.1 Phthalic anhydride and phenolphthalein as an intermediate to other organic compounds.³⁶⁵

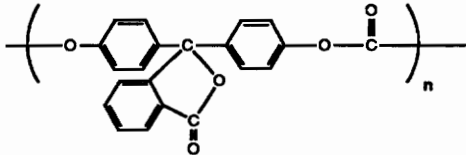
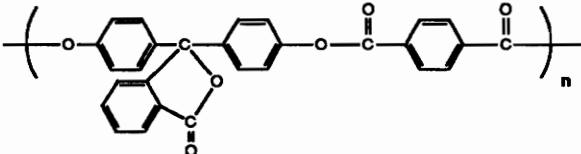
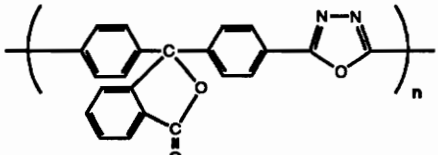
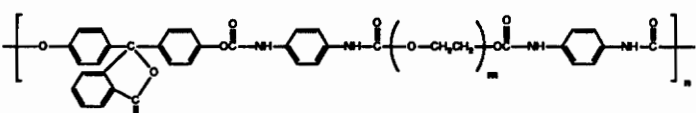
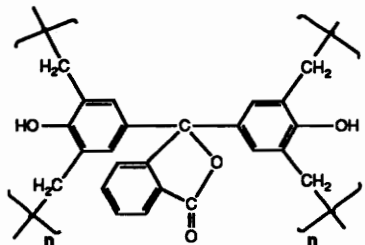
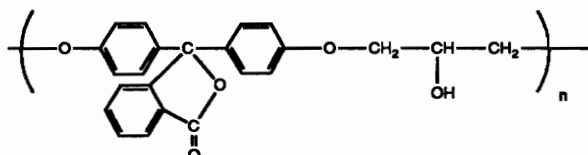


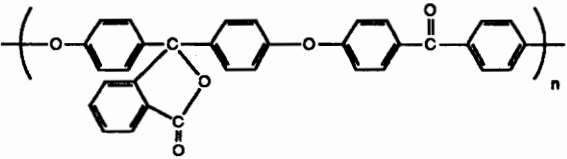
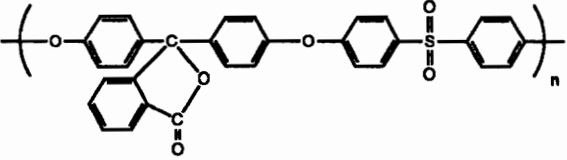
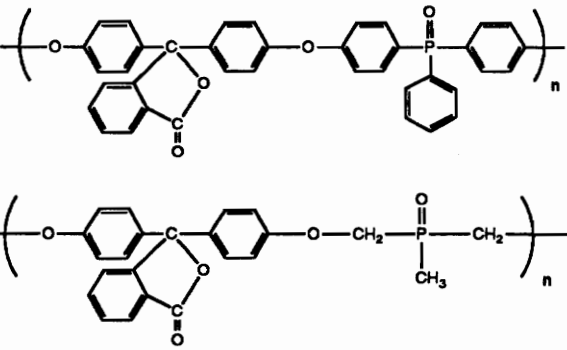
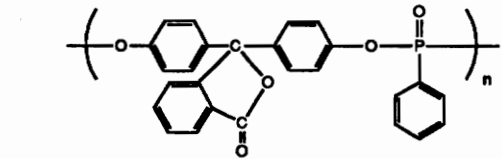
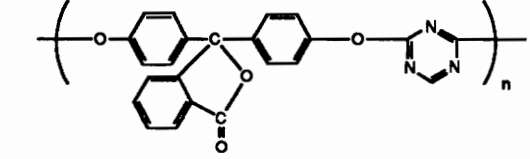
Scheme 2.2.1.2 Synthesis of novel bisphenols using phenolphthalein as a starting material.³⁶⁶⁻³⁶⁸

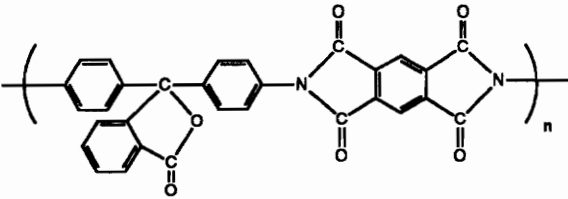
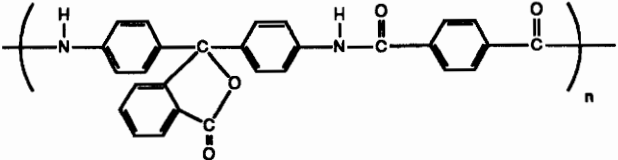
2.2.2 Survey of Phenolphthalein-Polymer Literature

Phenolphthalein is typically used in polymers where bisphenol A is the standard bisphenol. Most incorporation of phenolphthalein into the polymer backbone has included polycarbonates, polyesters, and poly(arylene ether)s (e.g. ketones and sulfones). Other polymers containing phenolphthalein range in variety and structure as shown in Table 2.2.2.1. Instead of grouping polyethers as one category in this table, ketones, sulfones, and two phosphine oxide examples are shown separately, since sulfones and phosphine oxides are the focus of this research.

Table 2.2.2.1 Examples of phenolphthalein in polymers.

Polymer Class	Structure	General Refs.
Carbonate		365, 369-381
Ester		365,369, 370,375, 377,381-407
Oxadiazole		365
Urethane		408
Phenol formaldehyde		409-411
Hydroxy ether		370,412, 413

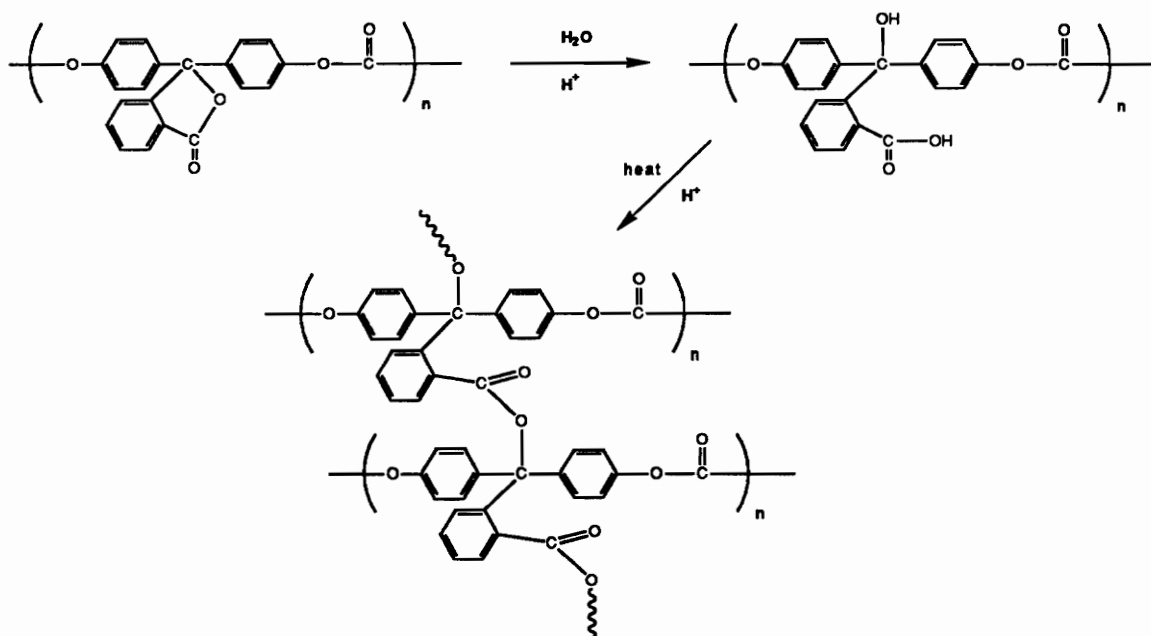
<p>Arylene Ether</p> <p>a) Ketone</p>		<p>368,384, 414-442</p>
<p>b) Sulfone</p>		<p>181,281, 282,368, 371,389, 395,413, 421,423, 426,434- 436,441, 443-455</p>
<p>c) Phosphine oxide</p>		<p>456</p> <p>457</p>
<p>Phosphonate</p>		<p>458</p>
<p>Cyanurate</p>		<p>459-461</p>

Imide		365,462
Amide		365,462

Advances have been made in our laboratories on phenolphthalein-containing poly(arylene ether sulfone)s^{219,220,301} and (phosphine oxide)s.^{210,212,215-218} These advances will be discussed in detail in Section 4.0.

2.2.3 Contributions of Phenolphthalein to Polymer Properties

Phenolphthalein has contributed significantly to the overall thermal properties of polycarbonate and polyester, and has been studied extensively by Lin *et al.*³⁷⁵⁻³⁷⁸ Phenolphthalein-related polymers are able to produce a higher degree of crosslinking during pyrolysis and as a result, lead to higher char yields. This cross-linking mechanism has been proposed as shown in Scheme 2.2.3.1.³⁷⁸

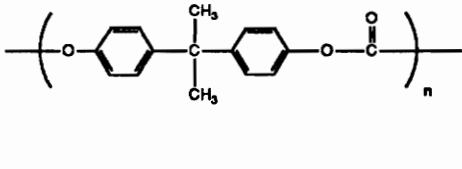
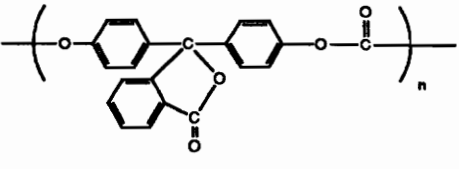


Scheme 2.2.3.1 Mechanism of cross-linking by hydrolytic degradation of phenolphthalein-polycarbonate.³⁷⁸

In both polycarbonates and polyesters, the phenolphthalein polymers have a significant increase in overall thermal properties compared to the bisphenol A systems as shown in Tables 2.2.3.1 and 2.2.3.2. Higher limiting oxygen index (LOI) values correlate with better flame resistance. The LOI of phenolphthalein polymers is higher than bisphenol A containing polymers. This characteristic is directly linked to the increased char yield of the phenolphthalein-containing systems. An increase in char yield is often reflected in decreased flammability of the polymeric system. This generalization is better understood if one considers the highly crosslinked structure on the polymer surface. The flammable volatile products in the inner polymer matrix have difficulty in diffusing through the char layer, resulting in lower flammability. Another factor is the heat transfer to the inner

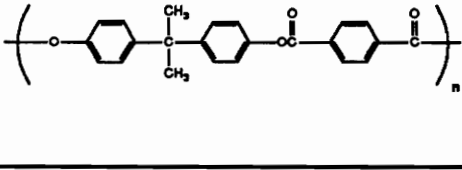
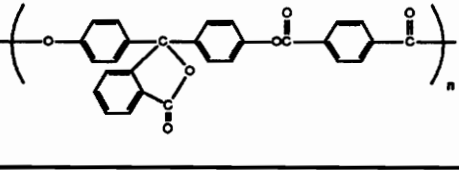
polymer mass is reduced as a result of the poor thermal conductivity of the char layer, which slows down the pyrolysis rate.³⁷⁷

Table 2.2.3.1 Comparison of bisphenol A vs. phenolphthalein polycarbonate.³⁷⁷

Property		
% Char yield (800 °C, N ₂)	21	54
LOI	26	38
T _g (°C) [T _m]	155 [230]	270
[η] ^a	0.27	0.31

a) measured at 30 °C in phenol/sym-tetrachloroethane (60/40)

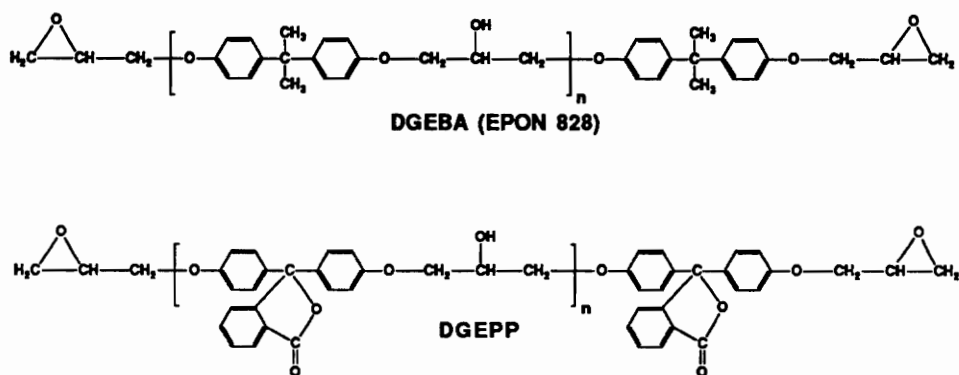
Table 2.2.3.2 Comparison of bisphenol A vs. phenolphthalein polyester.³⁷⁷

Property		
% Char yield (800 °C, N ₂)	29	45
LOI	26	36
T _g (°C) [T _m]	223 [317]	260
η _{inh} ^a	0.61	0.40

a) measured at 30 °C in phenol/sym-tetrachloroethane (60/40)

The improved thermal stability of phenolphthalein-containing polymers has not only been reported for polycarbonates^{375,378,380} and polyesters,^{375,377,382,393,394,396,400} but also for poly(arylene ether ketone)s,^{368,384,414,417,418,430,432,438-440} poly(aryl ether sulfone)s,^{368,445,453} and polycyanurates.⁴⁵⁹⁻⁴⁶¹ Reasons for the increased thermal stability of the phenolphthalein-polymers over the bisphenol A systems most likely include the crosslinking ability of the phenolphthalein lactone as shown previously in Scheme 2.2.3.1, as well as the increased rigidity of the polymeric backbone. This concept will be discussed in detail for poly(arylene ether)s in Section 4.1.

The last area in which phenolphthalein has been used in place of bisphenol A for improved thermal properties is that of epoxy resins.⁴⁶³⁻⁴⁶⁸ Traditionally, the diglycidyl ether of bisphenol A (DGEBA) is utilized as the main component in epoxy curing resins for composite materials. Phenolphthalein has also been reacted with epichlorohydrin to form the diglycidyl ether of phenolphthalein (DGEPP) as shown in Scheme 2.2.3.2. The flammability of the DGEBA is a major hazard. As a result, the DGEPP resin can be used as a substitute since it is much more flame-resistant. The flame resistance of this DGEPP resin is attributed to the char formation of the ring-opening of the lactone as described previously for polycarbonate in Scheme 2.2.3.1.⁴⁶⁴



Scheme 2.2.3.2 Use of DGEPP as an epoxy resin.

In addition to this increased flame resistance, the onset of cure for DGEPP is ~50-75 °C higher as compared to the DGEBA resin. This increased curing temperature is attributed to the complexation of the lactone moiety with the trimethoxyboroxane Lewis acid catalyst that is used to initiate cure.⁴⁶⁴ As a result of this complexation, the catalyst interaction with the epoxide ring is decreased, therefore the initial cure temperature of the DGEPP resin shifted to a higher degree.⁴⁶⁴

Recently, Zhang and Jun have studied the effect of radiation-induced crosslinking of phenolphthalein-based poly(arylene ether ketone)s.^{439,441,455} They have determined that at high temperatures (~300 °C), these systems can be crosslinked by removal of the cardo group (i.e. pendant heterocyclic lactone). As a result, the T_g value of the phenolphthalein poly(arylene ether ketone) increased 9 °C higher (236 °C) over that of unirradiated material (227 °C).⁴⁴¹

Due to the limitations of this review, applications of phenolphthalein-containing polymers will not be discussed in detail, but the following areas have been extensively investigated in the literature. These applications include the use of phenolphthalein-based poly(arylene ether)s as tougheners in epoxy and cyanate ester resins,^{219,220,301,419,421,425,427,446} and as membranes for liquid and gas separation.^{407,417,420,435,436,442,445,451,452}

2.3 Phosphorus in Polymers

2.3.1 Introduction

Excellent reviews have already been done in the area of phosphorus polymers.^{311,469-471} The major focus of this review is the chemistries used to incorporate phosphorus into the polymer.

The nomenclature used to classify organophosphorus compounds is shown in Figure 2.3.1.1.

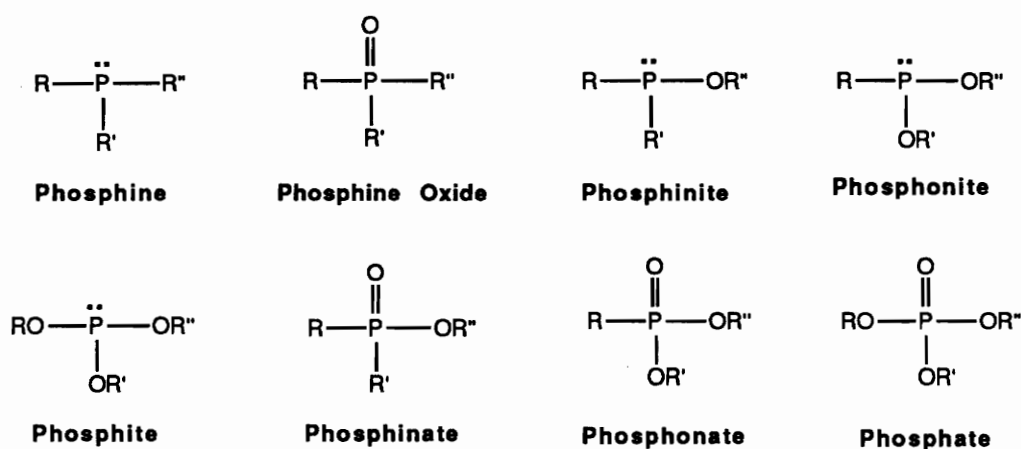
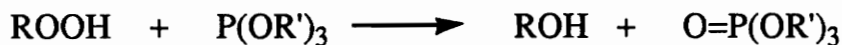


Figure 2.3.1.1 Classes of organophosphorus moieties.

Trivalent phosphorus compounds have wide application as non-discoloring antioxidants to stabilize polymers against chain scissioning and aging during processing and fabrication. Phosphites and phosponites are used as antioxidants in which their role is that of hydroperoxide decomposition as shown in Scheme 2.3.1.1. Often times, phosphite esters are used in conjunction with sterically hindered phenols.⁴⁷²



Scheme 2.3.1.1 Hydroperoxide decomposition by trivalent phosphorous compounds.

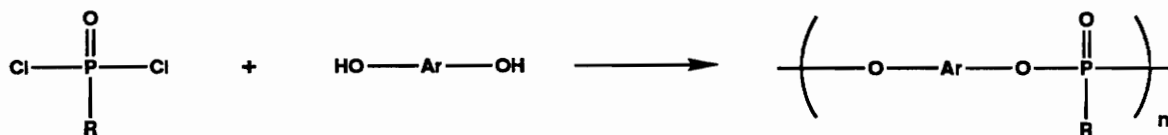
Phosphites have also been used to complex metallic impurities in polymers thereby improving color. Phosphite and phosphonite stabilizers are usually added to polymers in the range of 0.05 - 1% by weight.

2.3.2 Synthetic Routes to Incorporate Phosphorus Into Polymers

Due to the limitations of this review and the enormous amount of examples in which phosphorus has been incorporated into polymers, only a few examples will be cited for each synthetic route. The goal of this review is to inform the reader of the variety of synthetic techniques that can be utilized to incorporate phosphorus into polymers.

2.3.2.1 Phosphorus as the Electrophile

The most common incorporation of phosphorus into the polymer backbone is by halogen displacement from phosphorus in its pentavalent state by a nucleophilic species (e.g. phenoxide).⁴⁷³⁻⁴⁷⁵ As a result, a phosphorus-oxygen bond is formed which is hydrolytically unstable. An example of this chemistry is seen by the polymerization of a bisphenol with a substituted phosphonic dichloride.

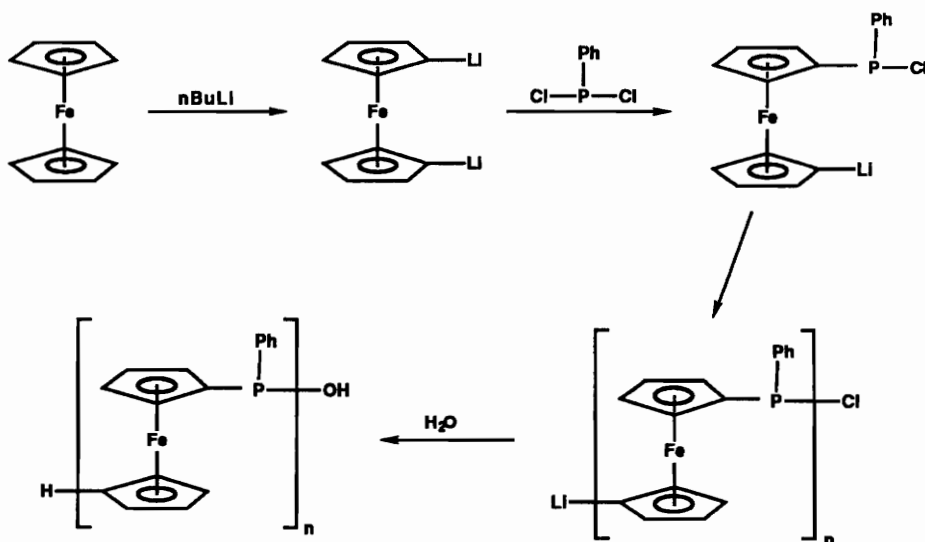


R = alkyl, aryl, alkyloxy, aryloxy

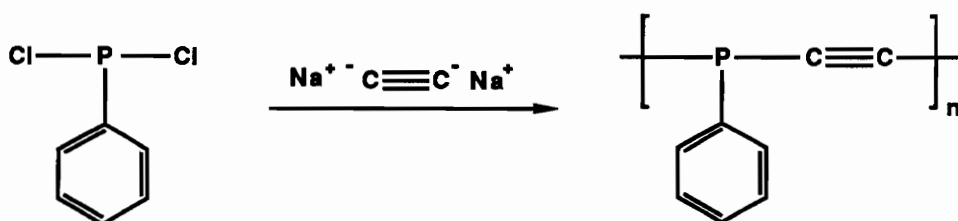
Scheme 2.3.2.1.1 Formation of a phosphorus-containing polyether with the electrophilic site at phosphorus.

An example of a trivalent phosphorus as an electrophile in polymer formation is the synthesis of poly[1,1'-ferrocenylene(phenylphosphine)] as shown in Scheme 2.3.2.1.2.^{476,477} This polymer was utilized for the formation of novel metal chelates which are exceptionally stable catalysts. Due to the linear nature of these polymers, the catalysts are homogenous under a wide variety of reaction conditions yet can be easily made insoluble for recovery purposes. These high molecular weight polymers were stable up to 350 °C in air.

Rahman *et al.* also utilized trivalent phosphorus as an electrophilic site with the synthesis of a simple conducting polymer containing only phosphorus and carbon in the backbone as shown in Scheme 2.3.2.1.3.⁴⁷⁸ Thermal studies indicated that this polymer was stable up to 300 °C in air with a T_g of 155 °C. This polymer has also been synthesized using phosphorus as a nucleophile as discussed in Section 2.3.2.2.



Scheme 2.3.2.1.2 Synthesis of poly[1,1'-ferrocenylene(phenylphosphine)].^{476,477}

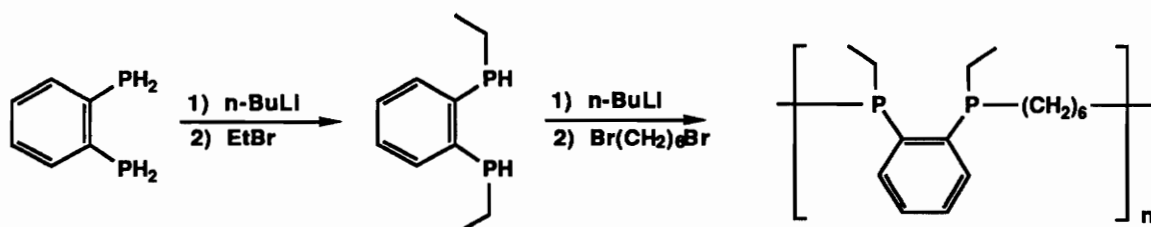


Scheme 2.3.2.1.3 Synthesis of Poly(phenylphosphine acetylene).⁴⁷⁸

2.3.2.2 Phosphorus as the Nucleophile

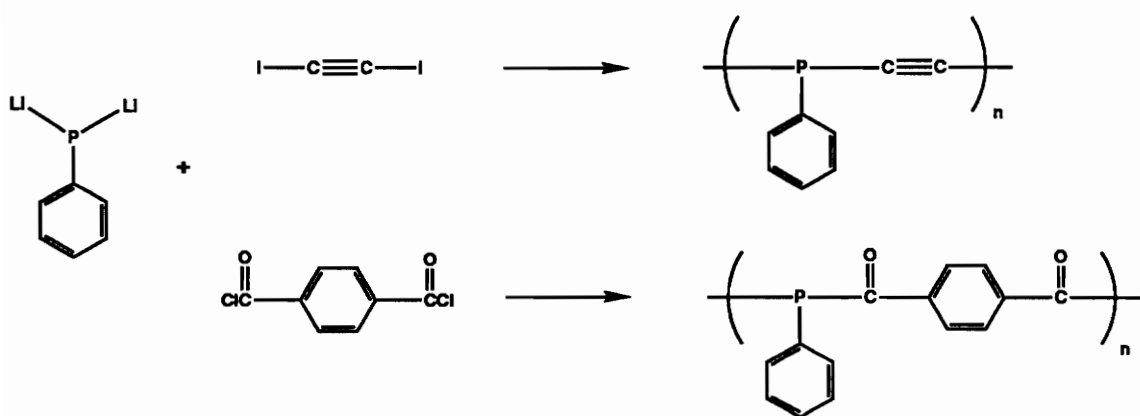
Phosphorus in its trivalent state has a lone pair of electrons contributing to its nucleophilicity. One example of using phosphorus as a nucleophile to make polymers is 1,2-bisphosphinobenzene.^{479,480} It was reacted with a dihaloalkane to give a linear, low molecular weight poly[1,2-bis(dialkylphosphino) benzene] as shown in Scheme 2.3.2.2.1. This polymer was a viscous, colorless oil with a degree of polymerization between 30 and 48. No thermal analysis was done on this polymer since the focus was to investigate the

complexation with nickel perchlorate to determine the electrochemical activity. The intent of synthesizing the 1,2-bisphosfinobenzene was to make a polymer for use as a metal chelater.



Scheme 2.3.2.2.1 Synthesis of poly(alkyl phosphine)s using phosphorus as the nucleophile.^{479,480}

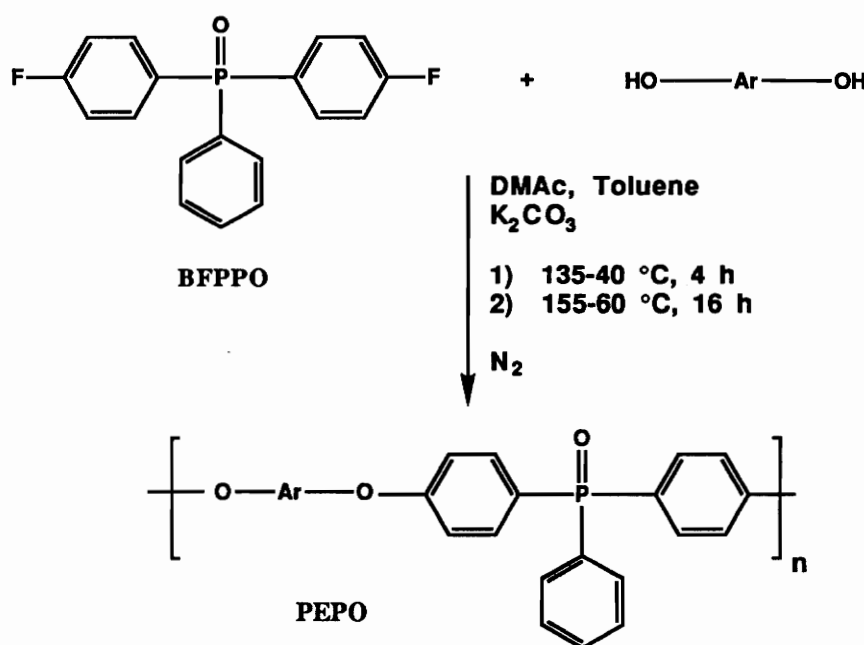
Phosphorus has also been used as a nucleophile in the synthesis of a poly(acetylene phosphine) made for electroconductive polymer applications.⁴⁸¹ This polymer is soluble in polar organic solvents and has excellent thermooxidative stability. Poly(aryl ketone phosphine) was also made by this method as shown in Scheme 2.3.2.2.2.^{481,482}



Scheme 2.3.2.2.2 Synthesis of poly(phosphine acetylene) and poly(phosphine ketone) using phosphorus as the nucleophile.^{481,482}

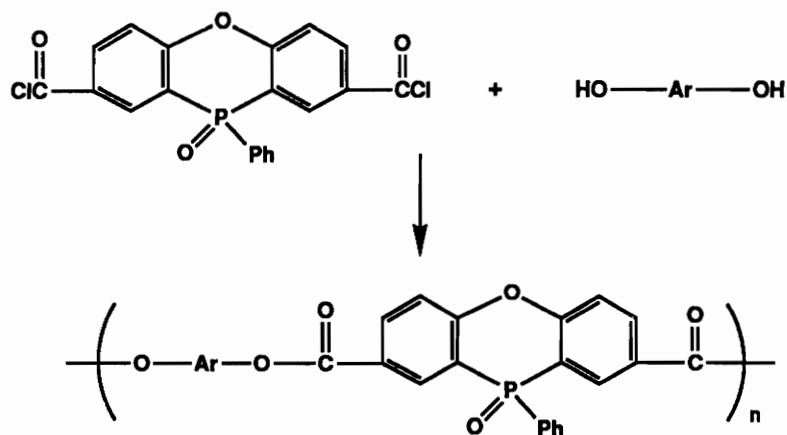
2.3.2.3 Phosphorus in Monomers

This synthetic technique is the one utilized exclusively in this research.²¹⁵⁻²¹⁸ By incorporating phosphorus into a monomer, one can utilize chemistries to form phosphorus-aryl bonds which are hydrolytically and thermally stable. An example of the synthesis of a poly(arylene ether phosphine oxide) (PEPO) by reacting bis(4-fluorophenyl phenyl) phosphine oxide (BFPPO) with a bisphenol is shown in Scheme 2.3.2.3.1.^{198,199,201-203,215-218,311}



Scheme 2.3.2.3.1 Synthesis of poly(arylene ether phosphine oxide) using a phosphorus-containing monomer.

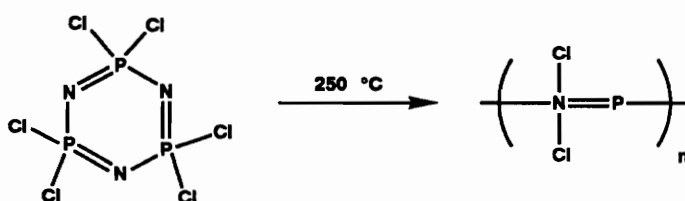
Linear polymers containing phosphorus-carbon heterocycles have been synthesized using a phenoxaphosphine oxide monomer. A specific example of the use of this phosphorus containing monomer is the interfacial synthesis of polyesters by reacting the diacid chloride with a bisphenol as shown in Scheme 2.3.2.3.2.⁴⁸³



Scheme 2.3.2.3.2 Synthesis of a polyester using a phenoxaphosphine oxide ring-containing monomer.⁴⁸³

2.3.2.4 Ring-opening of Phosphorus-Containing Cyclic Monomers

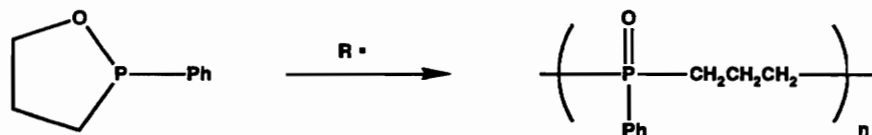
In 1897, Stokes reported the synthesis of polyphosphazine, known as 'inorganic rubber', which was the first known phosphorus-containing polymer.⁴⁸⁴ The open-chain polyphosphazines have been reviewed extensively.⁴⁸⁵⁻⁴⁸⁷ The synthesis of these materials is a ring-opening process as shown in Scheme 2.3.2.4.1.



Scheme 2.3.2.4.1 Synthesis of polyphosphazines *via* a ring-opening polymerization.

The thermodynamic driving force of most ring-opening polymerizations is the relief of ring strain. However, the free radical ring-opening polymerization of cyclic

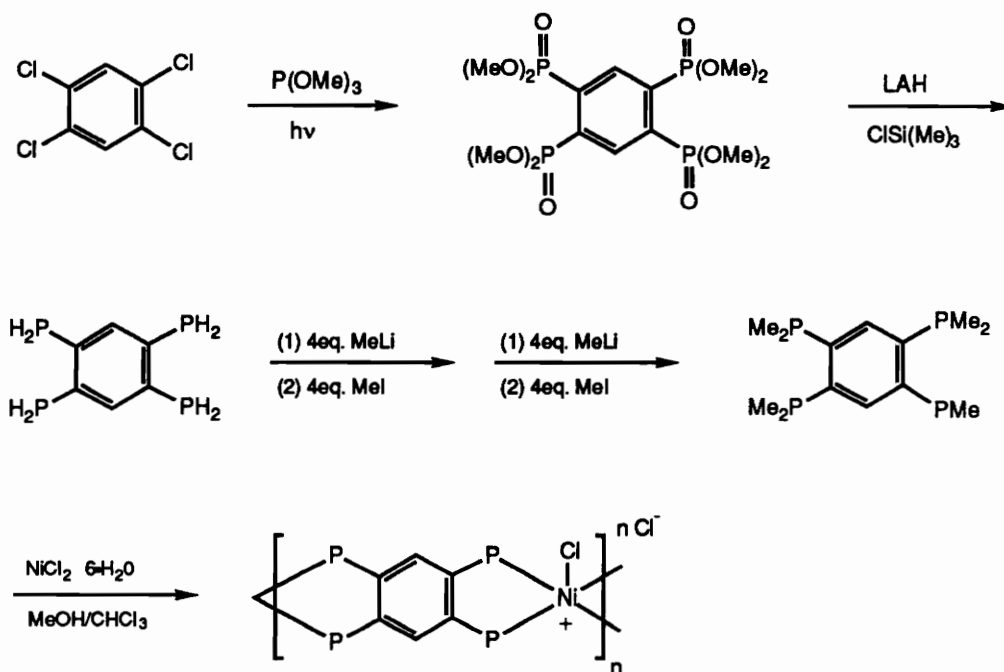
phosphinites is driven by the oxidation of phosphorus to its pentavalent state (Scheme 2.3.2.4.2).⁴⁸⁸ This rearrangement is an example of the well-known Arbuzov reaction.



Scheme 2.3.2.4.2 Free radical catalyzed ring-opening polymerization of a cyclic phosphorus monomer *via* the Arbuzov-type reaction.⁴⁸⁸

2.3.2.5 Metal-Phosphine Coordination

Recently, Fox *et al.* synthesized a nickel-phosphine coordination polymer as shown in Scheme 2.3.2.5.1.⁴⁸⁹ No thermal data was given on this polymer as the interest focused on the electrical properties.

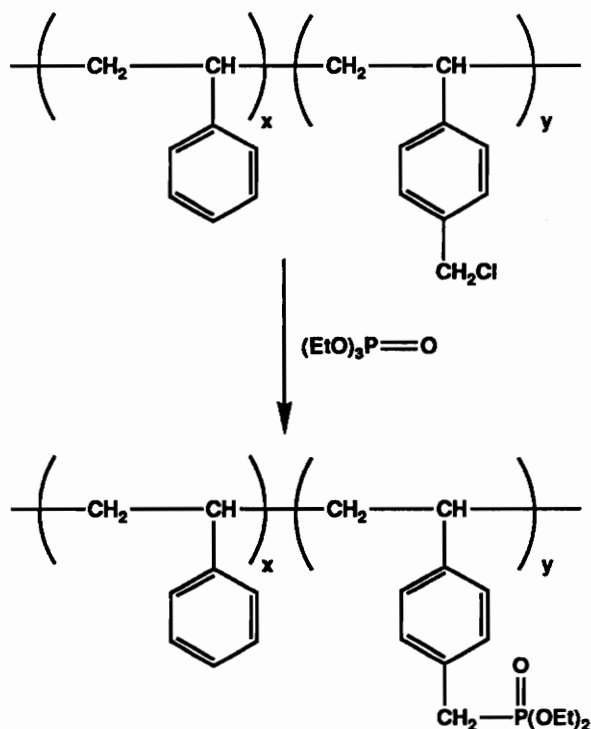


Scheme 2.3.2.5.1 Synthesis of nickel-phosphine coordination polymer.⁴⁸⁹

2.3.2.6 Post-Reaction of Phosphorus in Pendant Polymer Moieties

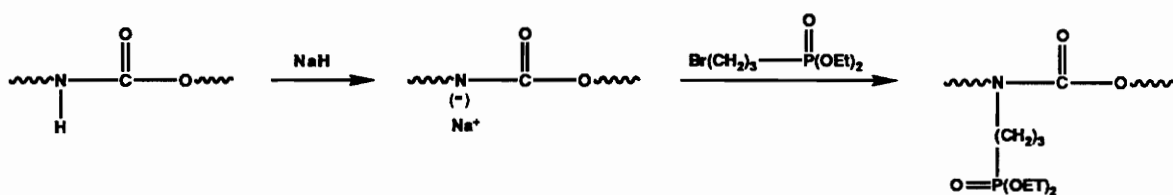
Many examples in the literature incorporate trivalent phosphorus into the polymer as pendant substituents.⁴⁹⁰⁻⁴⁹³

The last mechanism that will be covered here is to demonstrate the attachment of phosphorus onto the polymer chain utilizing reactive pendant moieties. This process is exemplified by the reaction of a phosphoryl ester group onto polystyrene as shown in Scheme 2.3.2.6.1.⁴⁹⁴ These polymers are useful as chelating agents, ion exchange resins and fire retardants.



Scheme 2.3.2.6.1 Post-reacting a phosphoryl ester group onto polystyrene.⁴⁹⁴

Phosphorus-containing polyurethanes have also been synthesized by the post-polymerization reaction of 3-bromopropylphosphate with a urethane polyanion as shown in Scheme 2.3.2.6.2.²⁹¹



Scheme 2.3.2.6.2 Synthesis of phosphorus-containing polyurethane by a post-reaction of 3-bromopropylphosphate.²⁹¹

In summary, phosphorus-containing polymers have been prepared by at least six methods: 1) using phosphorus as an electrophilic site, 2) nucleophilic displacement of halogen by phosphorus, 3) using phosphorus-containing monomers, 4) ring-opening phosphorus containing cyclic monomers, 5) metal-phosphine coordination polymers, and 6) post-reacting phosphorus on pendant moieties.

2.4 Research Logic

The objectives of this work include the following:

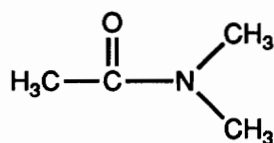
- 1) Synthesize a high temperature stable poly(arylene ether)
- 2) Make a stiffer chain poly(arylene ether) that has an increased modulus than that of typical poly(arylene ether)s (e.g. bisphenol A based systems) to be used in composite applications
- 3) Synthesize amide-containing bisphenols derived from phenolphthalein
- 4) React these bisphenols with an activated dihalide to make high MW poly(arylene ether)s
- 5) Characterize these novel polymers in terms of intrinsic viscosity, thermal and mechanical properties
- 6) Demonstrate the pendant lactone ring of phenolphthalein PAE provides reactive functionality for chemical modification
- 7) Further characterize the PAE reaction mechanism under various basic conditions using HPLC-UV/vis
- 8) Synthesize PAE of varying molecular weights, structures, and endgroups for reactive toughening of epoxy and cyanate ester resins

3.0 EXPERIMENTAL

3.1 Purification of Solvents

3.1.1 N,N-Dimethylacetamide (DMAc)

Chemical Structure:



Supplier: Fisher Scientific

Molecular Formula: C₄H₉NO

Molecular Weight, g/mol: 87.14

Boiling Point, °C/mm Hg: 164 / 760

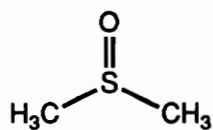
Density, g/cc: 0.937

Purification Procedure:

DMAc was purified by vacuum distillation with a water aspirator at ~60 °C after drying over calcium hydride. The constant boiling fraction was collected as a colorless liquid in a round bottom (RB) flask. The flask was then purged with nitrogen and sealed with a rubber septum.

3.1.2 Dimethylsulfoxide (DMSO)

Chemical Structure:



Supplier: Fisher Scientific

Molecular Formula: C₂H₆OS

Molecular Weight, g/mol: 78.13

Boiling Point, °C/mm Hg: 189 / 760

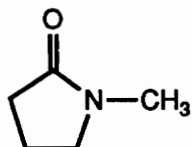
Density, g/cc: 1.101

Purification Procedure:

DMSO was distilled over calcium hydride, then again over phosphorus pentoxide. After vacuum distillation with a water aspirator at ~80 °C, the constant boiling fraction was collected as a colorless liquid in a RB flask. The flask was then purged with nitrogen and sealed with a rubber septum.

3.1.3 1-Methyl-2-pyrrolidinone (NMP)

Chemical Structure:



Supplier: Fisher Scientific

Molecular Formula: C₅H₉NO

Molecular Weight, g/mol: 99.13

Boiling Point, °C/mm Hg: 205 / 760

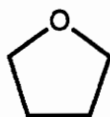
Density, g/cc: 1.033

Purification Procedure:

NMP was purified by vacuum distillation with a water aspirator at ~80 °C after drying over calcium hydride and/or phosphorus pentoxide. The constant boiling fraction was collected as a colorless liquid and stored under a dry nitrogen in a flask sealed with a rubber septum.

3.1.4 Tetrahydrofuran (THF)

Chemical Structure:



Supplier: Fisher Scientific

Molecular Formula: C₄H₈O

Molecular Weight, g/mol: 72.11

Boiling Point, °C/mm Hg: 67 / 760

Density, g/cc: 0.886

Purification Procedure:

Because THF is an ether solvent, extra care was taken to use bottles that contained 0.025% 2,6-di-*t*-butyl-4-methylphenol inhibitor. Upon distilling over sodium and benzophenone, THF was collected and purged with nitrogen. The flask was sealed with a rubber septum.

3.1.5 General Solvents and Reagents

The following solvents were used as received from Fisher Scientific: methanol, ethanol, acetone, toluene, chlorobenzene, methylene chloride, chloroform, anhydrous diethyl ether, and hexanes.

The following reagents were obtained from Fisher Scientific and used as received: anhydrous potassium carbonate, potassium hydroxide, magnesium turnings, anhydrous cobalt chloride, anhydrous magnesium sulfate, and concentrated sulfuric acid.

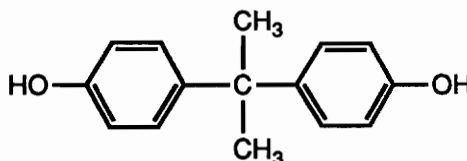
Reagents obtained from Aldrich Chemical and used as received were: *p*-toluene sulfonic acid monohydrate (98%), potassium *tert*-butoxide (95%), *p*-bromofluorobenzene (99%), aniline hydrochloride (97%), aniline (99%), ammonium hydroxide (28%), 4-nitrophenylhydrazine (98%, 10% H₂O), and 4-benzoyl biphenyl (99%).

Lastly, phenylphosphonic dichloride (97%) was obtained from Janssen and was used without further purification.

3.2 Preparation and Purification of Monomers

3.2.1 Bisphenol A (BIS A)

Chemical Structure:



Supplier: The Dow Chemical Company

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

Molecular Weight, g/mol: 228.27

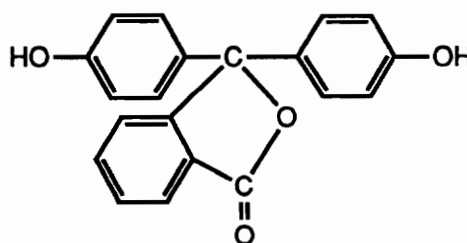
Melting Point, °C: 156-157

Purification Procedure:

Bis A was dried under vacuum prior to use and needed no further purification.

3.2.2 Phenolphthalein [2,2-bis(4-hydroxyphenyl)phthalide] (PP)

Chemical Structure:



Supplier: Aldrich

Molecular Formula: $C_{20}H_{14}O_4$

Molecular Weight, g/mol: 318.32

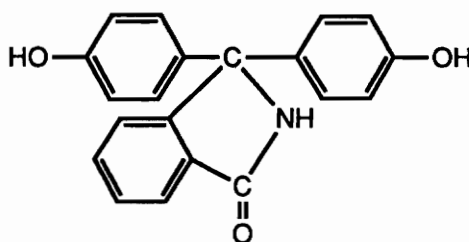
Melting Point, °C: 262-3

Purification Procedure:

PP was dried under vacuum prior to use and needed no further purification. The purity was determined to be 99.9% by HPLC.

3.2.3 Phenolphthalimidine [3,3-bis(4'-hydroxyphenyl)phthalimidine] (PI)

Chemical Structure:



Supplier: Synthesized in our laboratories.

Molecular Formula: $C_{20}H_{15}NO_3$

Molecular Weight, g/mol: 317.34

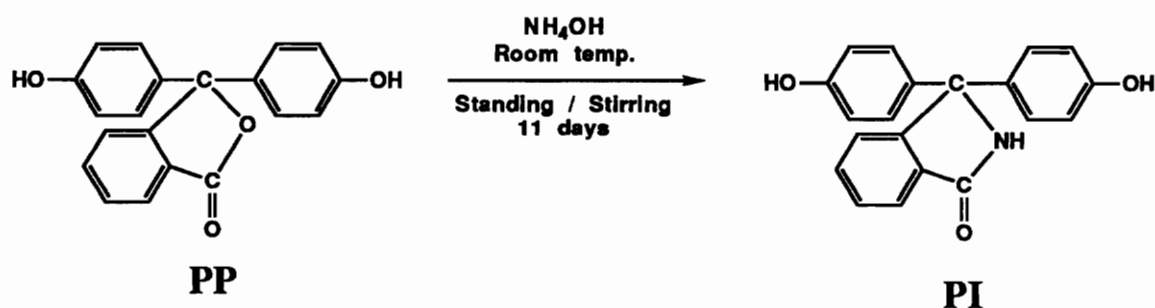
Melting Point, °C: 281-3

Synthesis Procedure:

Phenolphthalein (10 g) was dissolved in 100 ml of 28% ammonium hydroxide as shown in Scheme 3.2.3.1. The mixture was kept in a sealed 2 L bottle to keep the ammonia in solution. The deep purple mixture was then allowed to stand at room temperature with a brief stirring everyday for 11 days as suggested by Lin and Pearce.²²⁴

The color changed to a dull red-brown during this period and some product precipitated out of solution. The solution was poured into a stirring mixture of concentrated hydrochloric acid and ice, and the product was collected in quantitative yield and washed with water. The amide was dissolved in hot ethanol and, upon treatment with charcoal, water was added to start crystallization. The desired aminated product was

obtained in 79% yield. Upon repeated purification with activated charcoal and recrystallizations from ethanol/water, monomer grade white crystals were obtained, after drying at 150 °C, with a melting point of 281-3 °C (lit. 281-2 °C).^{377,495} Spectroscopic analyses of this material are given in Appendix 8.2: IR (Figure 8.2.1); ¹H NMR (Figure 8.2.2); ¹³C NMR (Figure 8.2.3). Elemental analysis calculated for C₂₀H₁₅NO₃: C, 75.7; H, 4.7; N, 4.4. Found: C, 75.4; H, 4.6; N, 4.4.

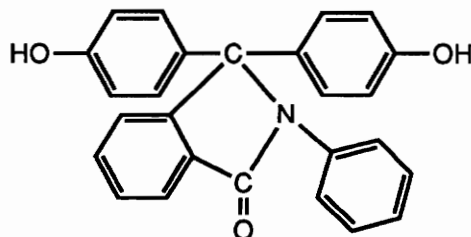


Scheme 3.2.3.1 Synthesis of phenolphthalimidine.

Purification of this monomer requires at least two recrystallizations from ethanol/water. This compound must be dried under vacuum at a temperature >150 °C in order to cleave the complex with ethanol. This monomer is unique in that it contains a somewhat acidic amide proton.

3.2.4 Phenolphthalein-anilide [N-phenyl-3,3-bis(4'-hydroxy phenyl)phthalimidine] (PA)

Chemical Structure:



Supplier: Synthesized in our laboratories.

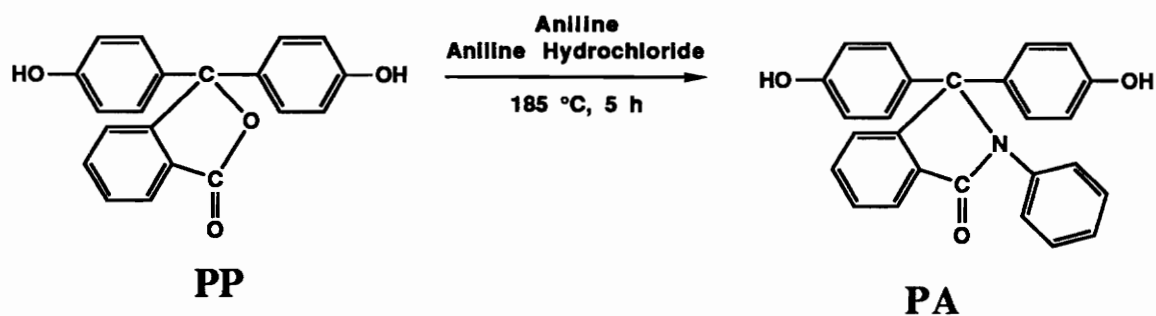
Molecular Formula: $C_{26}H_{19}NO_3$

Molecular Weight, g/mol: 393.44

Melting Point, °C: 292-3

Synthesis Procedure:

A mixture of phenolphthalein (20 g), aniline hydrochloride (20 g), and 60 ml of aniline was refluxed for 5 h under nitrogen as shown in Scheme 3.2.4.1



Scheme 3.2.4.1 Synthesis of phenolphthalein-anilide.

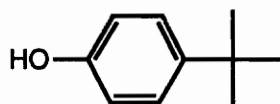
The dark solution was then stirred into a mixture of 100 g ice and 70 g of concentrated HCl. The violet crystalline product was separated by filtration and washed with water. The crystals were then dissolved in ice-cold 10% sodium hydroxide solution. The solution

was treated with activated carbon, then filtered. By dropwise addition of concentrated HCl into the stirred batch, the color changed to a bright pink, then to a pure white thick slurry with a pH of 3-4. The precipitated phenolphthalein-anilide (PA) was then washed to neutrality with water and dried under vacuum at 70 °C. The crude crystals gave a m.p. of 288-91 °C with a yield of 80%. They were then double recrystallized from ethanol/water and dried under vacuum at 150 °C. The resulting monomer grade crystals showed a melting point of 293 °C (lit. 279-80 °C)^{377,496}. Spectroscopic analyses of this material are given in Appendix 8.2: IR (Figure 8.2.4); ¹H NMR (Figure 8.2.5); ¹³C NMR (Figure 8.2.6). Elemental analysis calculated for C₂₆H₁₉NO₃: C, 79.4; H, 4.8; N, 3.6. Found: C, 79.0; H, 4.7; N, 3.6.

The melting point obtained by our laboratories was ~10°C higher than that reported in the literature.³⁷⁷ Due to the low viscosities reported for the polymers obtained by Lin and Pierce,³⁷⁷ it is suspected that their PA was not as pure as that obtained by us. The PA compound was also dried at >150 °C to break-up the ethanol complex with the molecule.

3.2.5 4-*tert*-Butylphenol (*t*-Bu)

Chemical Structure:



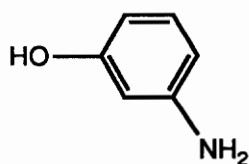
Supplier:	Aldrich
Molecular Formula:	C ₁₀ H ₁₄
Molecular Weight, g/mol:	150.22
Melting Point, °C:	98-101

Purification Procedure:

This monomer (*t*-Bu) was sublimed prior to use.

3.2.6 3-Aminophenol (*m*-AP)

Chemical Structure:



Supplier: Aldrich

Molecular Formula: C₆H₇NO

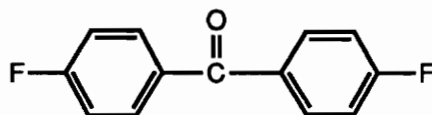
Molecular Weight, g/mol: 109.13

Purification Procedure:

This monomer (*m*-AP) was sublimed prior to use.

3.2.7 4,4'-Difluorobenzophenone (DFB)

Chemical Structure:



Supplier: ICI

Molecular Formula: C₁₃H₈F₂O

Molecular Weight, g/mol: 218.20

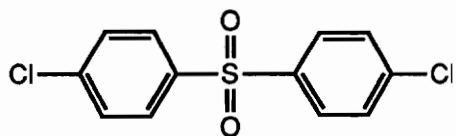
Melting Point, °C: 102-105

Purification Procedure:

DFB was recrystallized from a saturated solution in a mixture of deoxygenated ether/pet. ether. The white crystals were then separated by filtration and dried under vacuum at 50 °C prior to use.

3.2.8 4,4'-Dichlorodiphenylsulfone (DCDPS)

Chemical Structure:



Supplier: Amoco Chemical

Molecular Formula: $C_{12}H_8Cl_2O_2S$

Molecular Weight, g/mol: 287.16

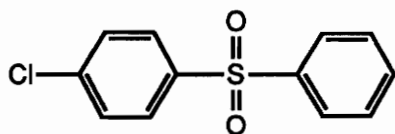
Melting Point, °C: 148.9

Purification Procedure:

This monomer was purified by recrystallization from toluene after treatment with activated charcoal. Upon filtering through Celite, the resulting clear uncolored DCDPS/toluene solution was cooled slowly. After sitting overnight, the resulting white crystals were separated by filtration, crushed, and vacuum dried at 75 °C.

3.2.9 4-Chlorodiphenyl sulfone (4-CDPS)

Chemical Structure:



Supplier: Aldrich

Molecular Formula: $C_{12}H_9ClO_2S$

Molecular Weight, g/mol: 252.72

Melting Point, °C: 90-94

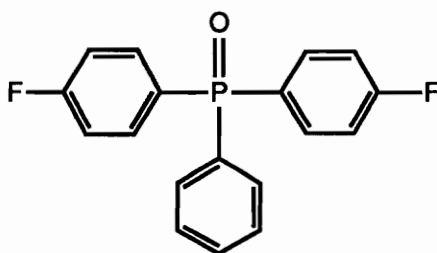
Purification Procedure:

This monomer was purified by recrystallization from toluene after treatment with activated charcoal. Upon filtering through Celite, the resulting clear uncolored

DCDPS/toluene solution was cooled slowly. After sitting overnight, the resulting white crystals were separated by filtration, crushed, and vacuum dried at 75 °C.

3.2.10 4,4'-Bis(fluorophenyl)phenyl Phosphine Oxide (BFPPO)

Chemical Structure:



Supplier: Synthesized in our laboratories.

Molecular Formula: C₁₈H₁₃F₂OP

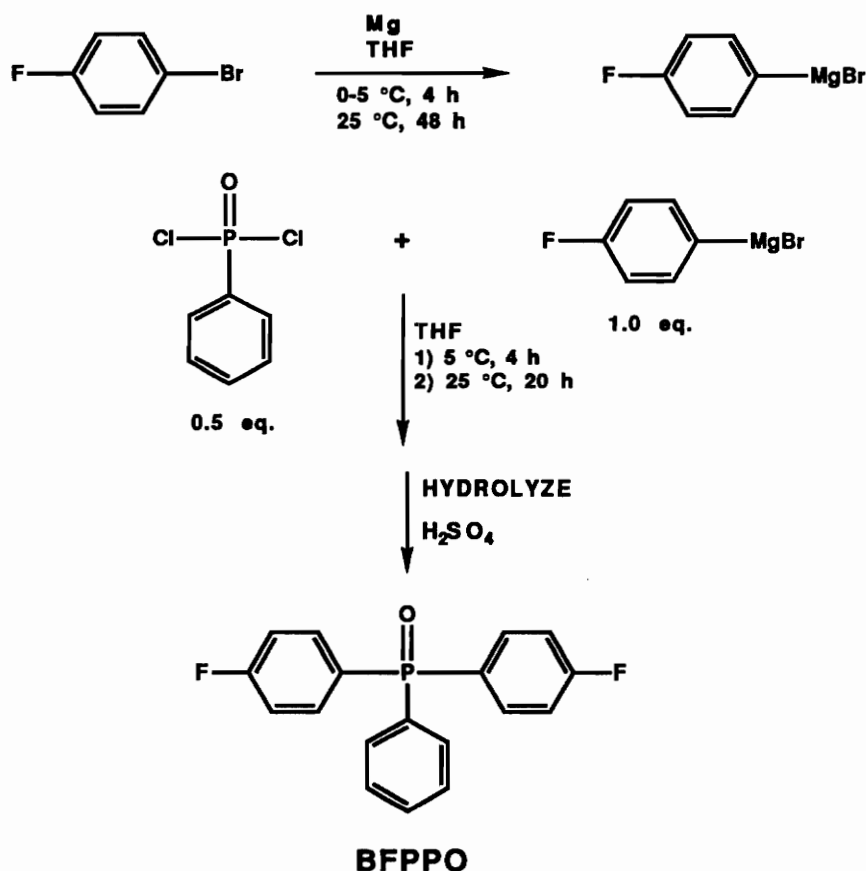
Molecular Weight, g/mol: 314.28

Melting Point, °C: 124-126

Purification Procedure:

This monomer was synthesized and purified by a variation of known Grignard techniques as shown in Scheme 3.2.10.1.^{168,311,497,498}

For example, 85.1 g (3.5 mol) magnesium turnings (Aldrich 99%) and 3.5 L freshly distilled tetrahydrofuran (THF) (Baker, 99+%) were added to a flame dried 5 L 4-neck flask equipped with a mechanical stirrer, addition funnel, and nitrogen inlet. The solution was cooled with an ice water bath to 5 °C and 618.7g (3.5 mol) *p*-bromofluorobenzene (Aldrich, 99%) was added dropwise over a period of 3-4 h. The mixture was stirred at room temperature overnight to give a gray cloudy solution. Improved yields were obtained when the Grignard solution was made in 50% solids, which resulted in the Grignard product crystallizing out of solution. When the mixture reached ambient temperature, the Grignard solution was stirred for a total of 48 h.



Scheme 3.2.10.1 Synthesis of Bis(4-fluorophenyl)phenyl phosphine oxide (BFPPO).

Next, 351.8 g (1.75 mol) phenylphosphonic dichloride (Janssen, 97%) was added dropwise at 5 °C over 3-4 h. The Grignard reagent went into solution as the reaction exothermed. The reaction was allowed to stir at room temperature overnight to give a yellow clear solution. Aqueous sulfuric acid (10%) was added until the solution was acidic. Water was then added until two layers formed (~1.5 L) and the THF layer was decanted. The water layer was washed well with ether, and all the organic layers were combined. The organic layer was then dried over anhydrous magnesium sulfate (Fisher), filtered, and the THF removed to yield a light yellow solid in quantitative yield. Monomer

grade material was achieved by distilling twice with a Kugelrohr apparatus as shown in Figure 3.2.10.1.

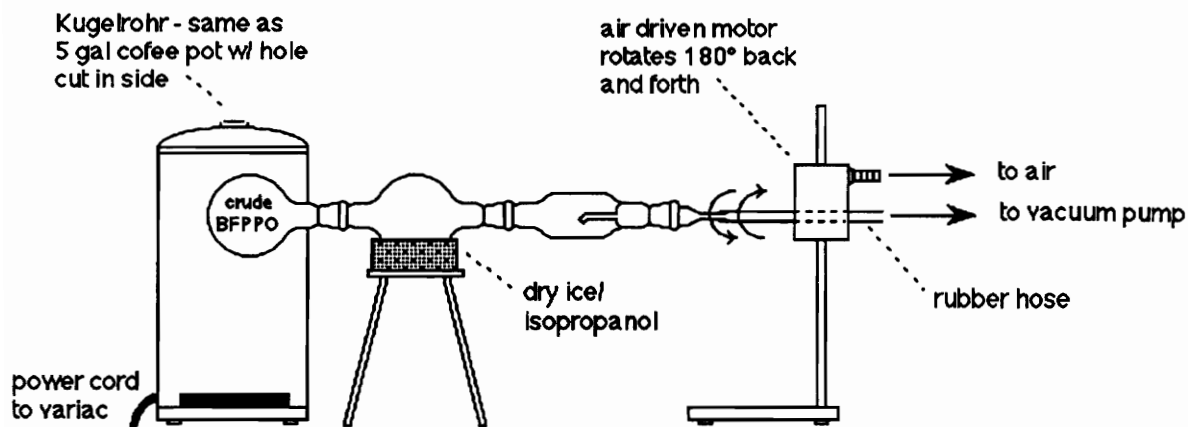


Figure 3.2.10.1 Kugelrohr distillation apparatus used to purify BFPPPO.

The purified material was removed from the Kugelrohr flask by melting the BFPPPO with a heat gun. The BFPPPO was further purified with activated charcoal and recrystallized from THF and hexane. The resulting monomer grade white crystals were achieved with an overall yield of 85-90% with a melting point of 124-26 °C (lit. 124-26).^{168,311,497,498} Spectroscopic analyses of this material are given in Appendix 8.2: IR (Figure 8.2.7); ¹H NMR (Figure 8.2.8); ¹³C NMR (Figure 8.2.9). Elemental analysis calculated for C₁₈H₁₃F₂OP: C, 68.8; H, 4.1. Found: C, 68.7; H, 4.0.

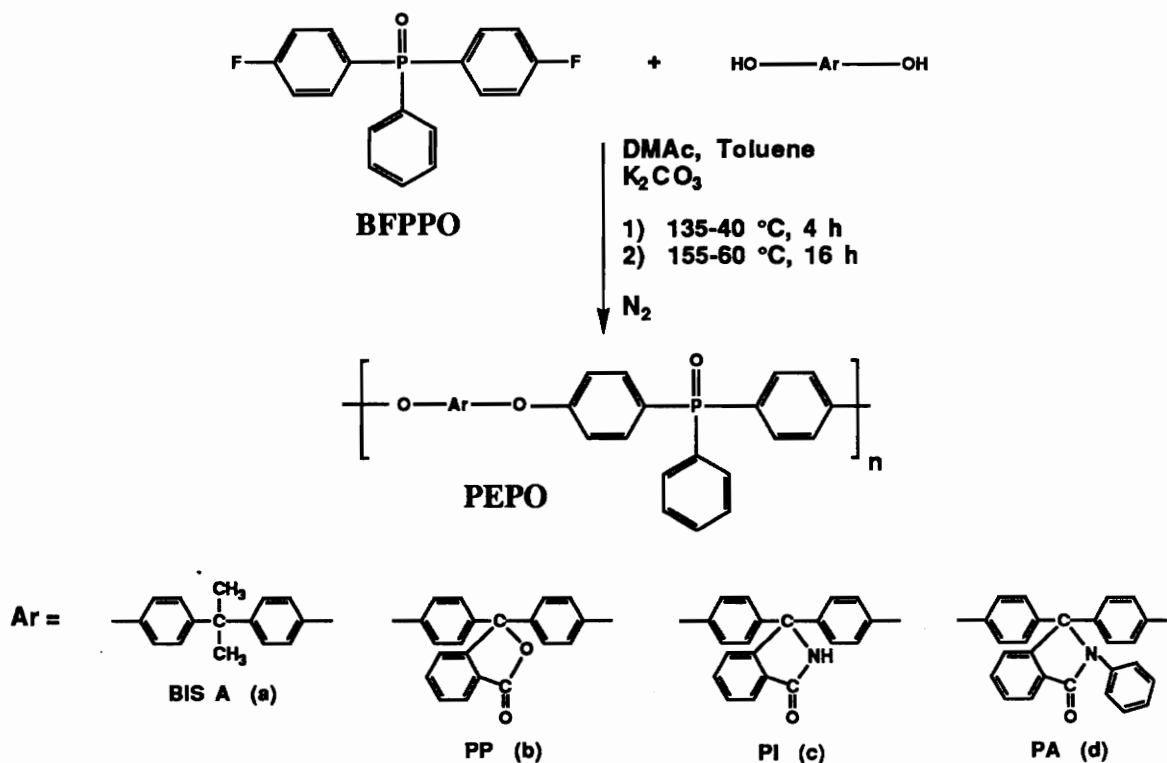
3.3 *Synthesis of Polymers*

3.3.1 High Molecular Weight Poly(arylene ether)s

High molecular weight poly(arylene ether phosphine oxide)s (PEPO) were synthesized as shown in Scheme 3.3.1.1. The synthesis of BIS A-PEPO will be used as an example of the typical procedure used (Scheme 3.3.1.1a). A 1 L flask was equipped with a Dean-Stark trap, overhead stirrer, nitrogen inlet, and a thermometer. Bis(4-fluorophenyl) phenyl phosphine oxide (BFPPO) 31.4280g (0.1 mol) was added to the vessel followed by 22.8920 (0.1 mol) BIS A and 15% excess K_2CO_3 (15.9 g, 0.115 mol). The polymerization was carried out at approximately 15% solids. Freshly vacuum distilled N,N-dimethylacetamide (DMAc) (Aldrich, 99+%) (350 ml) was then added followed by toluene (100 ml) which acts as an azeotroping agent. The temperature of the reaction was raised to 135-40 °C for a period of 4 h. During this time, an azeotrope of toluene and water was collected in the Dean-Stark trap. The reaction was then heated to 160 °C for 16 h to yield a very viscous light brown solution. After cooling, chloroform (70 ml) was added to dilute the mixture and the salts filtered off. A few drops of glacial acetic acid was added to the clear light brown mixture in order to neutralize the solution. The polymer was then precipitated by addition to a 3:1 ratio of methanol/water in a Waring blender. Upon drying, the white fibrous polymer was dissolved in chloroform to make a 10% solution. After a second precipitation from 3:1 methanol/water, the polymer was filtered and dried in a vacuum oven at 175 °C for 12 h. This polymer was soluble in chlorinated solvents, THF, and dipolar aprotic solvents. Spectroscopic analyses of BIS A-PEPO are given in Appendix 8.2: IR (Figure 8.2.16); 1H NMR (Figure 8.2.17); ^{13}C NMR (Figure 8.2.18).

High molecular weight PEPO based on derivatives of PP (Scheme 3.3.1.1b,c,d) were synthesized by the same procedure as given for BIS A, except for PI-PEPO (Scheme

3.3.1.1c) which required 65% excess K_2CO_3 (22.8 g, 0.165 mol) in order to make high molecular weight polymer. Reasons for this will be discussed in Section 4.1.1. Spectroscopic analyses (IR, 1H NMR, and ^{13}C NMR) of PP, PI, and PA-PEPO are given in Appendix 8.2 (Figures 8.2.19 - 8.2.27). Other characterization on these polymers is discussed in Section 4.1.1.



Scheme 3.3.1.1 Synthetic route to high molecular weight PEPO.

High molecular weight poly(arylene ether sulfone)s (PES) were also prepared by the same process as described previously for the phosphine oxides. These polymers (including characterization) will be discussed in Section 4.1.2. Spectroscopic analyses (IR, 1H NMR, and ^{13}C NMR) of BIS A, PP, PI, and PA-PES are given in Appendix 8.2 (Figures 8.2.28 - 8.2.39).

3.3.2 Controlled Molecular Weight Poly(arylene ether)s

The molecular weight of polymers were controlled by two methods. The first method for controlling the molecular weight is by adding an excess of either the bisphenol or the activated dihalide. As a result, polymers were prepared having either phenolic or halogen end-groups. The second method is by adding a monofunctional end-capper to the reaction. This end-capper is typically a substituted phenol (e.g. *m*-aminophenol or *t*-butyl phenol). Using this method, polymers were prepared that were terminated with either amine or with non-reactive *t*-butyl functionalities.

The synthetic procedure for controlled molecular weight oligomer/polymers is the same as described previously for the high molecular weight systems with the exception that a calculated amount of either monofunctional end-capper or excess reagent was added. The calculations for determining the amount of end-capper and reagents for controlled molecular weight polymers are described in Appendix 8.1.

3.4 Model Study Conditions

3.4.1 Model Compound

All model compound reactions utilized a 100 mL three-neck RB flask equipped with a magnetic stirrer, sampling port, Dean-Stark trap, nitrogen inlet, and a thermometer. Throughout the reaction, aliquots were collected periodically. In each reaction, time zero was when the 4-chlorodiphenylsulfone (4-CDPS) was added. The aliquots were immediately quenched with an equal volume of glacial acetic acid and sealed in small vials for HPLC analysis. The results from this model study will be discussed in Section 4.2.

3.4.1.1 Bisphenol A + 4-Chlorodiphenylsulfone Model Reaction

K₂CO₃ Reaction. The synthetic conditions for this reaction can be seen in Scheme 3.4.1.1.1a. The conditions are described as follows: BIS A (2.26 g, 9.90 mmol) was added to the reaction flask followed by the weak base, K₂CO₃ (1.57 g, 11.36 mmol). An internal standard, 4-benzoylbiphenyl (0.26 g, 1.00 mmol), was also added. Lastly, freshly distilled DMAc (50 mL) was added to make a 15% solution followed by toluene (25 mL) which acted as an azeotroping agent. The reaction was heated to 135 °C and azeotroped for 4 h to dehydrate the system. (This 4 h dehydration time is not necessary, because a weak base is used, but was done to maintain consistency with the KOH reactions.) After 4 h, the reaction was cooled to 100 °C and the 4-CDPS (5.50 g, 21.76 mmol) added to begin the reaction. Immediately a time 0 sample was taken. The reaction was then heated to 135 °C and toluene was refluxed again for 4 h, after which time the temperature was increased to 155 °C, and the toluene was removed *via* the Dean-Stark trap. The temperature of 155 °C was maintained for 16 h. To isolate the model compound formed, the reaction mixture was cooled and the salts filtered. The mixture was then precipitated in a 50/50 mixture of methanol and water. The white crystalline product was then recrystallized from toluene/hexane to give pure BIS A-BDPS in 67% yield and m.p. = 180-83 °C (lit. 182-83 °C)³³³. Spectroscopic analyses of this material are given in Appendix 8.2: IR (Figure 8.2.10); ¹H NMR (Figure 8.2.11); ¹³C NMR (Figure 8.2.12). Elemental analysis calculated for C₃₉H₃₂O₆S₂: C, 70.9; H, 4.8. Found: C, 70.7; H, 4.7.

The reaction kinetics determined from this model study will be discussed in Section 4.2.1.

3.4.1.2 Phenolphthalein + 4-Chlorodiphenylsulfone Model Reaction

The model compound reaction using PP was run under the same conditions and molar amounts as described previously for the BIS A model reaction. The only difference was in the K_2CO_3 reaction, the color turned a medium purple, whereas with KOH, the solution became viscous and deep purple in color. The K_2CO_3 reaction is shown previously in Scheme 3.4.1.1.1b and the KOH reactions are shown in Scheme 3.4.1.1.2b. At the end of the K_2CO_3 reaction, the mixture was acidified with acetic acid. The mixture was then poured into 3:1 v/v methanol/water. The crude white precipitate was separated by filtration and dried in a vacuum oven at 60 °C (<10 mm Hg). The yield of crude product was 84% (m.p. = 106-8 °C). Spectroscopic analyses of this material are given in Appendix 8.2: IR (Figure 8.2.13); 1H NMR (Figure 8.2.14); ^{13}C NMR (Figure 8.2.15). Elemental analysis calculated for $C_{44}H_{30}O_8S_2$: C, 70.4; H, 4.0. Found: C, 69.3; H, 4.0.

The kinetics determined from this model reaction will be discussed in Section 4.2.2.

3.4.1.3 Bisphenol A + Phenolphthalein + 4-Chlorodiphenylsulfone Model Reaction

In the reactions where the relative reactivities of BIS A and PP were being compared with K_2CO_3 as the base, the previously mentioned conditions in Section 3.4.1.1 were used to maintain consistency for accurate comparisons. The results from this mixed reaction will be discussed in Section 4.2.3. The following are variations from the standard individual studies:

K_2CO_3 Reaction. BIS A (1.129 g, 4.94 mmol) and PP (1.574 g, 4.94 mmol) were added to the same reaction vessel, followed by K_2CO_3 (1.57 g, 11.36 mmol). This mixture was dehydrated for 4 h at 135 °C with azeotroping toluene. The reaction was then cooled to 100 °C and 4-CDPS (5.50 g, 21.76 mmol) was added to start the reaction.

KOH Reactions. BIS A (1.129 g, 4.94 mmol) and PP (1.574 g, 4.94 mmol) were added to the same reaction vessel with either 1.0 eq. KOH (0.622 g, 12% H₂O, 9.90 mmol) or 2.0 eq. KOH (1.274 g, 12% H₂O, 19.80 mmol). This mixture was dehydrated for 4 h at 135 °C with azeotroping toluene. The reaction was then cooled to 100 °C and 4-CDPS (5.50 g, 21.76 mmol) was added to start the reaction.

3.4.2 Model Polymers

All model polymerizations utilized a 100 mL three-neck RB flask was equipped with a mechanical stirrer, sampling port, Dean-Stark trap, nitrogen inlet, and a thermometer. Throughout the reaction, aliquots were withdrawn periodically. These aliquots were immediately quenched with an equal volume of glacial acetic acid and sealed in small vials for both HPLC and GPC analysis.

3.4.2.1 Bisphenol A + 4-Dichlorodiphenylsulfone Model Polymer

K₂CO₃ Reaction. The conditions for the synthesis of high molecular weight bisphenol A based poly(arylene ether sulfone) (BIS A-PES) were the same as described previously for BIS A-PEPO in section 3.3.1 with the following exceptions: BIS A (2.5794 g, 11.30 mmol) and K₂CO₃ (1.796 g, 12.99 mmol) followed by DMAc (40 mL) and toluene (30 mL), were added to the reaction flask and heated to 135 °C, then azeotroped for 4 h to dehydrate the system. This was done to maintain consistency with the KOH reactions. The reaction was then cooled to 100 °C before DCDPS (3.2444 g, 11.30 mmol) was added. This enabled the reaction to have a time zero at the time the DCDPS was added for aliquot analysis. The reaction was then heated to 135 °C for 4 h, then 155 °C for 16 h. Spectroscopic analyses of this material is given in Appendix 8.2: IR (Figure 8.2.28); ¹H NMR (Figure 8.2.29); ¹³C NMR (Figure 8.2.30).

KOH Reactions. To make BIS A-PES with KOH as the base, the BIS A (2.5794 g 11.30 mmol) was dehydrated with either 1.0 eq. KOH (0.7309 g, 11.30 mmol) or 2.0 eq.

KOH (1.4546 g, 22.70 mmol) for 4 h, then cooled to 100 °C before the DCDPS (3.2444 g, 11.30 mmol) was added to the flask. The reaction conditions were the same as those mentioned previously in Section 3.4.1.1 for the model compound KOH study.

3.4.2.2 Phenolphthalein + 4-Dichlorodiphenylsulfone Model Polymer

These reaction conditions and molar amounts were used exactly as mentioned in Section 3.4.2.1 for the BIS A model polymer reaction. The bases used for the three PP model polymerizations were 1.15 eq. K_2CO_3 , 1.0 eq. KOH and 2.0 eq. KOH. Spectroscopic analyses of this material is given in Appendix 8.2: IR (Figure 8.2.31); 1H NMR (Figure 8.2.32); ^{13}C NMR (Figure 8.2.33).

3.4.3 Model Study Calculations to Determine % Conversion

The kinetic plots were constructed by taking the time 0 sample peak area data and making the area obtained for BIS A equal 100% and the area obtained for 4-CDPS equal to 105%. Since the final 23 h sample showed no BIS A and no Mono-adduct, complete conversion to Di-adduct was assumed. Thus the area obtained for the Di-adduct after 23 h was set at 100%. Assuming that response is linear between 0 and 100% for the concentration range studied, allows calculation of the amount of Mono-adduct by mass balance. An internal standard (ISTD) was added to the model reactions because toluene was being removed. Normalization of the peak areas with the ISTD was performed as follows:

$$\frac{\text{Area bisphenol at time 0}}{\text{Area ISTD}} - \frac{\text{Area bisphenol at time X}}{\text{Area ISTD}} = \% \text{ bisphenol converted}$$

$$\frac{\text{Area di-adduct at finish}}{\text{Area ISTD}} - \frac{\text{Area di-adduct at time X}}{\text{Area ISTD}} = \% \text{ di-adduct formed}$$

$100 - (\% \text{ bisphenol converted} + \% \text{ di-adduct formed}) = \% \text{ mono-adduct formed.}$

Since an area is obtained for the mono-adduct peak, and the calculated amount of the mono-adduct is known, a response factor was calculated for the mono-adduct in each sample. An average mono-adduct response factor was then determined for all of the samples collected. This average response factor was used to determine a measured value of mono-adduct in each sample. A comparison of the calculated vs. the measured level of mono-adduct in each model reaction on BIS A is shown under three basic conditions in Figure 3.4.3.1. The excellent agreement confirms the good precision of technique.

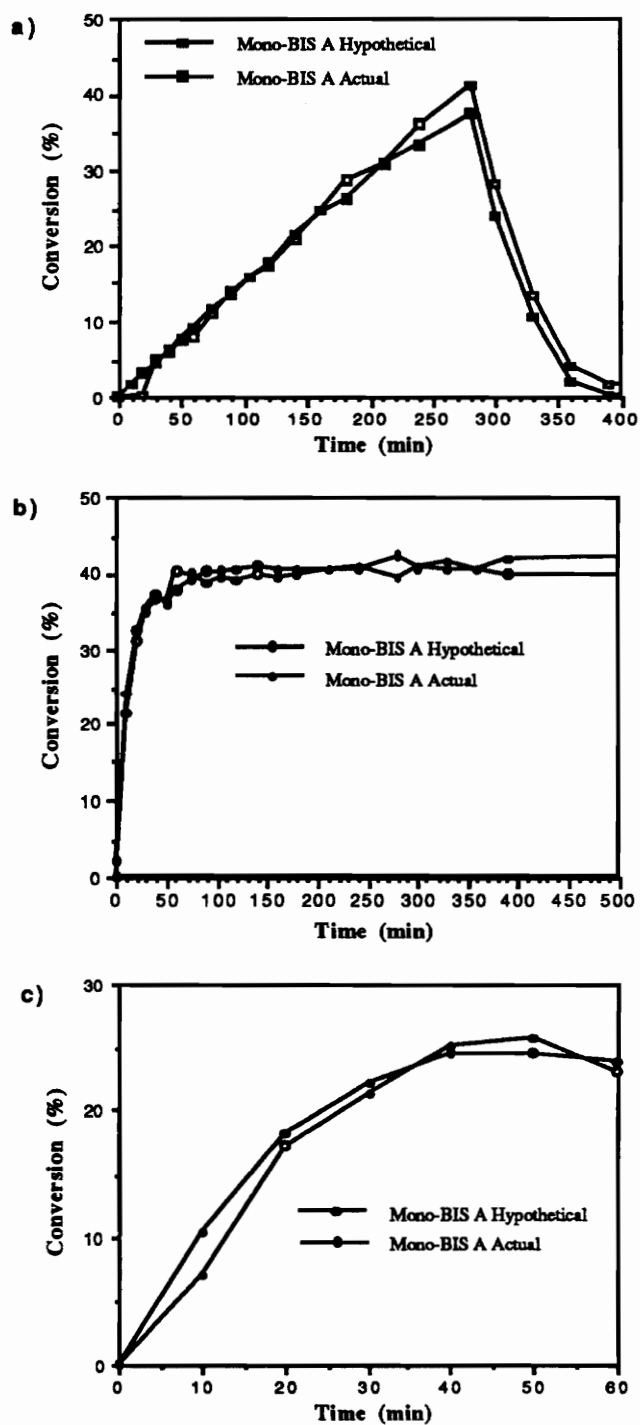


Figure 3.4.3.1 The comparison of the hypothetical vs. actual curves for the formation of Mono-BIS A under different basic conditions: a) 1.15 mole K_2CO_3 , b) 1.0 mole KOH, and c) 2.0 mole KOH.

3.5 Preparation of Metal Complexed Poly(arylene ether) Films

Five different poly(arylene ether)s were used to determine the degree of complexing with one metal salt, cobalt chloride (CoCl_2). The polymer structures, acronyms, and molecular weights for the repeat units are shown in Table 3.5.1. The poly(arylene ether)s chosen for this study were all controlled molecular weight systems with $M_n \sim 20,000$ g/mol. Each was made by the procedure described previously in Section 3.3.2 with the bisphenol in excess. As a result, each system was -OH terminated.

The reasoning behind deciding which polymers to evaluate, the molecular weight to use, the metal salt, and the mole % added will be discussed in Section 4.3.1.

The following formula was used to determine the amount of cobalt chloride (CoCl_2) to add to the polymer:

$$[\text{Mass of polymer (g) / Molecular weight of repeat unit (g/mol)}] *$$

$$[\text{Mole \% metal / 100}] * \text{Formula weight of } \text{CoCl}_2 \text{ (g/mol)} = \text{Amount of } \text{CoCl}_2 \text{ to use (g)}$$

For example, to prepare a 20 mole % CoCl_2 BIS A-PEPO film, the following procedure was used: 20 kg/mol hydroxy end-capped BIS A-PEPO (1.0 g, 19.90 mmol) and DMAc (5 mL) were added to a 20 mL vial to make a 20% solution. This polymer solution was stirred until homogeneous, then filtered through a 0.45 μm PTFE disposable filter. To this filtered solution, anhydrous CoCl_2 (0.0517 g, 0.398 mmol) was added and the blue solution stirred until homogeneous (~6-12 h). The polymer/metal salt solution was then poured onto a glass plate and placed in a closed tank at 60 °C with a constant nitrogen purge. After ~ 2 days, the resulting film was placed in a vacuum oven at ambient temperature for 4 h. Slowly the temperature was increased to 175 °C over a period of 12 h, and held at this temperature for another 12 h. The dried film was optically clear and deep

blue in color. Other metal salt modified polymer films (Table 3.5.1) were prepared by the same method. Polymers containing either phosphorus or phenolphthalein (e.g. BIS A-PEPO, PP-PEPO, PP-PES) resulted in optically clear, homogenous blue films. Polymers without these moieties (e.g. BIS A-PES, BIS A-PEK) resulted in films in which the metal salt precipitated. As a result, these films were brittle and opaque. Characteristics of these materials will be further discussed in Section 4.3.1.

Table 3.5.1 Poly(arylene ether)s used in metal complexation studies.

Acronym	Polymer Repeat Unit Structure	Molecular Weight of Repeat Unit (g/mol)
BIS A - PEPO		502.56
PP - PEPO		592.59
BIS A - PES		442.53
PP - PES		532.56
BIS A - PEK		406.49

3.6 Chemical Modification of Phenolphthalein-based Poly(arylene ether)s

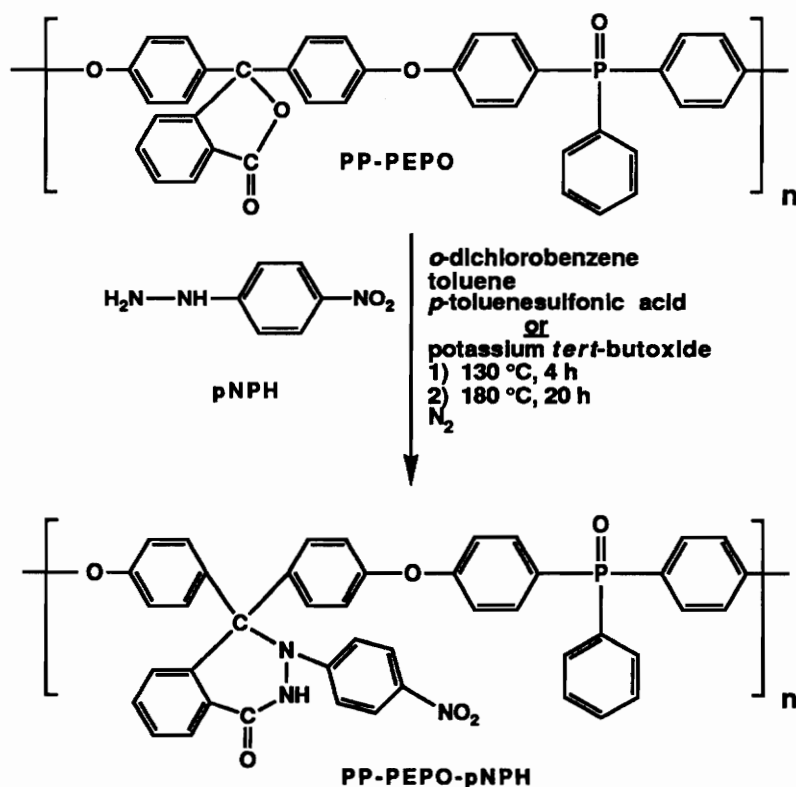
3.6.1 PP-PEPO Derivatization

Several different reaction conditions were evaluated to determine the optimal conditions for derivatization of phenolphthalein-based poly(arylene ether phosphine oxide) (PP-PEPO) with *p*-nitrophenylhydrazine (pNPH).

The PP-PEPO that was used as the base material for the derivatization was controlled to 15 kg/mol. The Carothers equation was utilized to determine the amount of excess PP that was needed to obtain hydroxy end-groups as shown in Appendix 8.1. The synthetic procedure used for 15K PP-PEPO was described previously in Section 3.3. The intrinsic viscosity (η) was determined to be 0.31 dL/g in chloroform at 25 °C for the 15K PP-PEPO.

The first reaction that was tried was the derivatization of 15K PP-PEPO with *p*-nitrophenylhydrazine (pNPH) (Aldrich, 98%, 10% H₂O). The following conditions were utilized as shown in Scheme 3.6.1.1. A 500 mL flask was equipped with a Dean-Stark trap, overhead stirrer, nitrogen inlet, and a thermometer. 15 K PP-PEPO (10 g, 16.9 mmoles) was added to the vessel followed by *o*-dichlorobenzene (500 mL). The temperature of the reaction was raised to 70 °C with constant stirring until the polymer went into solution. pNPH (30.0 g, 169.0 mmol, 10x molar excess) was then added followed by toluene (100 mL) which acts as an azeotroping agent. The temperature of the reaction was raised to 135-40 °C for a period of 4 h. During this time, an azeotrope of toluene and water was collected in the Dean-Stark trap. The reaction was then heated to 175 °C and *p*-toluenesulfonic acid monohydrate (*p*-TSA) (catalytic amount) was added. The temperature was maintained between 175-80 °C for 20 h to yield a deep yellow/brown homogeneous solution. After cooling, the reaction mixture was precipitated in hexane and filtered to

obtain a mixture of polymer and unreacted chromophore. This mixture was then stirred in boiling methanol for 2 h to dissolve the unreacted chromophore. After filtering, the polymer was dried, resulting in a dark brown powder. The polymer was then placed in a Soxhlet extractor and extracted with methanol for 24 h. The resulting hard polymer chunks were then dissolved in chloroform and precipitated in methanol two times. After filtering, the polymer was dried in a vacuum oven at 130 °C for 24 h. The resulting PP-PEPO-pNPH (8 g) was tan in color. This material was soluble in chlorinated solvents, THF, and polar aprotic solvents. The intrinsic viscosity (η) was determined to be 0.29 dL/g in chloroform at 25 °C. The extent of incorporation of the chromophore was ~10 mole % as determined by elemental analysis: (calculated for 100% derivatization: N, 5.77; found: N, 0.56). Spectroscopic analyses of this material is given in Appendix 8.2: IR (Figure 8.2.40); ^1H NMR (Figure 8.2.41); ^{13}C NMR (Figure 8.2.42). GPC-UV/vis analysis is shown in Section 4.3.2.



Scheme 3.6.1.1 Derivatization of PP-PEPO with pNPH under acid or base conditions.

Other reactions included the use of potassium *tert*-butoxide (*t*-BOK) in a base catalyzed derivatization of PP-PEPO. The reaction conditions described previously were used with the exception of using 20 K PP-PEPO (2.0 g, 3.38 mmol), pNPH (1.75 g, 5.79 mmol), and *t*-BOK (0.65 g, 5.8 mmol) in place of *p*-TSA. After addition of *t*-BOK to the dehydrated polymer/chromophore solution, the reaction color immediately turned dark brown and black polymer precipitated on the sides of the reaction vessel. The reaction was then heated again to 180 °C and refluxed for 6 h. Workup for the derivatized polymer was the same as described previously. Final product was coffee-ground like in consistency and color. This material was not soluble in chlorinated solvents, THF, and polar aprotic solvents, hexafluoroisopropanol, or *m*-cresol. Elemental analysis determined there was

25.8 mole % incorporation of chromophore in the PP-PEPO backbone. Suggested reasons as to the behavior of this material as well as refinements in this technique will be discussed in Section 4.3.2.

3.6.2 PP-PES Derivatization

Derivatization of phenolphthalein-poly(arylene ether sulfone) (PP-PES) was also tried. In an effort to achieve higher % derivatization without precipitation of the polymer from the reaction medium, DMSO was used as solvent. For example, a 100 mL flask was equipped with a Dean-Stark trap, overhead stirrer, nitrogen inlet, and a thermometer. 15K PP-PES (3.0 g, 5.6 mmoles) was added to the vessel followed by freshly distilled DMSO (50 mL). pNPH (1.076 g, 6.20 mmol), was then added followed by toluene (25 mL) which acts as an azeotroping agent. The temperature of the reaction was raised to 135-40 °C for a period of 4 h. During this time, an azeotrope of toluene and water was collected in the Dean-Stark trap and the color of the reaction remained homogeneous and orange in color. The reaction was then cooled to 40 °C and potassium *tert*-butoxide (0.732 g, 6.20 mmol) was added. Immediately, the reaction turned a deep purple, then brown while staying homogeneous. The temperature was heated again to 135 °C and refluxed again for 4 h. At this time the toluene was removed *via* the Dean-Stark trap, and the reaction was heated to 155 °C for 20 h to yield a brown homogeneous solution. After cooling, the reaction mixture was precipitated in a mixture of methanol/water (50/50) and filtered to obtain a brown powder which was analyzed using GPC-UV/vis. The GPC-UV/vis analysis (Section 4.3.2) showed that the polymer had been degraded.

3.7 Reactive Poly(arylene ether)s (PAE) as Tougheners in Cyantate Ester and Epoxy Blends

3.7.1 Reactive PAE Used in Epoxy Blends

Poly(arylene ether)s were synthesized to act as thermoplastic modifiers for toughening epoxy resins. Many different amorphous poly(arylene ether)s were synthesized with varying molecular weights, structures, and end-groups which will be discussed in more detail in Section 4.3.3.1. These polymers were synthesized according to the conditions discussed previously in Section 3.3.

A series of functionalized polymers containing chlorine, *t*-butyl, hydroxy, or amine end-groups were dissolved in epoxy resin and cured. The phase morphology was investigated specifically to determine the interaction of the thermoplastic modifier with epoxy network upon cure. Fracture toughness studies were done to determine the mechanical properties of the toughened epoxy systems.

An example of the resin blend preparation is as follows.³²² The degassed DGEBA epoxy resin system was mixed with the thermoplastic modifier (e.g. BIS A-PES-NH₂) and curing agent, diaminodiphenyl sulfone (DDS), then stirred at 140 °C until a clear mixture was obtained. In all resin mixtures, the molar ratio of epoxy resin to amine curing agent was maintained at 2:1 to allow for complete network formation. The degassed clear resin mixture was poured into a preheated silicone rubber mold at 130 °C and cured in an air convection oven with a pre-optimized cure cycle: 4 h at 130 °C, 2 h at 220 °C, slow cooling in oven. Loadings of thermoplastic modifier up to 30 wt. % were possible within the epoxy blend. Further characterization will be discussed in Section 4.5.3.1.

3.7.2 Reactive PAE Used in Cyanate Ester Blends

Poly(arylene ether)s were synthesized to act as thermoplastic modifiers for toughening cyanate ester resins. The polymers that were investigated were controlled molecular weight materials and will be discussed in more detail in Section 4.3.3.2. They were synthesized according to the procedure as discussed previously in Section 3.3.

To make the resin blend, the amorphous poly(arylene ether)s were dissolved in molten AroCy B-10 melt at 90-100 °C to obtain a homogeneous melt. The melt was degassed under vacuum to remove any volatiles or entrapped air. As soon as degassing was complete, the catalyst, (250 ppm Al(acac)/2 pph nonyl phenol) was added with stirring and the reaction was further degassed. The hot resin was subsequently poured into pre-heated (100 °C) silicone rubber molds for fracture toughness, tensile dog-bone, and dynamic mechanical analysis specimens. The melts were then cured using a cure protocol of 3 h at 104 °C, 1 h at 200 °C and 2 h at 250 °C.^{219,220}

3.8 Characterization Methods

3.8.1 Nuclear Magnetic Resonance (NMR)

3.8.1.1 Proton (¹H) NMR

Proton (¹H) NMR spectra were obtained on either a Varian 400 MHz instrument or a Bruker 300 MHz normally in CDCl₃ or deuterated DMSO depending on solubility of the material. All spectra were referenced to tetramethylsilane (TMS) at 0 ppm.

This method was not only used to characterize structure, but also to calculate the number average molecular weight $\langle M_n \rangle$ of *t*-butyl phenyl functionalized poly(arylene ether)s. In this case, the aliphatic protons of the *t*-butyl group were ratioed relative to the

aromatic protons to provide an estimate of $\langle M_n \rangle$. This method was based on the assumption that there are two targeted end-groups per chain.

A specific example for how this technique can be used is in the case of *t*-butyl terminated biphenol-based poly(arylene ether phosphine oxide) (BP-PEPO-*t*-Bu) (Figure 3.8.1.1.1).

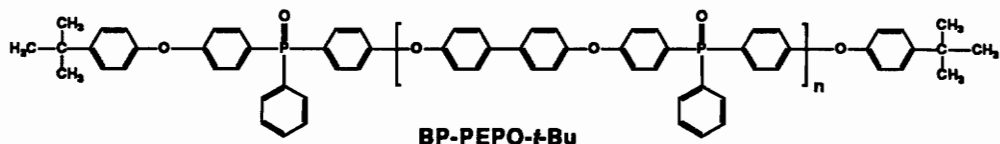


Figure 3.8.1.1.1 Structure of *t*-butyl terminated BP-PEPO for M_n determination by ^1H NMR.

In the ^1H NMR spectra of BP-PEPO, two sets of peaks can be integrated to determine $\langle M_n \rangle$, the end-group methyl protons (1.3 - 1.4 ppm), and the polymer and end-group aromatic protons (7.0 - 7.8 ppm). The aromatic peaks were integrated without including the chloroform peak at 7.24 ppm. The following equations further explain this process.

$$\frac{\text{Value for integrated aromatic region}}{\text{Value for integrated aliphatic region}} = \frac{\# \text{ aromatic protons per chain}}{\# \text{ aliphatic protons per chain}} = \frac{\# \text{ aromatic protons}}{18}$$

The number (#) of aromatic protons can be solved for, since there are three other knowns. Once this value has been determined, the number of repeat units (X) can be solved with the following equation:

$$\frac{\# \text{ aromatic protons}}{18} = \frac{Z * X + Y}{18} = \frac{21 * X + 21}{18} = \frac{\text{Value for integrated aromatic region}}{\text{Value for integrated aliphatic region}}$$

where: X = # repeat units; Y = # aromatic protons in end-groups; Z = # aromatic protons
in repeat unit

Lastly, the number of repeat units (X) was multiplied by the repeat unit molecular weight (460.472 g/mol). To this value, the molecular weight of the end-groups (574.7 g/mol) was added resulting in the total $\langle M_n \rangle$ for the polymer.

3.8.1.2 Carbon (^{13}C) NMR

Carbon (^{13}C) NMR spectra were obtained in the same manner as the proton NMR spectra.

3.8.2 Infrared Spectroscopy (IR)

Fourier Transform infrared spectra were obtained using a Perkin Elmer 1740 instrument. Polymers were analyzed as thin films placed in front of the IR beam, whereas monomers were ground, mixed with dry powdered KBr, and pressed into pellets for analysis.

3.8.3 Elemental Analysis

Atlantic Microlabs, Inc. analyzed both monomers and derivatized polymer samples (Section 4.3.2) for elemental analysis. All components were heated to 1000 °C during analysis.

3.8.4 Melting Point Apparatus

A melting point was taken on all solid monomers. The ground sample was placed in an open capillary vial and heated slowly in a melting point apparatus to determine a

melting point range. The formation of the meniscus was taken as the beginning melt temperature.

3.8.5 Intrinsic Viscosity (η)

Intrinsic viscosities were measured at 25 °C in a Cannon-Ubbelohde viscometer, typically using chloroform as the polymer solvent. Three polymer solutions of low polymer concentrations were prepared for analysis. The time, taken by the polymer solutions (t) and the pure solvent (t_0) through the graduated viscometer path-length, was measured. Assuming $t / t_0 = \eta / \eta_0$, the specific viscosity was defined as $[\eta]_{sp} = [(\eta/\eta_0) - 1]$ and the reduced viscosity as $[\eta]_{red} = \ln(\eta/\eta_0)$. Both (η_{sp} / c) and (η_{red} / c) were plotted against concentration (c) and extrapolated to zero concentration to give the intrinsic viscosity $[\eta]$.

3.8.6 Titration of Functional Oligomers

To determine the molecular weight of hydroxy and amine terminated functionalized poly(arylene ether) oligomers, a titration technique was utilized.³²⁰ The MCI GT-05 Automatic Titrator (Cosa Instruments Corp.) in conjunction with a standard glass-body combination electrode with Ag/AgCl reference electrode was used. The polymer solutions in NMP were titrated against approximately 0.025N methanolic solution of tetramethylammonium hydroxide (TMAH). The TMAH was standardized by titration against an aqueous solution of potassium hydrogen phthalate (KHP) of known concentration. The titration procedure involved titrating a solution of a known weight (w) of the polymer in NMP versus TMAH of standardized normality (N). The $\langle M_n \rangle$ was estimated using the formula $[M_n = (2000w)/(N*(B-BI))]$ where B represents the volume of TMAH used up by the polymer solution and BI represents the blank titration value. If P_i and P_e represent the initial and end-point milli-volt potentials of the actual titration profile,

then the blank titration value was estimated as the amount of titrant used up by NMP alone to undergo the potential change ($P_e - P_i$). $\langle M_n \rangle$ was estimated as an average of 3-4 different titrations for each molecular weight.

3.8.7 Differential Scanning Calorimetry (DSC)

DSC was performed on either a DuPont 912 instrument or a Perkin Elmer 7 series thermal analysis instrument. The reported glass transition temperatures (T_g) from DSC were obtained on the samples which had been cold pressed and secured in crimped aluminum pans. Scans for amorphous polymers were run at 10 °C / min to a temperature greater than the T_g , quench cooled to room temperature, and reanalyzed at 10 °C / min. The T_g values reported are those from second scans.

3.8.8 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) of polymeric samples was performed using a Dupont 951 or a Perkin Elmer 7 series thermal analysis instrument. Typically, a heating rate of 10 °C in an atmosphere of air was utilized. The temperature at which the polymeric sample had a 5% weight loss was taken as the value for which the samples were compared. Each sample was taken up to a temperature of 750 °C to determine char yield.

3.8.9 Stress-Strain Measurements

The mechanical properties of the poly(arylene ether)s were measured *via* tensile tests on an Instron 1123 equipped with a strain gauge extensometer (Instron 2630-013). The dog-bone shape samples (ASTM D-638 #5) were cut out of the solution cast films with thicknesses ranging from 3-10 mils. The samples were tested at room temperature at a cross head speed of 0.5" / min, following ASTM Standard D-638. Approximately 10 samples were tested and the results averaged.

3.8.10 Transmission Electron Microscopy (TEM)

A Philips 420T STEM at 100 kV was used to analyze samples that were embedded in epoxy, cured at 60 °C overnight, then microtomed with a Reichert-Jung Ultracut E Microtome. This process was used to analyze poly(arylene ether)s that were doped with CoCl_2 to evaluate the morphology of metal distribution within the polymer matrix. This will be discussed in Section 4.3.1.3.

3.8.11 Gel Permeation Chromatography (GPC)

3.8.11.1 Molecular Weight Determination

For molecular weight determination, samples were analyzed on a Waters 150C ALC/GPC chromatograph equipped with differential refractive index detector and a Viscotek Model 100 viscosity detector connected in parallel. N-methylpyrrolidinone (HPLC grade) containing 0.5 wt. % LiBr filtered through 0.5 μm Nylon filter served as a mobile phase. The conditions for GPC analysis were as follows. Two stainless steel columns (7.8 x 300) mm were packed with Waters μSyrage l HT (10^3 \AA and 10^4 \AA) having a mean particle diameter of 10 μm . The flow rate was 1.0 mL/min and the injection volume was 200 μL . A temperature of 60 °C was utilized for both for GPC and detector. Samples prepared to known concentration ($\sim 3 \text{ mg/mL}$) were dissolved in the mobile phase and filtered through 0.2 μm PTFE disposable filter prior to analysis. Determination of absolute molecular weight averages and distribution of the poly(arylene ether) samples was based on the concept of universal calibration. Eighteen different monodisperse polystyrene standards were used to construct the calibration curve.

3.8.11.2 Model Polymerization Analysis

A Hewlett Packard HP1090 GPC equipped with a diode-array detector was utilized for the analysis of the model polymerizations as discussed in Sections 3.4.2 and 4.2.5.

The following conditions were used for this model study:

Mobile phase:	DMF + 0.4% by wt. LiNO ₃
Flow rate:	1 mL/min.
Column:	7.6 mm x 300 mm Polymer Laboratories PL gel mixed bed with 5 micron particles
Detector:	Diode-Array
Detection wavelength:	270 nm

3.8.11.3 Polymer Derivatization Analysis

This instrument was also used to characterize the polymers derivatized with chromophores. Signals were collected at 270 and 400 nm. UV/vis spectra were collected at a rate of 1 spectra / second. These spectra were then used to construct a three dimensional GPC plot (i.e. wavelength vs. absorbance vs. time). This characterization will further be discussed in Section 4.3.2.

3.8.12 High Performance Liquid Chromatography (HPLC)

3.8.12.1 Model Compound Kinetic Study

High performance liquid chromatography was performed on a Hewlett Packard 1090 instrument equipped with a UV-vis detector (HPLC-UV/vis). This instrument was utilized to determine the reaction kinetics of the model compound reactions as discussed in Sections 3.4.1 and 4.2. The following conditions were used for this model compound study:

Mobile phase: Acetonitrile/water

Gradient:

<u>Time (min)</u>	<u>Volume % Acetonitrile</u>	<u>Volume % Water</u>
0	50	50
20	100	0

Flow rate: 1 mL/min.

Column: 4.6 mm x 150 mm Keystone Scientific ODSII with 5 micron particles

Detector: Diode-Array

Detection wavelength: 230 nm

The retention time of the internal standard, benzoyl biphenyl, was such that it did not interfere with any other peaks in the spectrum. As a result, the area of each reaction peak was divided by the area of the internal standard peak, thus normalizing each sample. Although several signals were collected at various wavelengths, 230 nm was chosen as the wavelength at which all the components in the reaction gave a reasonable absorbance, therefore all kinetic data was based upon the absorbance at this wavelength.

The purity of new monomers was also determined by this gradient technique.

3.8.12.2 Model Polymerization Kinetic Study

High performance liquid chromatography was also used to analyze a model polymerization as discussed in Sections 3.4.2 and 4.2.5. This analysis was also performed on a Hewlett Packard 1090 instrument equipped with a UV/vis detector (HPLC-UV/vis). The following conditions were used for this model polymerization study:

Mobile phase: Tetrahydrofuran/water

Gradient:

<u>Time (min)</u>	<u>Volume % THF</u>	<u>Volume % Water</u>
0	60	40
15	100	0

Flow rate: 1 mL/min.

Column: 4.6 mm x 150 mm Keystone Scientific ODSII with 5 micron particles

Detector: Diode-Array

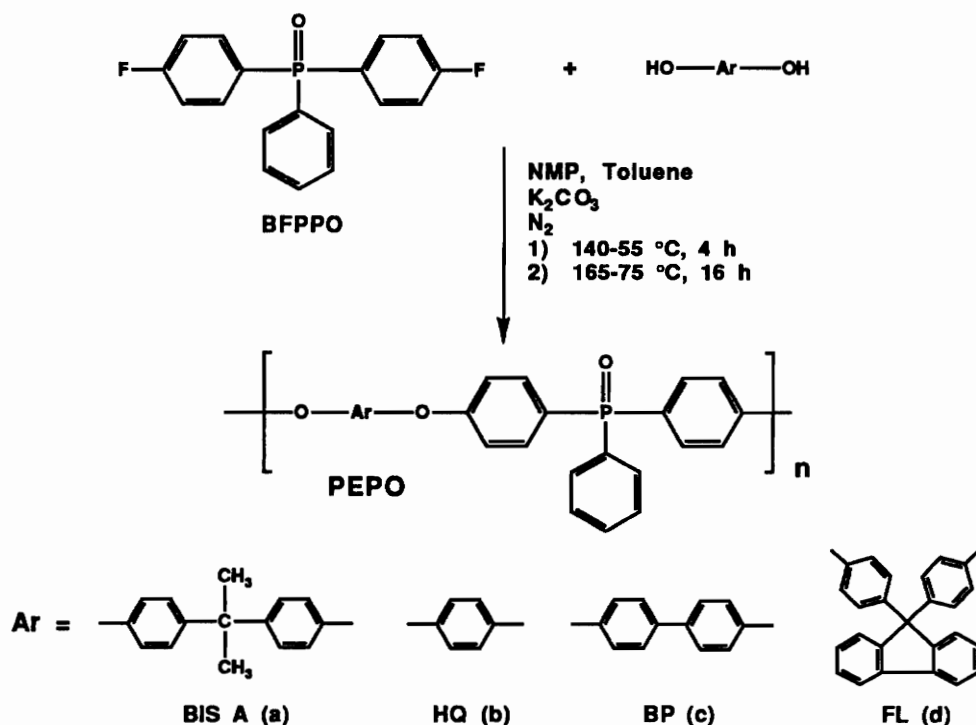
Detection wavelength: 260 nm

4.0 RESULTS AND DISCUSSION

4.1 Polymer Synthesis and Characterization

4.1.1 High Molecular Weight Poly(arylene ether phosphine oxide)s (PEPO)

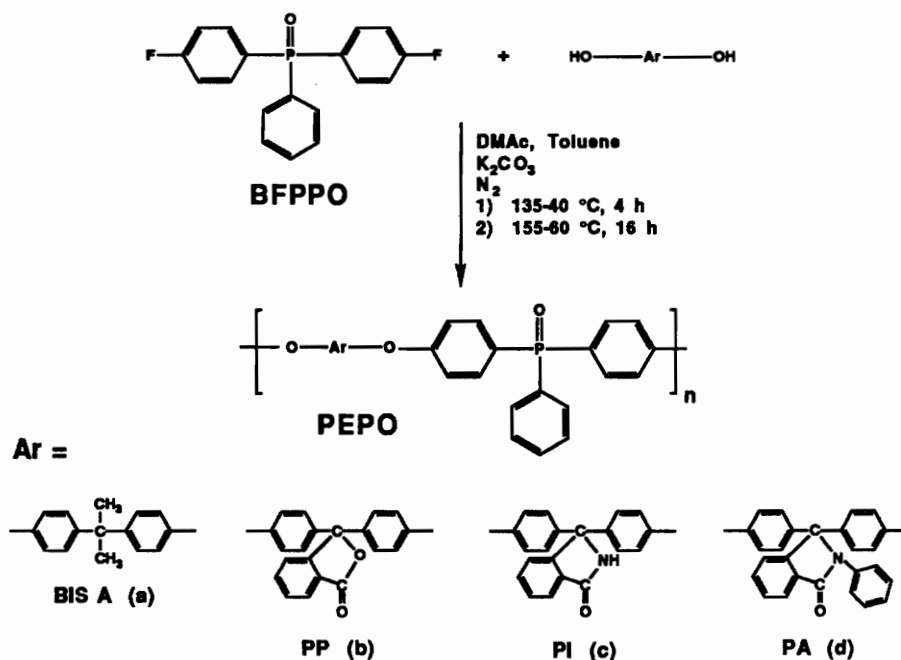
Poly(arylene ether phosphine oxide)s (PEPO) were synthesized by nucleophilic aromatic substitution step polymerization of bis(4-fluorophenyl)phenyl phosphine oxide (BFPPPO) with various bisphenols including bisphenol A (BIS A), hydroquinone (HQ), 4,4'-biphenol (BP), and fluorenone bisphenol (FL) as shown in Scheme 4.1.1.1. These novel polymers possess high temperature stability, flame resistance, and resistance to oxygen plasma.^{199,203,206}



Scheme 4.1.1.1 Examples of common poly(arylene ether phosphine oxide)s (PEPO).

Phenolphthalein and its derivatives are heterocyclic bisphenols that useful building blocks for condensation polymers. Phenolphthalein and related structures are known to most chemists as acid-base indicators, drugs and dyes, etc. In this study, the synthesis and characterization of PEPO made using phenolphthalein and its aminated derivatives are discussed (Scheme 4.1.1.2). It was postulated that the combination of phosphorus and phenolphthalein in the polymer backbone would lead to new heat resistant macromolecules with increased mechanical properties.

Upon successful preparation of these phenolphthalein derived bisphenols, as discussed previously in Section 3.2, novel high molecular weight PEPO were easily prepared by nucleophilic aromatic substitution step polymerization as outlined in Scheme 4.1.1.2b,c,d. The BIS A-PEPO (Scheme 4.1.1.2a) was synthesized and characterized for comparison against the heterocyclic-containing polymers based on phenolphthalein and derivatives.



Scheme 4.1.1.2 Synthesis of PEPO by condensation of BFPPPO with bisphenol A, phenolphthalein and its amide derivatives.

All polymerizations were conducted in freshly distilled DMAc, which was previously dried over calcium hydride. DMAc was used as the solvent in place of N-methylpyrrolidinone (NMP) as utilized previously for polymers of this type synthesized in our laboratories (Scheme 4.1.1.1). The resulting polymers obtained from this process (Scheme 4.1.1.2a-d) were much whiter in color, whereas polymers obtained from the NMP process contained slight brown discoloration most likely from decomposition products of this solvent. Potassium carbonate (K_2CO_3) was added in 15% excess based on the molar amount of bisphenol that was needed for the synthesis of PEPO. For PI-PEPO, a 65% excess of K_2CO_3 was needed to produce high molecular weight polymer. This is most likely due to the amide nitrogen interacting with K_2CO_3 , thereby requiring extra base for deprotonating the bisphenol.

The bisphenol and activated dihalide were added in 1:1 stoichiometry to achieve high molecular weight macromolecules. The polymerizations were carried out at approximately 15% solids. The reaction was dehydrated at 135-40 °C by azeotropic distillation with toluene. The reaction was then heated to 160 °C for 16 h. Upon cooling, chloroform was added to dilute the mixture. After filtering the salts, the polymers were precipitated two times in a 75/25 mixture of methanol/water using a Waring blender. The polymers were then dried at 175 °C under vacuum for 12 h. The resulting white, fibrous polymers were soluble in both chlorinated and polar aprotic solvents except PI-PEPO which was only soluble in polar aprotic solvents. The insolubility of PI-PEPO in chlorinated solvents is likely due to interchain hydrogen bonding.

Spectroscopic analyses (1H NMR, ^{13}C NMR, IR) of PEPO are shown in Appendix 8.2 (Figures 8.2.16 - 8.2.27). The four high molecular weight polymers (Scheme 4.1.1.2a-d) were characterized as discussed in the following sections.

4.1.1.1 Viscosity and GPC Data for PEPO

Intrinsic viscosities for these PEPO homopolymers were obtained to gain a qualitative understanding of their molecular weights. The final polymerization mixtures were very viscous, and the resulting isolated polymers were fibrous in nature. This is an indication that high molecular weight materials were being made. This was further verified with the high values obtained from the intrinsic viscosity results.

In order to obtain a quantitative comparison for the intrinsic viscosity values, GPC was utilized for the PEPO materials. Determination of absolute molecular weight averages and distributions of the poly(arylene ether) samples was based on the concept of universal calibration. Eighteen different monodisperse polystyrene standards were used to construct the calibration curve. The results for the molecular weight characterization for PEPO's are listed in Table 4.1.1.1.1.

Table 4.1.1.1.1 Intrinsic viscosity and GPC analysis of poly(arylene ether phosphine oxide)s. (Structures shown in Scheme 4.1.1.2)

polymer	$[\eta]$ ^{25°C} CHCl ₃ (dl/gm)	GPC ^{60°C} NMP+LiBr			
		$[\eta]$ ^{60°C} NMP+LiBr (dl/gm)	$\langle Mw \rangle$ (kg/mol)	$\langle Mn \rangle$ (kg/mol)	Mw/Mn
BIS A-PEPO	0.44	0.41	55.9	27.7	2.0
PP-PEPO	0.56	0.50	83.2	41.5	2.0
PI-PEPO	0.40	0.39	72.5	33.2	2.2
PA-PEPO	0.47	0.45	77.4	38.3	2.0

From the values given in Table 4.1.1.1.1, it is seen that the PEPO's are high molecular weight materials which are above the chain entanglement molecular weight. The strong correlation between the intrinsic viscosities done with a viscometer vs. those obtained by the GPC confirms the utility of the universal calibration. The PEPO's have similar molecular weights and appear to be well-defined high molecular weight systems for comparison. It is interesting to note that the PI-PEPO has a polydispersity which deviates from 2.0. This would indicate that the PI monomer has a side reaction during the step-growth polymerization, although high molecular weights are obtained.

4.1.1.2 Thermal and Mechanical Properties for PEPO

Thermal Analysis. The thermal properties of the BIS A, PP, PI, and PA-PEPO were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) as shown in Table 4.1.1.2.1. DSC analysis of the poly(arylene ether)s, showed no indications of crystallinity. Dynamic TGA indicates excellent thermal stability at temperatures up to 525 °C in air. The glass transition temperatures (T_g) for the phenolphthalein-based polymers all have values >265 °C .

It can be seen from the results in Table 4.1.1.2.1 that PP-PEPO has a 67 °C increase in glass transition (T_g) as compared to the typical BIS A-PEPO. This is likely due to a combination of the increased backbone rigidity and interchain cohesion, due to the pendant heterocycle along the polymer backbone. Other interesting trends include a 9 °C increase in T_g of PA-PEPO as compared to PP-PEPO. This suggests an increase in the stiffness of the backbone as a result of the N-phenyl moiety. Lastly, it can be seen that PI-PEPO has a 45 °C increase in T_g over PP-PEPO and a 34 °C increase over PA-PEPO. The PI-PEPO has an amide hydrogen present in the pendant heterocycle. The significantly higher T_g is likely due to the interchain hydrogen bonding ability of this amide group.³⁷⁷

Table 4.1.1.2.1 Thermal characterization for poly(arylene ether phosphine oxide)s.

polymer	$[\eta]$ ^{25°C} CHCl ₃ (dl/gm)	TGA (°C) ^a 5% Wt. loss in air	T _g (°C) ^b
BIS A-PEPO	0.44	507	200
PP-PEPO	0.56	496	267
PI-PEPO	0.40	484	312
PA-PEPO	0.47	522	278

a) Scan rate of 10 °C/min.

b) Determined from second scan at 10 °C/min.

Another interesting characteristic of phenolphthalein is its ability to ring-open and crosslink at high temperatures as discussed previously in Section 2.2.3. As a result, polymers containing this moiety have much higher char yields than that of typical poly(arylene ether)s (e.g. bisphenol A based systems).³⁷⁵⁻³⁷⁸ This phenomena is also seen in a TGA analysis of PP-PEPO which has ~40% char yield at 700 °C as compared to BIS A-PEPO which has ~20% char remaining at 700 °C.

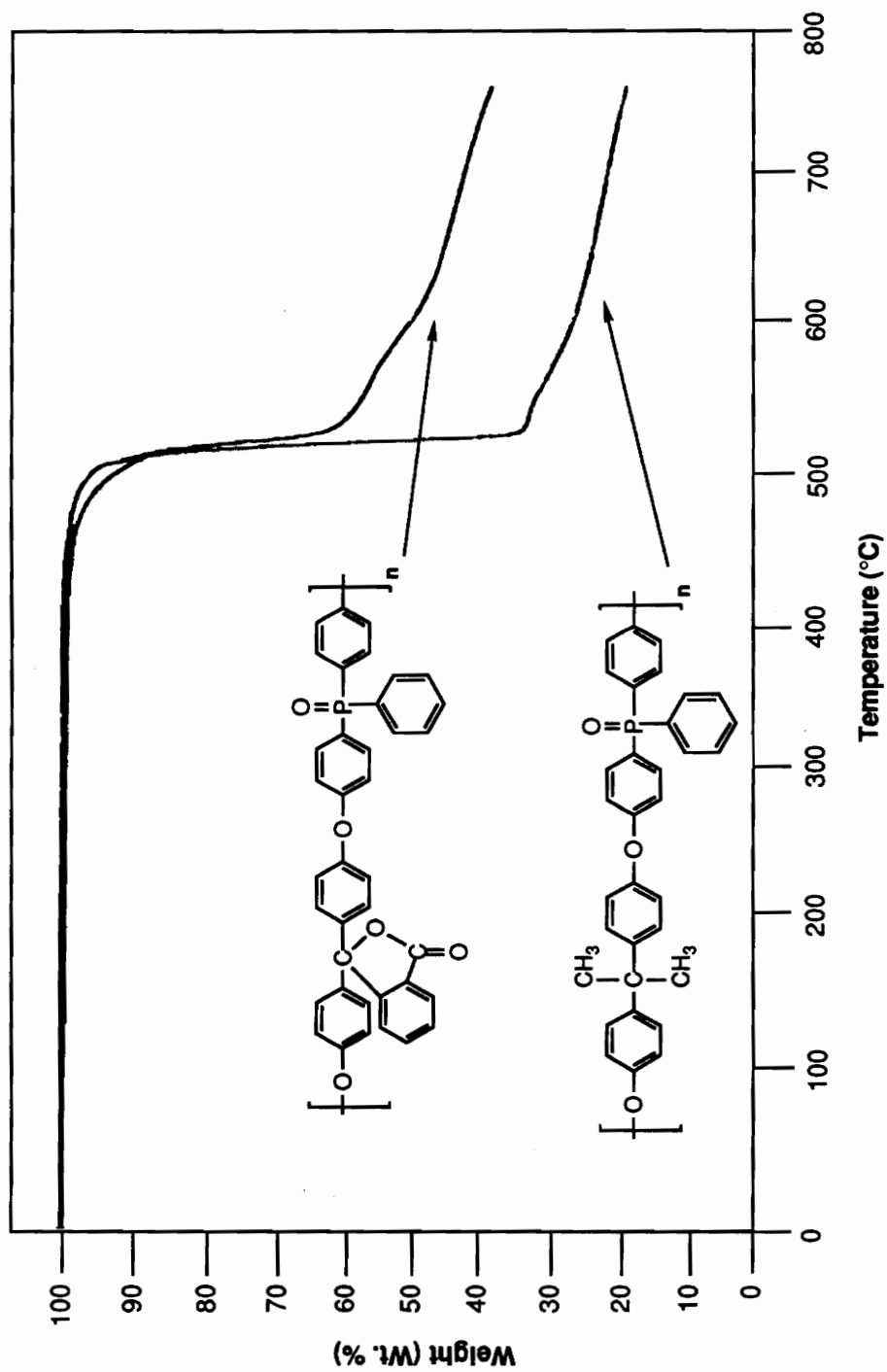


Figure 4.1.1.2.1 TGA analysis of BIS A-PEPO and PP-PEPO. (10 °C/min in air)

Mechanical Properties. Solution cast films of the BIS A, PP, PI, and PA-PEPO's indicated that they are amorphous, transparent, and rigid. These films were ductile, verifying that the polymers were well above the chain entanglement molecular weight. The films prepared from BIS A, PP, and PA-PEPO were cast from chloroform onto a glass plate, whereas the PI-PEPO was cast from DMAc. This was due to the fact that the PI-PEPO was not soluble in chloroform due to extensive inter-chain hydrogen bonding. The films were allowed to dry overnight at room temperature and placed in a vacuum oven where the temperature was slowly increased to 200 °C over a period of 3 days. The modulus was measured on an Instron using dogbone samples cut from the films. Approximately 10 samples were tested and the results were averaged as shown in Table 4.1.1.2.2.

Table 4.1.1.2.2 Mechanical properties of PEPO's.

polymer	GPC $\langle M_n \rangle$ (kg/mol)	Young's * Modulus (ksi)	% Strain * at Break
BIS A-PEPO	27.7	399 \pm 60.6	33 \pm 6.7
PP-PEPO	41.5	444 \pm 48.5	31 \pm 6.3
PI-PEPO	33.2	480 \pm 23.5	18 \pm 5.6
PA-PEPO	38.3	495 \pm 50.1	7 \pm 1.6

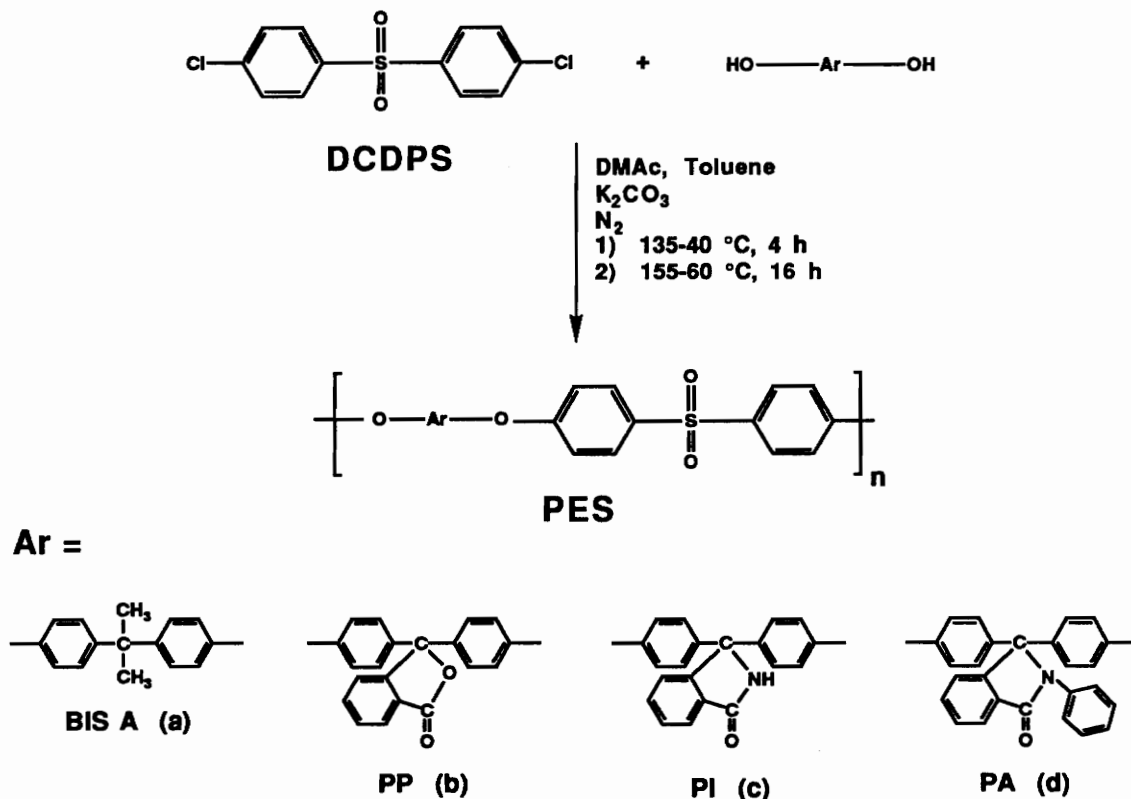
* Values from cast films: chloroform (BIS A, PP, PA-PEPO); DMAc (PI-PEPO)

Since these PEPO materials are high molecular weight as verified by GPC, the mechanical properties should be somewhat independent of molecular weight differences. It can be seen from these results that an improvement of ~10% in modulus is obtained by using PP in place of Bis A. Incorporating PI results in the modulus increasing another 10% which is likely due to increased inter-chain forces. Incorporating PA results in yet another increase of ~5%. This is attributed to both an increase in intermolecular forces as well as increased rigidity of the polymer backbone. The % elongation is similar for both BIS A and PP-PEPO, yet declines for PI and PA-PEPO. This is expected due to the increasing rigidity of the polymer backbone and inter-chain forces, thereby making it a more brittle system.

4.1.2 High Molecular Weight Poly(arylene ether sulfone)s (PES)

High molecular weight poly(arylene ether sulfone)s (PES) were prepared as outlined in Scheme 4.1.2.1 by the same conditions as described previously in Section 4.3.1 for the PEPO's.

These four high molecular weight PES materials were synthesized for comparison against the PEPO materials that were made with the same bisphenols. Spectroscopic analysis (^1H NMR, ^{13}C NMR, IR) of PES is given in Appendix 8.2. The characterization of these materials as well as comparisons against the PEPO materials will be discussed in the following sections.



Scheme 4.1.2.1 Synthesis of PES by condensation of DCDPS with bisphenol A, phenolphthalein and its amide derivatives.

4.1.2.1 Viscosity and GPC Data for PES

Intrinsic viscosities for these PES homopolymers were obtained to gain a qualitative understanding of their molecular weights. In order to obtain a quantitative comparison for the intrinsic viscosity values, GPC was utilized for the PES materials. Determination of absolute molecular weight averages and distribution of the poly(arylene ether) samples was based on the concept of universal calibration. Eighteen different monodisperse polystyrene standards were used to construct the calibration curve. The results for the molecular weight characterization for PES's are listed in Table 4.1.2.1.1.

Table 4.1.2.1.1 Intrinsic viscosity and GPC analysis of poly(arylene ether sulfone)s (PES).

polymer	$[\eta]$ ^{25°C} CHCl ₃ (dl/gm)	GPC ^{60°C} NMP+LiBr			
		$[\eta]$ ^{60°C} NMP+LiBr (dl/gm)	<Mw> (kg/mol)	<Mn> (kg/mol)	Mw/Mn
BIS A-PES	0.44 *	0.40 *	51.5	26.2	2.0
PP-PES	1.54 **	1.49 **	194	95.5	2.0
PI-PES	0.39	0.39	57.7	22.8	2.5
PA-PES	1.16	1.08	285	132	2.1

* Gel portion removed.

** Gel portion included.

From Table 4.1.2.1.1, it can be seen that BIS A, PP, PI and PA-PES are high molecular weight materials which are above the chain entanglement molecular weight. The strong correlation between the intrinsic viscosities obtained using a viscometer vs. those obtained by the GPC confirms the utility of the universal calibration by which these values were based. The PES's appear to have a large scatter in the molecular weights obtained. This scatter is due to the formation of an insoluble gel in the BIS A and PP-PES reactions. The gel in the BIS A system was filtered out prior to analysis, whereas very little gel formed in the PP-PES reaction and therefore it was not removed. With these differences, the PES systems are well above the chain entanglement molecular weight, thus can be used for comparison. It is interesting to note that the PI-PES system has a polydispersity which

deviates from 2.0 as was seen previously in Table 4.1.1.1.1 for the PI-PEPO. This would indicate that the PI monomer has a side reaction during the step-growth polymerization, although high molecular weight was obtained.

4.1.2.2 Thermal Properties of PES

The high molecular weight PES materials were analyzed with both TGA and DSC for comparison of thermal properties. These values are given in Table 4.1.2.2.1.

It is interesting to note that the BIS A, PP, PI, and PA-PES's showed the same trend in T_g 's as the corresponding PEPO structures as described previously in Table 4.1.1.2.1. As a result, the same explanations hold true for the variations in results. The fact that the T_g of these polymers can be raised by ~ 110 °C by incorporating PI vs. Bis A into the backbone is remarkable.

Table 4.1.2.2.1 Thermal characterization for poly(arylene ether sulfone)s.

polymer	$[\eta]$ ^{25°C} CHCl ₃ (dl/gm)	TGA (°C) ^a 5% Wt. loss in air	T_g (°C) ^b
BIS A-PES	0.44 [*]	505	188
PP-PES	1.54 ^{**}	496	267
PI-PES	0.39	491	296
PA-PES	1.16	528	280

* Gel portion removed. ** Gel portion included.

a) Scan rate of 10 °C/min.

b) Determined from second scan at 10 °C/min.

By comparing the results in Table 4.1.1.2.1 with Table 4.1.2.2.1, it can be seen that the T_g values for PP-PEPO and PP-PES are essentially the same. Likewise, the T_g 's are very close for PA-PEPO and PA-PES. A large difference can be seen in which the T_g for PI-PES is significantly lower (~ 16 °C) than PI-PEPO. This could indicate that the phosphine oxide group is more hydrogen bonded to the N-H moiety.

4.2 Model Study of Poly(arylene ether) Synthesis

4.2.1 Bisphenol-A + 4-Chlorodiphenylsulfone Model Compound Reaction

This model study was carried out using the same reaction conditions as the poly(arylene ether) polymerizations performed during this investigation. These conditions make it difficult to determine kinetic rate constants because of the following:

- 1) nonisothermal (135 - 155 °C)
- 2) concentration changes (toluene is removed)
- 3) heterogeneous (K_2CO_3 and bisphenate formed with KOH)
- 4) solvent (DMAc hydrolyzed by KOH)

However, since various stages of the reaction are isothermal, the calculation of rate constants may be possible and will be investigated at a later time.

This model study was done to accomplish a number of objectives. They are as follows:

- 1) determine advantages of using K_2CO_3 over KOH in a polycondensation process
- 2) investigate the reactivity differences of phenolphthalein (PP) and bisphenol A (BIS A) in both weak and strong base conditions
- 3) determine if the carboxylate moiety of the PP quinone participates in nucleophilic displacement

High Performance Liquid Chromatography (HPLC) was utilized to monitor the polycondensation process using a weak base, K_2CO_3 , vs. a stronger base, KOH. With this analytical technique, the loss of monomers, and appearance of intermediates and

products can be monitored vs. reaction time. In Figure 4.2.1.1, the components that were monitored during the BIS A model reaction are identified both by structure and acronym.

Figure 4.2.1.2 is an example of HPLC traces of aliquots which were taken at time 0, 5, and 10 h. Each aliquot was quenched with an excess amount of acetic acid before HPLC analysis. As a result, only the protonated species are observed in the kinetic evaluations. The three HPLC traces (of the twenty five collected for each reaction) shown in Figure 4.2.1.2 were chosen as a representative trend for the typical model study reaction. At time 0, only the starting materials (BIS A and the model activated halide, 4-CDPS) and the internal standard (ISTD) (4-benzoylbiphenyl) are visible. As the reaction proceeds to 5 h, the peak intensity of the BIS A and 4-CDPS starting materials decrease as they are consumed, while the Mono-BIS A intermediate and Di-BIS A product are forming as shown in Figure 4.2.1.2. At the end of 10 h, the reaction is complete as only Di-BIS A peak is observed. Some of the 4-CDPS remains at the end of the reaction due to 5 % excess being used to ensure complete reaction of the BIS-A.

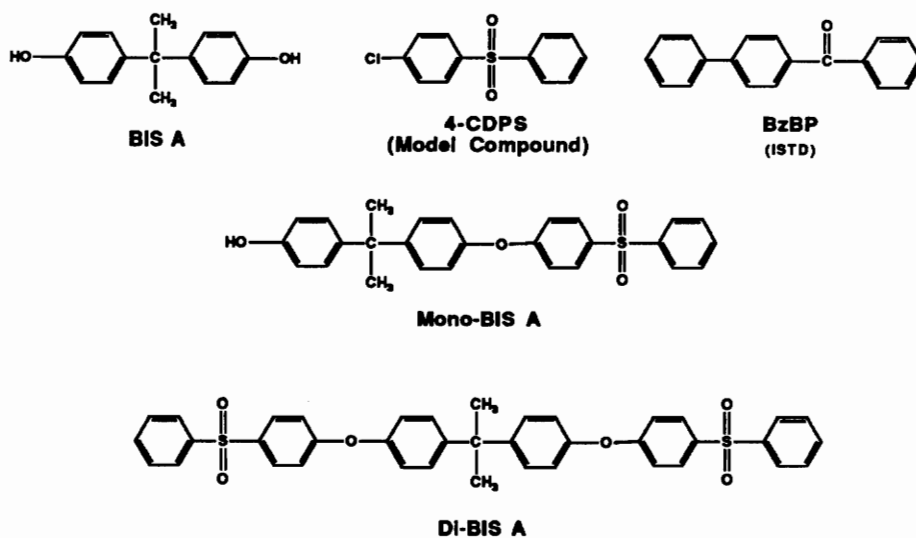
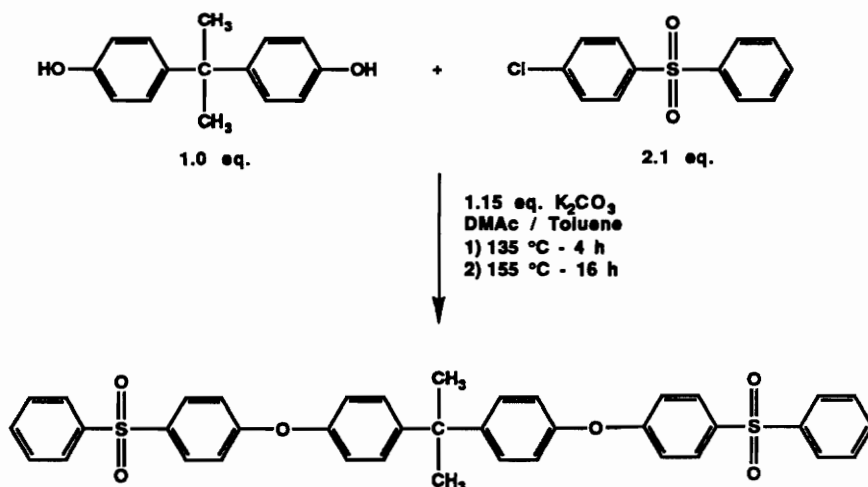


Figure 4.2.1.1 BIS A model compound study reactants, internal standard, proposed intermediate, and product as observed in HPLC.

The kinetic graphs shown in this model study were constructed by plotting the integrated areas from each peak obtained during the reaction vs. time. Calculations (Section 3.4.3) were carried out on the normalized values in order to plot all curves on a % conversion vs. time plot. As a result, the curves can be both quantitatively and qualitatively compared. The following descriptions of each reaction will attempt to do so.

In a polycondensation model study with K_2CO_3 , all reagents can be added to the flask at the beginning of the reaction. This is a major advantage as compared to strong base conditions, because the K_2CO_3 does not hydrolyze the activated halide. The conditions for the BIS A model study with K_2CO_3 as the base are shown in Scheme 4.2.1.1.



Scheme 4.2.1.1 Model compound study reaction conditions for reacting BIS A with 4-CDPS using K_2CO_3 .

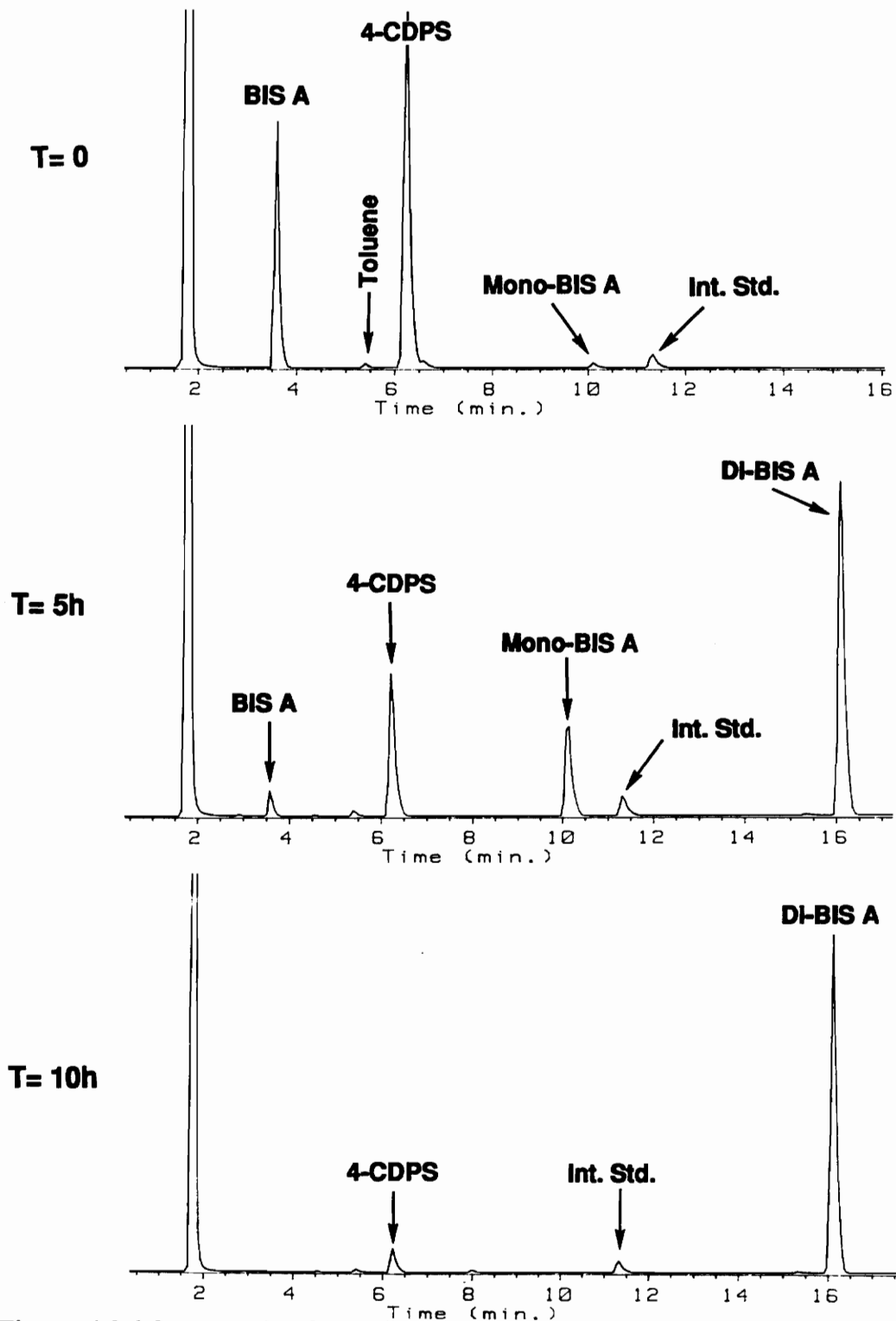
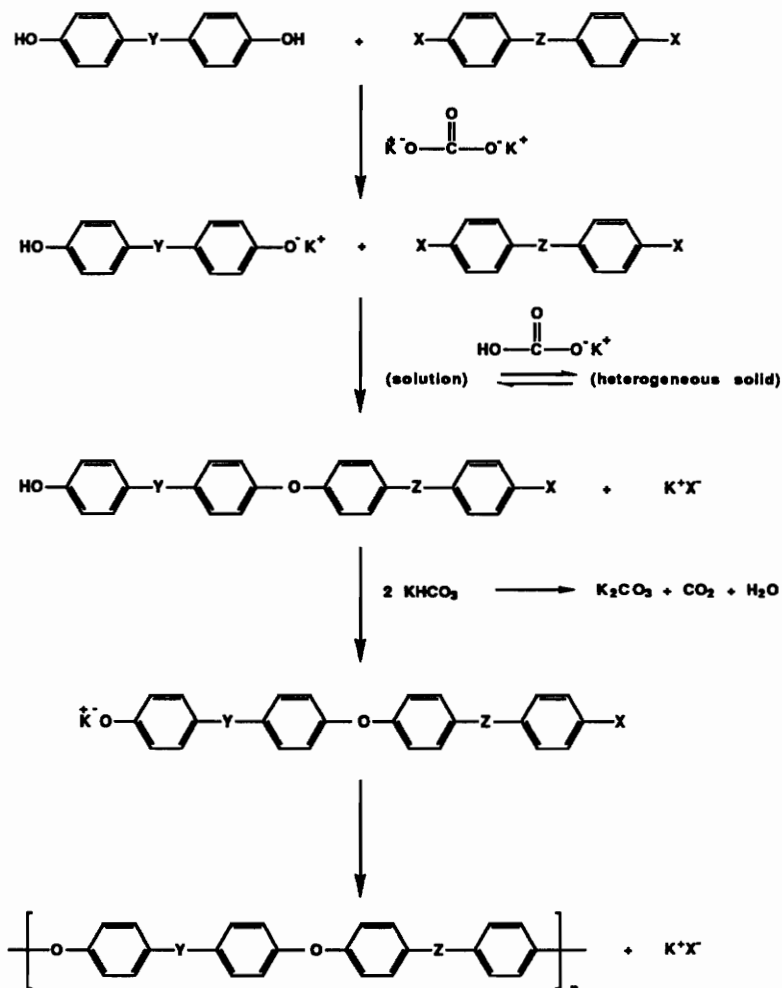


Figure 4.2.1.2 Example of HPLC trace taken from BIS A + 4-CDPS model compound study reaction with K_2CO_3 as the base.

The reaction temperature is increased from 135 °C to 155 °C at 240 min. This temperature increase plays an important role in the kinetics as the Di adduct forms slowly during the initial stages, then rapidly increases after 240 min. Viswanathan, Johnson, and McGrath^{104,105,315} proposed the mechanism shown in Scheme 4.2.1.2 for poly(arylene ether) synthesis using K_2CO_3 as base.



Scheme 4.2.1.2 Proposed mechanism for the formation of poly(arylene ether)s in a potassium carbonate (K_2CO_3) process.^{104,105,315}

It can be seen from this proposed mechanism (Scheme 4.2.1.2) that the weak base, potassium carbonate, is only strong enough to abstract one proton from the bisphenol. Potassium carbonate (K_2CO_3) is then converted to bicarbonate ($KHCO_3$) which is in equilibrium between solution and heterogeneous solid. Two moles of bicarbonate then react to regenerate one mole of K_2CO_3 as well as carbon dioxide, and water. The newly formed K_2CO_3 abstracts the remaining proton of the dimer to continue reacting with another mole of 4-CDPS.

The following differences can be described for each basic condition. K_2CO_3 is a weak base and is only strong enough to abstract one proton. Using 1.0 mole KOH, it is strong enough to abstract both protons, but only enough for 1/2 reaction. Using 2.0 mole KOH conditions, it is strong enough to abstract both protons, and enough for complete reaction. The assumption for complete reaction is that the KOH is completely consumed by the bisphenol and no side reactions occur with the activated halide or solvent.

It can be seen from Scheme 4.2.1.3 that strong base conditions, e.g. KOH, require two steps in which the base and bisphenol must be dehydrated first, then the activated halide added to the formed bisphenate. By using this two-step method, the strong base is consumed by the BIS A, thus none is available to hydrolyze the activated halide.

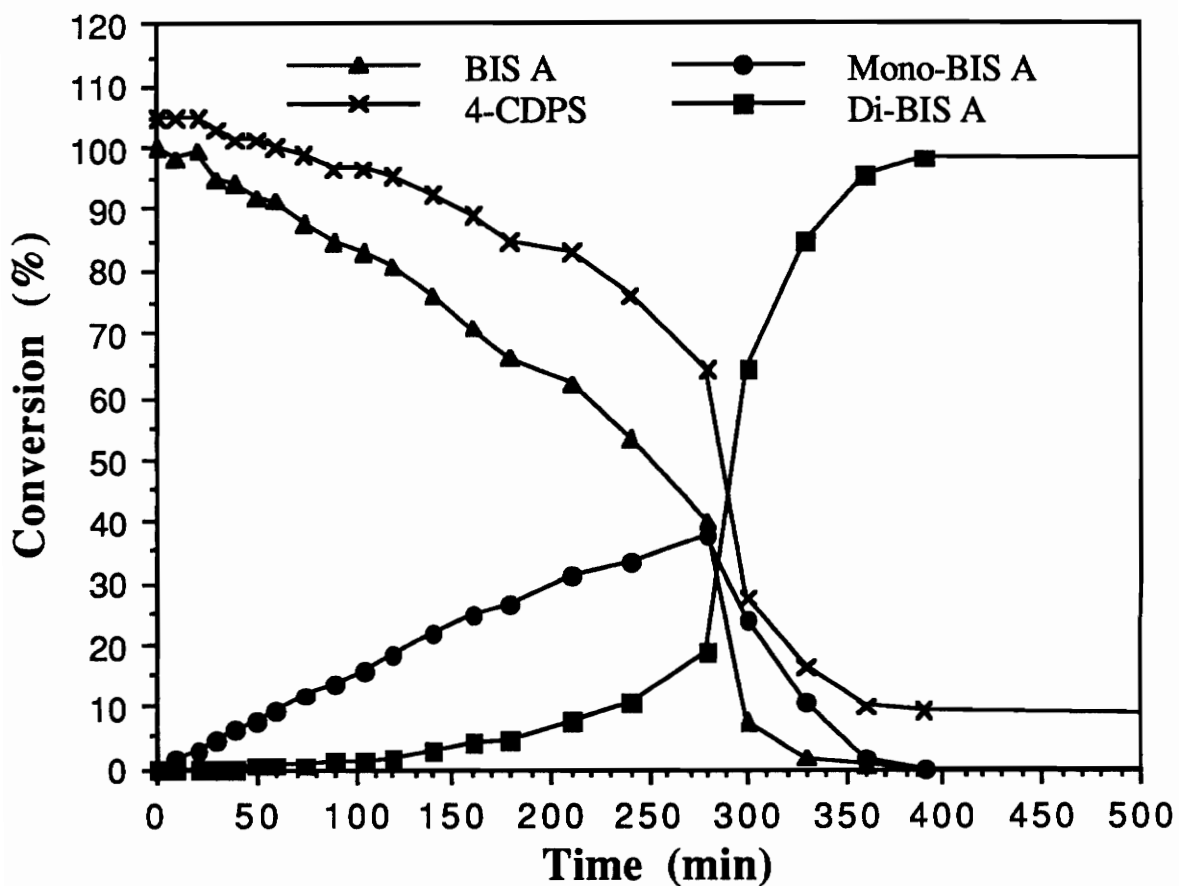


Figure 4.2.1.3 Kinetic plot of BIS A (1 mole) reacting with 4-CDPS (2.1 mole) using 1.15 mole K_2CO_3 .

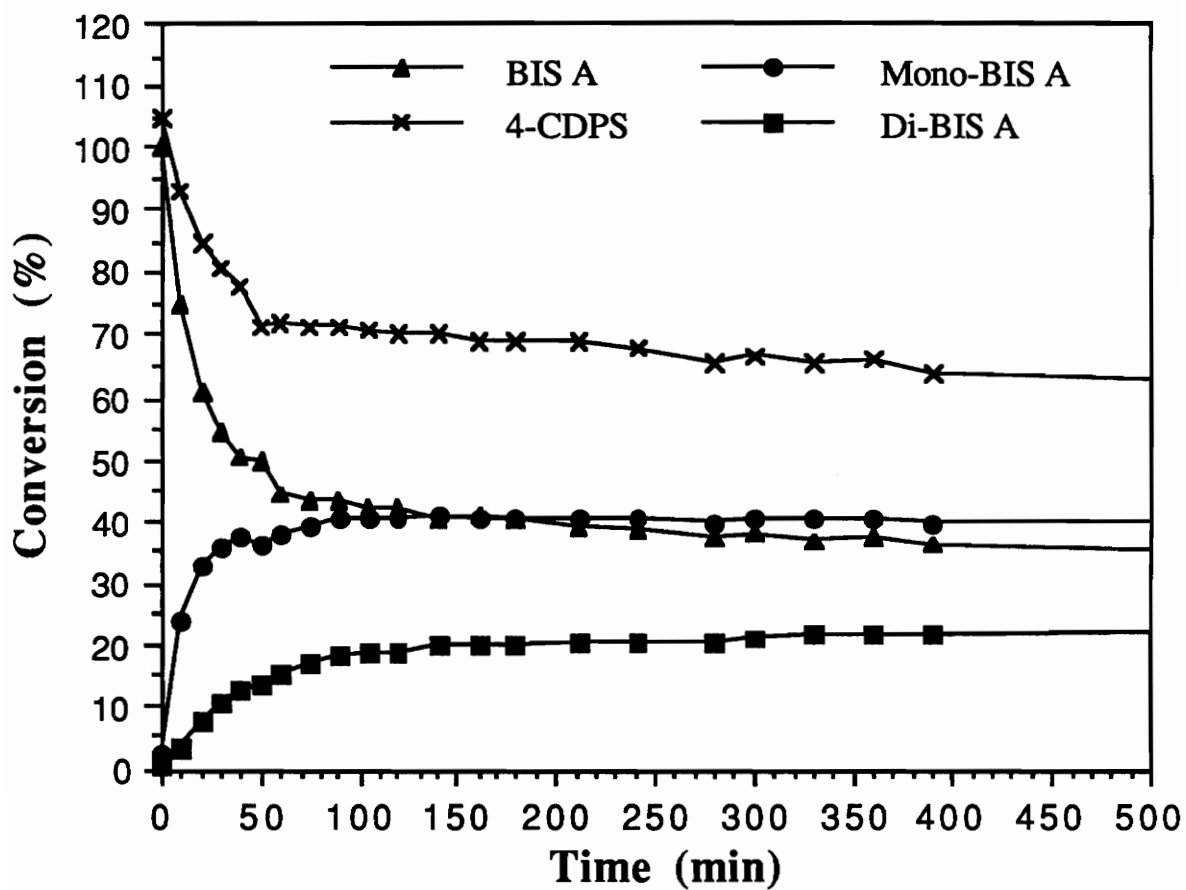


Figure 4.2.1.4 Kinetic plot of BIS A (1 mole) reacting with 4-CDPS (2.1 mole) using 1.0 mole KOH.

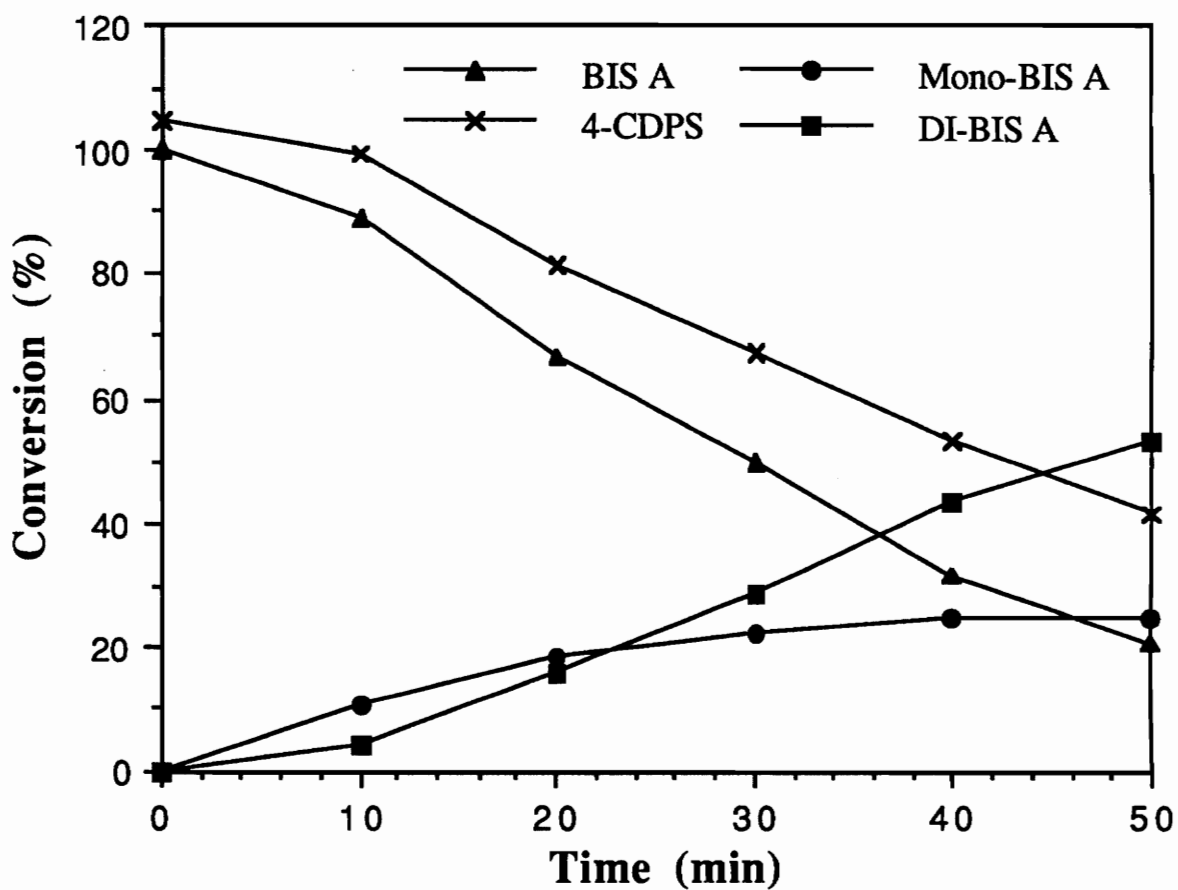


Figure 4.2.1.5 Kinetic plot of BIS A (1 mole) reacting with 4-CDPS (2.1 mole) using 2.0 mole KOH.

Other model studies were carried out to show the effect of 1.0 mole KOH (Figure 4.2.1.4) on the reaction kinetics as compared to 2.0 mole KOH (Figure 4.2.1.5). This comparison was also done to determine what effect the strength of the base has on the reaction kinetics. It is important to emphasize once again that the KOH reactions were completely dehydrated with the BIS A before addition of 4-CDPS as shown previously in Scheme 4.2.1.2. This is crucial to a successful study, because if these reactions are carried out with all components added initially, the base will hydrolyze the activated halide thus terminating the reaction.

With 1.0 mole of KOH (Figure 4.2.1.4), the reaction kinetics of BIS A with 4-CDPS are somewhat different than seen with the same reaction in the presence of K_2CO_3 (Figure 4.2.1.3). The loss of the BIS A does not reach zero due to the point that only half of the required amount of KOH was employed to complete the reaction. Since ~5% excess of 4-CDPS was used, a large amount of this material still remained by the end of the reaction. The most interesting trend lies in the initial formation of both the Mono and Di-BIS A adducts, whereas with the K_2CO_3 reaction, only Mono-BIS A is seen during the first 100 min. In Figure 4.2.1.4, both the Mono and Di-adducts level off as only half the required amount of KOH is available to carry the reaction to completion.

When 2.0 mole KOH are used (Figure 4.2.1.5), there is enough base to allow the reaction to go to completion assuming no interaction of the base with the activated halide or solvent, although in this reaction there was hydrolysis of DMAc. Figure 4.2.1.5 shows that the Mono-BIS A and Di-BIS A adducts are formed initially, with the disappearance of the Mono adduct as the Di adduct continues to form.

Figures 4.2.1.6-8 compares the formation and loss of the individual components under the three basic conditions previously shown in Figures 4.2.1.3-5. Figure 4.2.1.6 was constructed by taking the BIS A curves from Figures 4.2.1.3-5 and plotting them on the same graph. This way, the BIS A loss in each reaction can be compared. In the same

way, the rates of Mono-BIS A and Di-BIS A under the three basic conditions are shown on Figures 4.2.1.7 and 8, respectively.

With K_2CO_3 , a very slow consumption of the BIS A (Figure 4.2.1.6) takes place during the first hour of reaction. Under the strong base conditions of 1.0 and 2.0 mole KOH, the consumption of BIS A is quite rapid. This would indicate the formation of bisphenate due to the stronger basicity of KOH.

A kinetic plot showing the formation of Mono-BIS A intermediate with different bases is shown in Figure 4.2.1.7. The rate of Mono-BIS A formation under different basic conditions was determined from these curves to be: 1.0 mole KOH > 2.0 mole KOH > K_2CO_3 . This trend may be explained on the basis of phenate concentration. With 2.0 mole KOH, bisphenate forms and reacts immediately to form Di-BIS A, thus the Mono-BIS A intermediate builds to only a low level. With 1.0 mole KOH, mostly monophenate forms, thus a much higher concentration of Mono-BIS A is observed.

Comparison of Di-BIS A (Figure 4.2.1.8) under different basic conditions is interesting. With the weak base, K_2CO_3 , the Di adduct starts to form after 60 min., whereas with 2.0 mole KOH, the Di adduct forms immediately. This again shows how the strength of the base effects reaction rate. It is seen from the K_2CO_3 curve that after the reaction is heated from 135 °C to 155 °C at 240 min., the Di adduct rapidly approaches 100% conversion. This would indicate that at the lower temperature of 135 °C, mostly monophenate is formed which can react to form the Mono adduct. After heating to 155 °C, enough thermal energy is put into the system to allow the weak base to decompose the $KHCO_3$, regenerating K_2CO_3 .

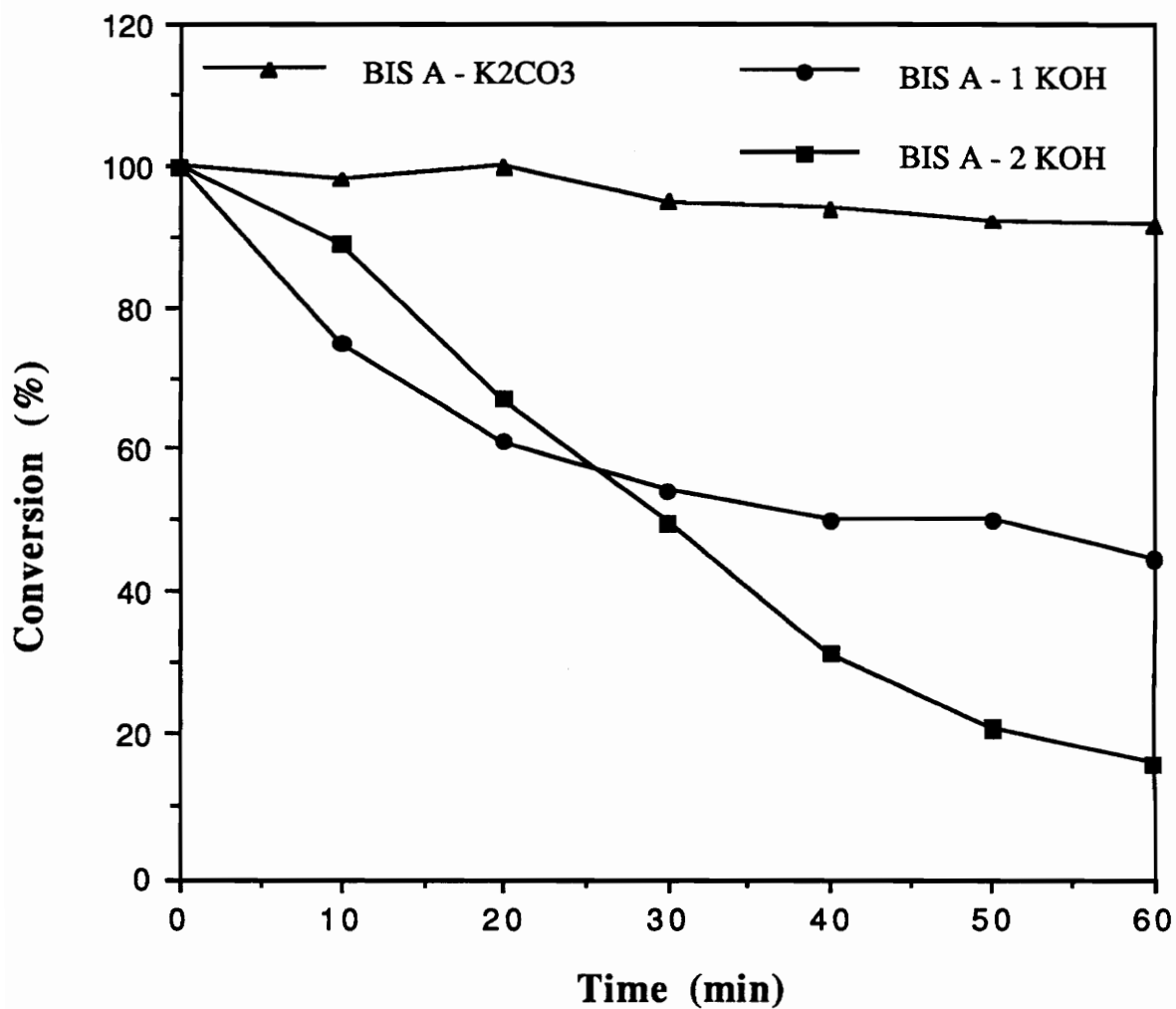


Figure 4.2.1.6 Kinetic plot comparing the BIS A loss in the condensation reaction using different basic conditions. (An overlay of the BIS A curves generated in Figures 4.2.1.3-5)

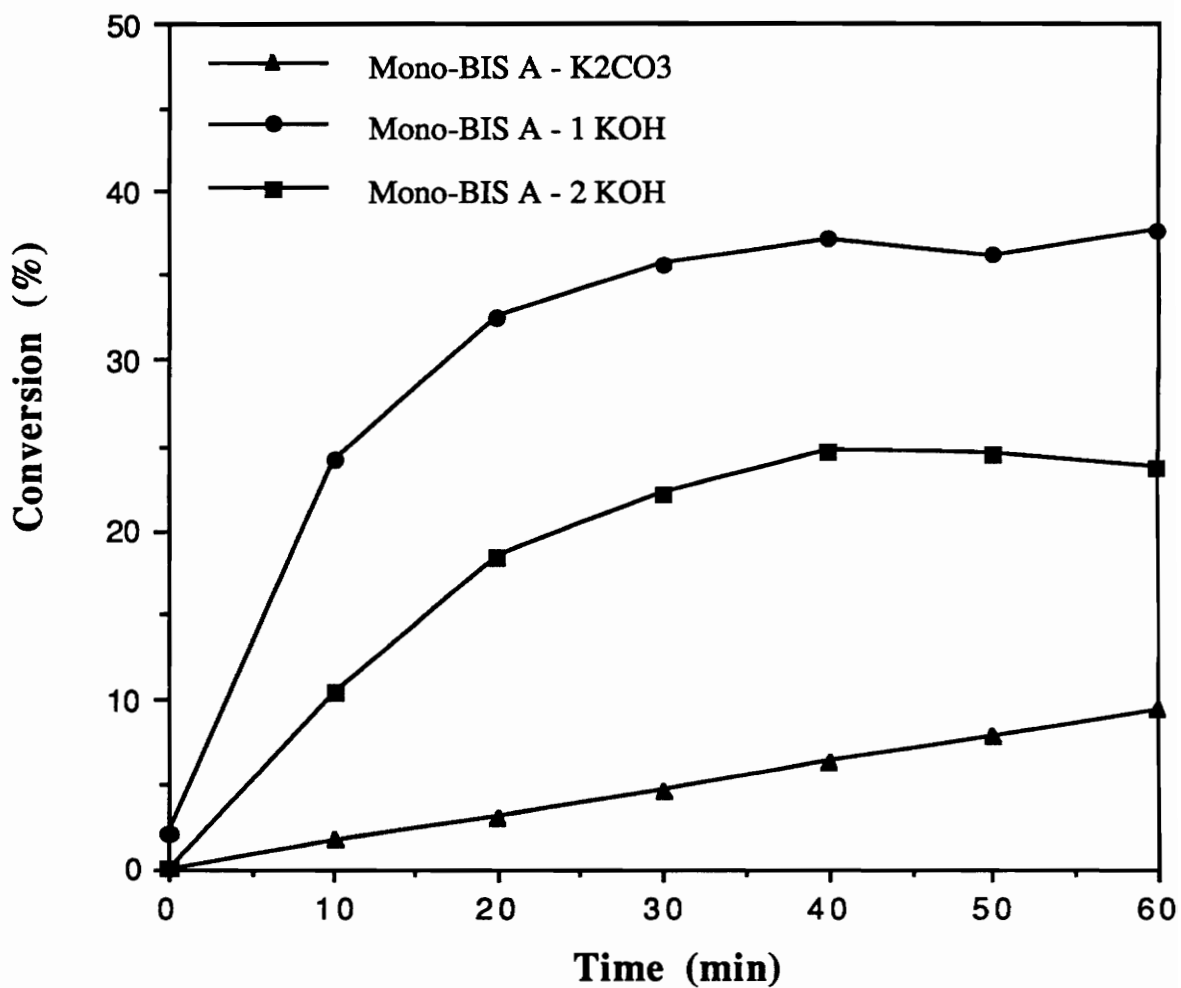


Figure 4.2.1.7 Kinetic plot comparing the Mono-BIS A level in the condensation reaction using different basic conditions. (An overlay of the Mono-BIS A curves generated in Figures 4.2.1.3-5)

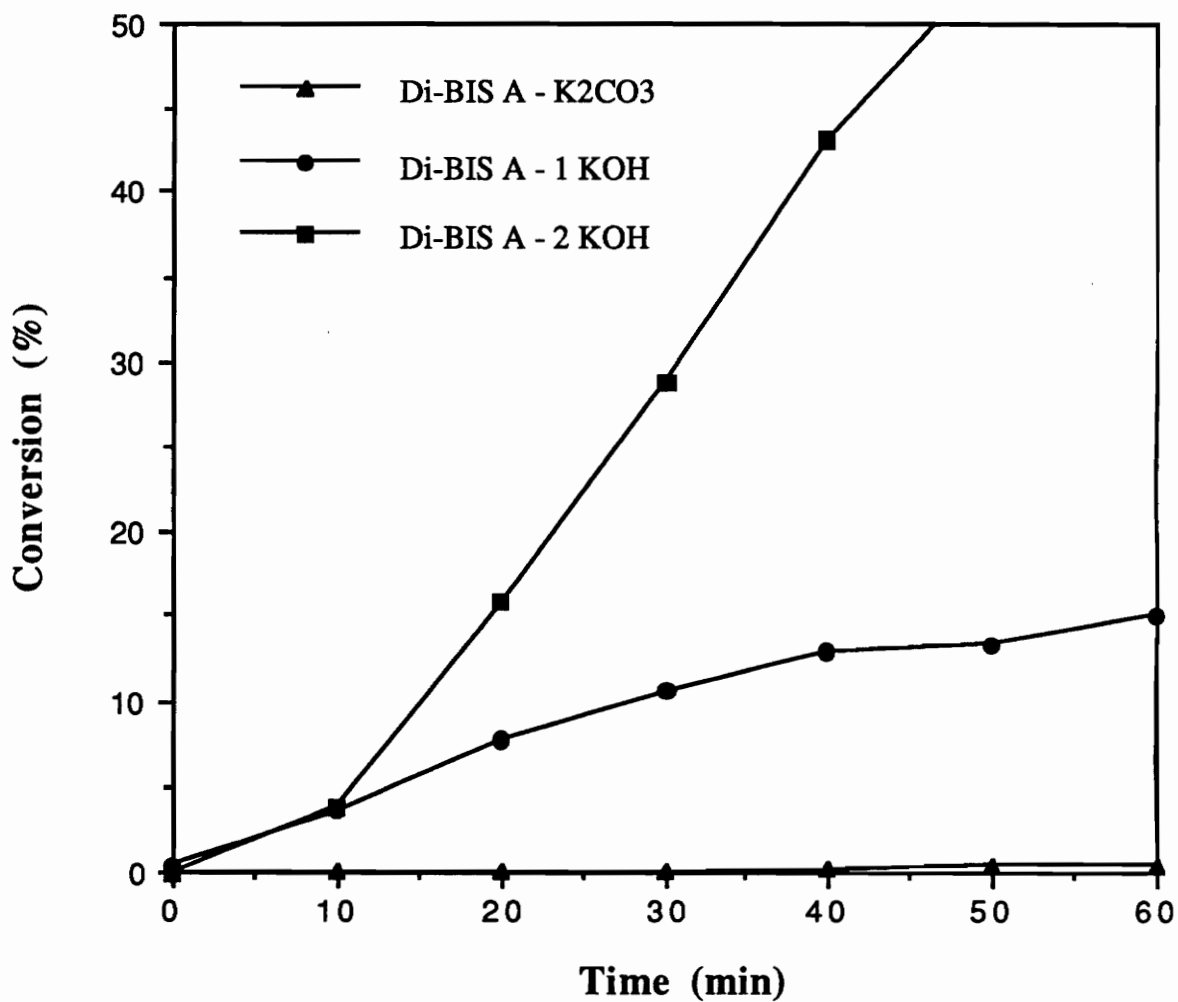
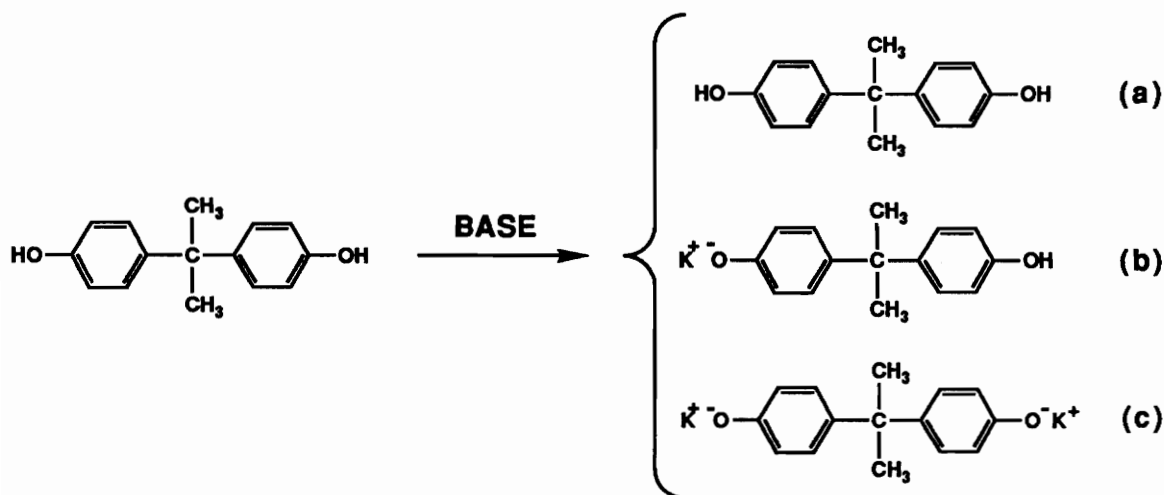


Figure 4.2.1.8 Kinetic plot comparing the Di-BIS A formation in the condensation reaction using different basic conditions. (An overlay of the Di-BIS A curves generated in Figures 4.2.1.3-5)

The results of the BIS A model study suggest the following:

- 1) using K_2CO_3 , the reaction proceeds at a much slower rate as compared to KOH
- 2) using 1.0 mole KOH, the Mono-BIS A formation proceeds at a much faster rate as compared to K_2CO_3 or 2.0 mole KOH, and the Mono adduct is formed at a much faster rate than the Di adduct
- 3) using 2.0 mole KOH, the Di-BIS A formation proceeds at a much faster rate as compared to both K_2CO_3 and 1.0 mole KOH

These observations suggest the hypothesis that with K_2CO_3 at 135 °C, mainly monophenate is formed. When 1.0 mole KOH is used, a high concentration of monophenate is formed. Lastly, with 2.0 mole KOH, bisphenate is formed at 135 °C which is confirmed by ~50% conversion to Di-BIS A after 1 h into the reaction. This hypothesis is shown in more detail in Scheme 4.2.1.4.



Scheme 4.2.1.4 Proposed derivatives of BIS A under different basic conditions.

The proposed relative amounts of BIS A and its salts under various basic conditions (Scheme 4.2.1.4) are given in Table 4.2.1.1.

Table 4.2.1.1 Relative amounts of proposed BIS A derivatives under different basic conditions.

BIS A Derivative (from Scheme 4.2.1.4)	K₂CO₃	1.0 mole KOH	2.0 mole KOH
(a)	Minor	Minor	Trace
(b)	Major	Major	Minor
(c)	Trace	Minor	Major

4.2.2 Phenolphthalein + 4-Chlorodiphenylsulfone Model Compound Reaction

Phenolphthalein (PP) is a bisphenol similar in structure to BIS A. Differences in structure include a heterocyclic lactone in PP where the isopropylidene group is located in BIS A. This structural difference adds to the unique characteristics of this bisphenol in both reaction mechanism and kinetics. In Figure 4.2.2.1, the components that were monitored during the PP model reaction are identified both by structure and acronym.

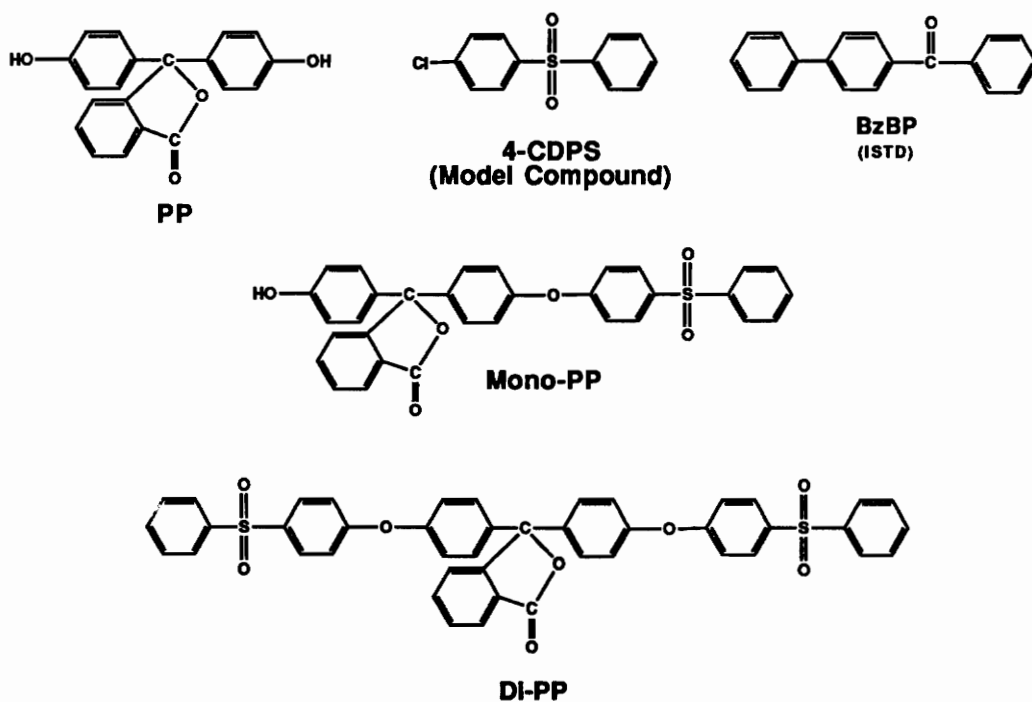
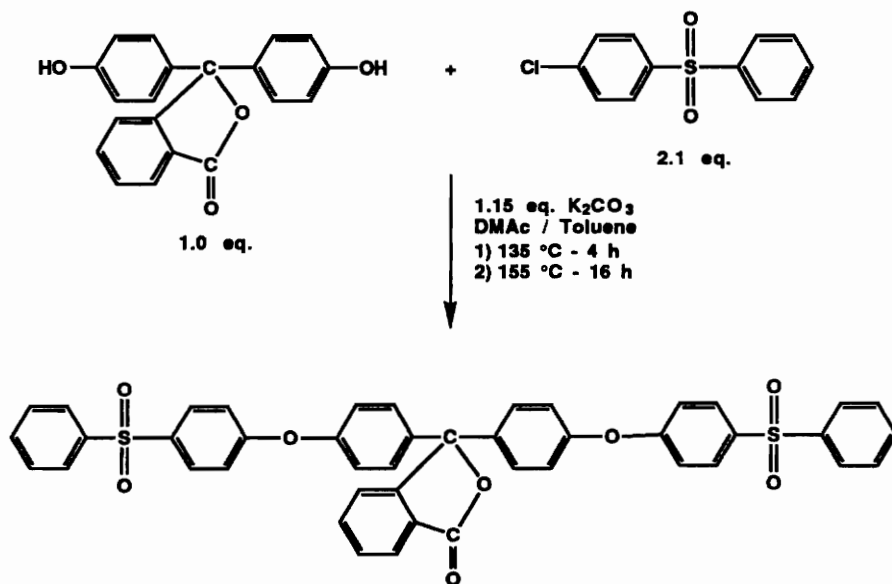


Figure 4.2.2.1 PP model compound study reactants, internal standard, proposed intermediate, and product as observed in HPLC.

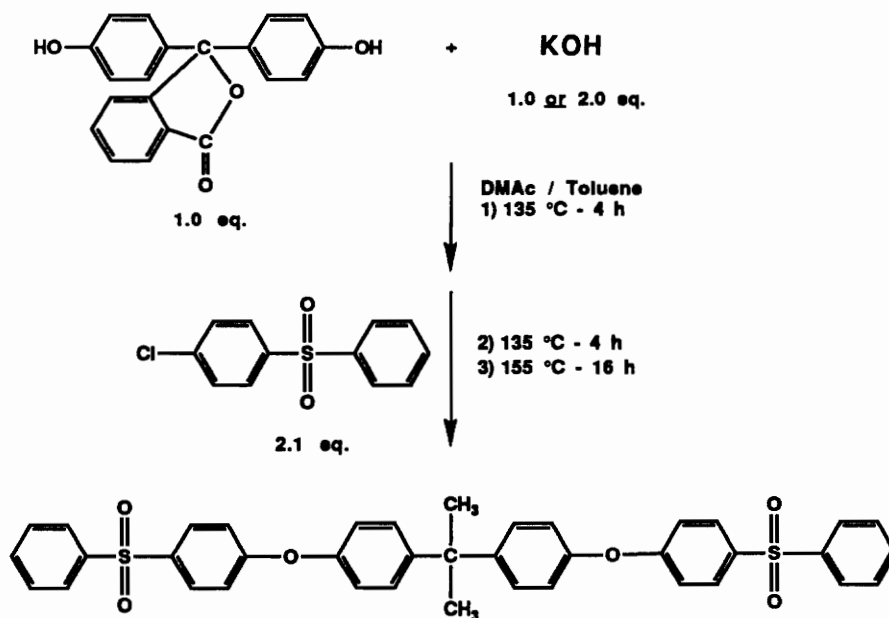
The conditions for the PP model compound study with K_2CO_3 as the base are shown in Scheme 4.2.2.1. These conditions were exactly the same as described previously for the BIS A model compound study to maintain consistency. Aliquots were sampled periodically throughout the reaction, neutralized with acetic acid, and analyzed using an HPLC.



Scheme 4.2.2.1 Model compound study reaction conditions for reacting PP with 4-CDPS under K_2CO_3 conditions.

It can be seen from Scheme 4.2.2.2 that the PP model compound reaction under strong base conditions, e.g. KOH, requires two steps in which the base and bisphenol must be dehydrated first, then the activated halide added to the isomeric mixture of PP. By using this two-step method, the strong base is consumed by the bisphenol, thus none is available to hydrolyze the activated halide.

The kinetics for the reaction of PP with 4-CDPS in K_2CO_3 are shown in Figure 4.2.2.2. The kinetics of this reaction are very similar to that of BIS A as shown previously in Figure 4.2.1.3. It can be seen in Figure 4.2.2.2 that under K_2CO_3 conditions, PP and 4-CDPS are consumed and approach zero as condensation between the two occurs. The curve representing 4-CDPS does not end at zero due to ~5% excess being utilized to ensure complete reaction of the bisphenol. An excellent correlation is seen as the Mono-PP adduct forms and disappears due to Di-PP adduct formation. The reaction temperature is increased from 135 °C to 155 °C at 240 min. This temperature increase plays an important role in the kinetics as the Di adduct forms slowly during the initial stages, then rapidly increases after 240 min.



Scheme 4.2.2.2 Model compound study reaction conditions for reacting PP with 4-CDPS under KOH conditions.

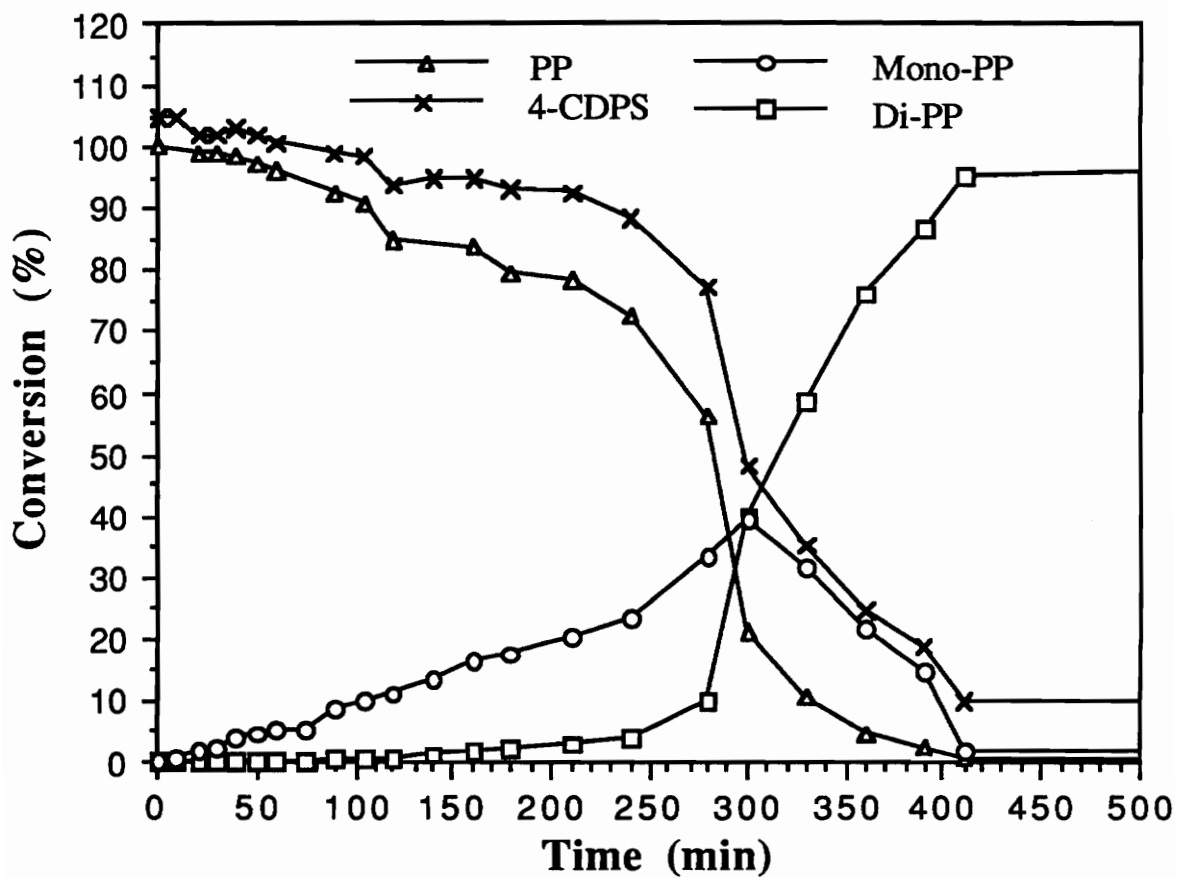


Figure 4.2.2.2 PP (1.0 mole) reacting with 4-CDPS (2.1 mole) using 1.15 mole K_2CO_3 .

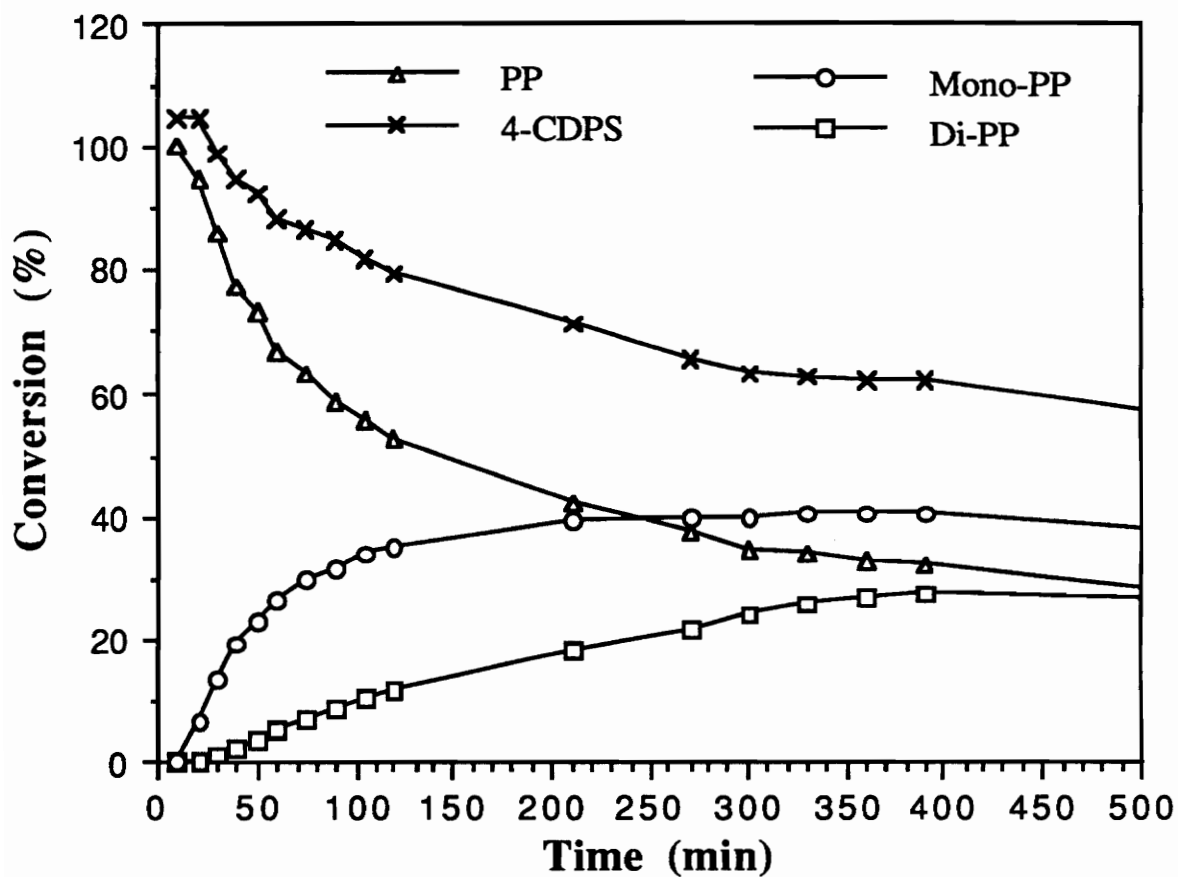


Figure 4.2.2.3 PP (1.0 mole) reacting with 4-CDPS (2.1 mole) using 1.0 mole KOH.

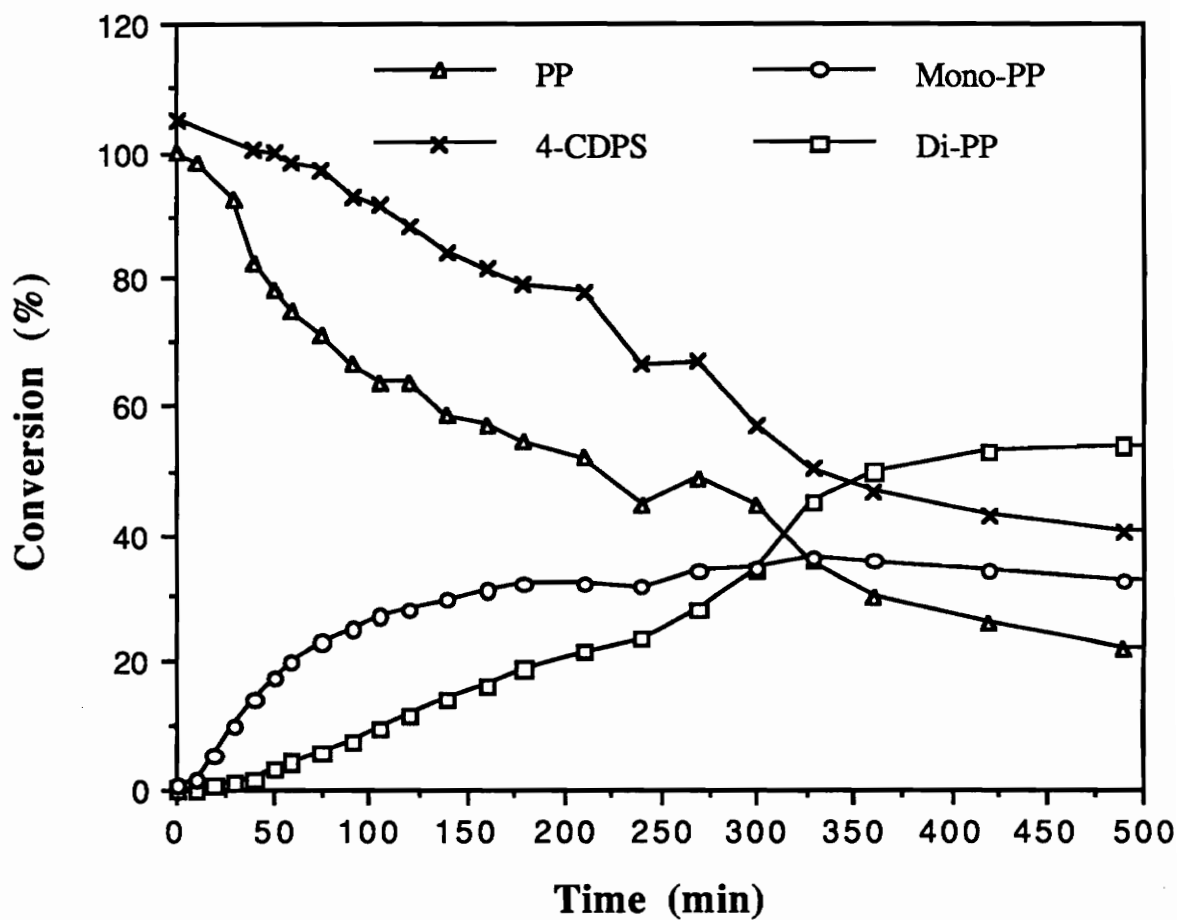


Figure 4.2.2.4 PP (1.0 mole) reacting with 4-CDPS (2.1 mole) using 2.0 mole KOH.

The kinetic plot of the PP model study reaction with 1.0 mole KOH is shown in Figure 4.2.2.3. It is seen that initially both PP and 4-CDPS approach zero and then level off as only half the base was available to carry the reaction to completion. Both Mono-PP and Di-PP adducts form initially which is to be expected due to the strong base conditions.

In Figure 4.2.2.4, the plot of the PP model reaction with 2.0 KOH gave interesting results. The reaction was slower than in the 1.0 KOH reaction in both consumption of starting materials and formation of intermediate and product. This is likely due to the precipitation of the di-potassium salt of PP from solution.

The results of the PP model study suggest the following:

- 1) using K_2CO_3 , the reaction proceeds at a much slower rate as compared to KOH
- 2) using 1.0 mole KOH, the Mono-BIS A formation proceeds at a faster rate as compared to K_2CO_3 or 2.0 mole KOH, and the Mono adduct is formed at a much faster rate than the Di adduct
- 3) using 2.0 mole KOH, the Di-BIS A formation proceeds at a much faster rate as compared to K_2CO_3

Figure 4.2.2.5 depicts in a different way what was previously shown in Figures 4.2.2.2-4. For example, Figure 4.2.2.5 was constructed by taking the PP curves from Figures 4.2.2.2-4 and plotting them on the same graph. This way, the PP loss in each reaction can be compared. Following the same reasoning, to compare the mono and di formation, the curves from Figures 4.2.2.2-4 were placed accordingly in Figures 4.2.2.6 and 7.

In looking at a plot of just PP loss under different basic conditions (Figure 4.2.2.5), it is seen that with K_2CO_3 , ~20% of PP is consumed during the first 4 h. Upon heating from 135 °C to 155 °C, the PP concentration rapidly approaches zero as it is converted to product. Under KOH conditions, the same trend is observed for both 1.0 and 2.0 mole KOH in which ~50% of PP is consumed during the first 4 h. It is important to

emphasize that the curves represent unreacted PP. Any quinones that were formed under strong KOH conditions were ring closed back to PP when the aliquots were quenched with acetic acid.

Figure 4.2.2.6 represents a kinetic plot of the formation of Mono-PP adduct under different basic conditions. The following reaction rates for Mono-PP formation is seen from the curves: 1.0 mole KOH > 2.0 mole KOH > K_2CO_3 . This trend will be used to formulate a proposed mechanism for how PP undergoes condensation with 4-CDPS to form the Mono adduct.

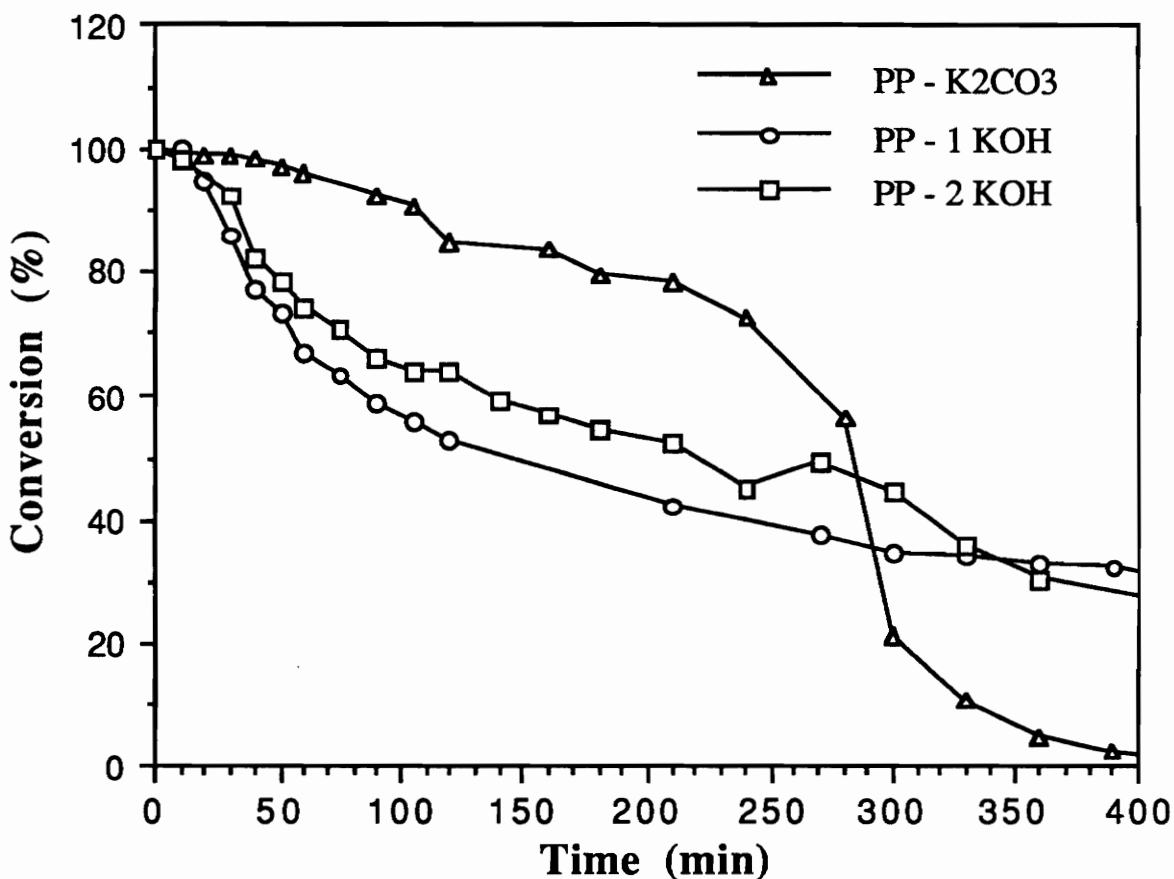


Figure 4.2.2.5 Kinetic plot comparing PP loss in the condensation reaction under different basic conditions. (An overlay of the curves generated in Figures 4.2.2.2-4)

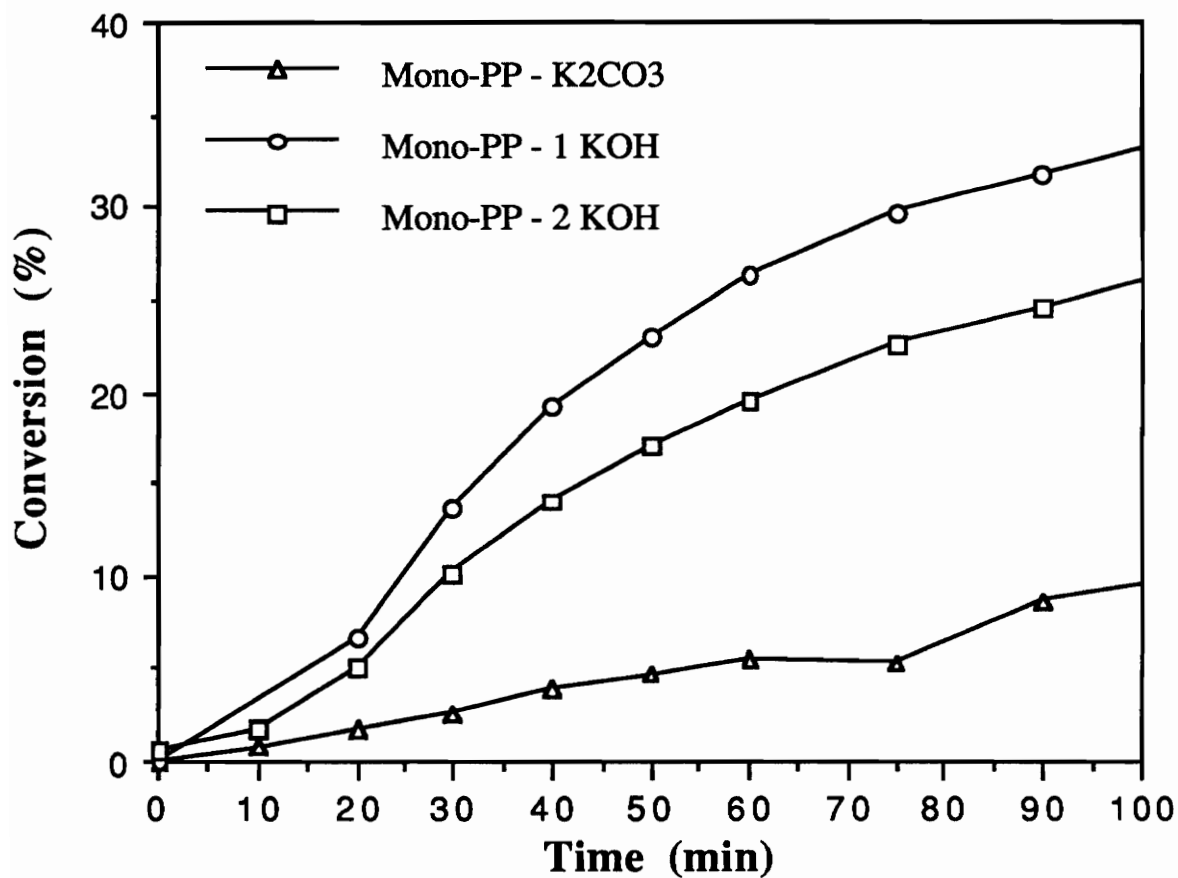


Figure 4.2.2.6 Kinetic plot comparing Mono-PP formation in the condensation reaction under different basic conditions. (An overlay of the curves generated in Figures 4.2.2.2-4)

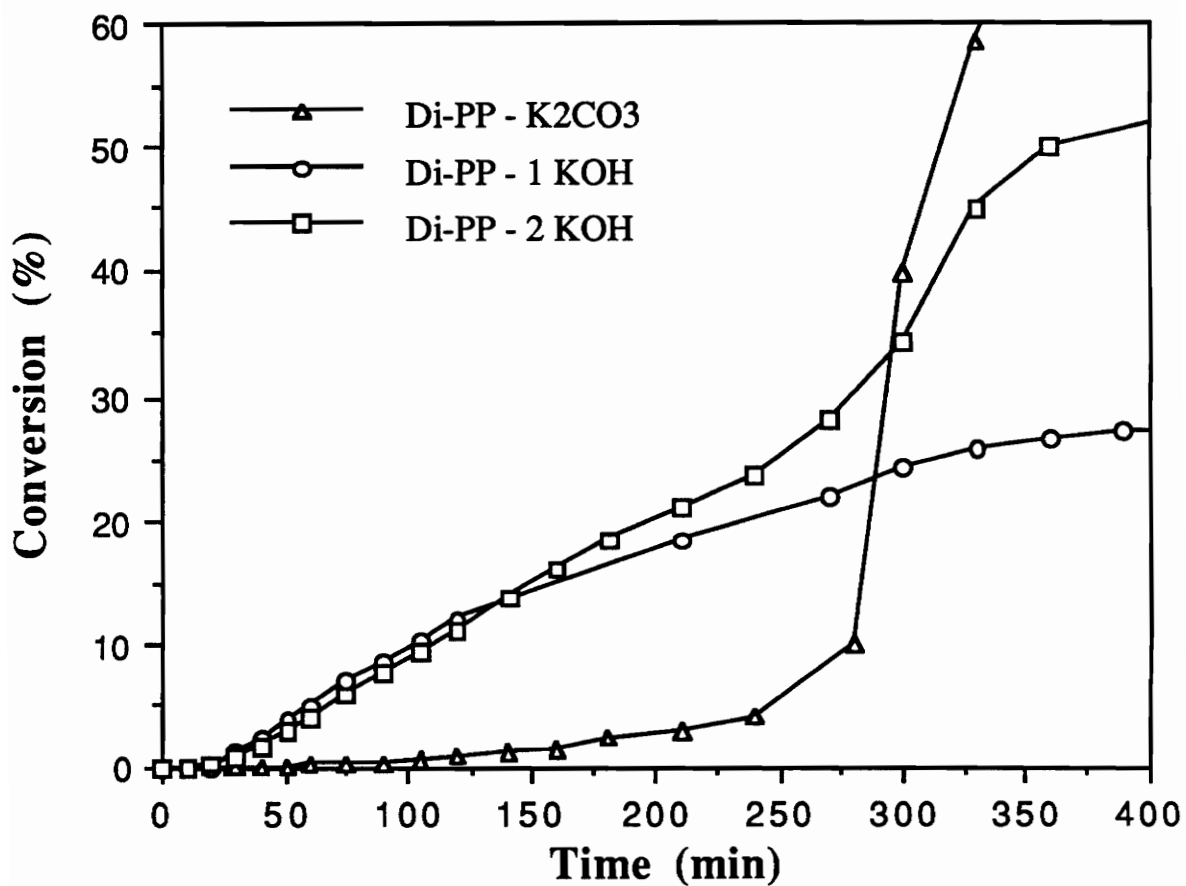
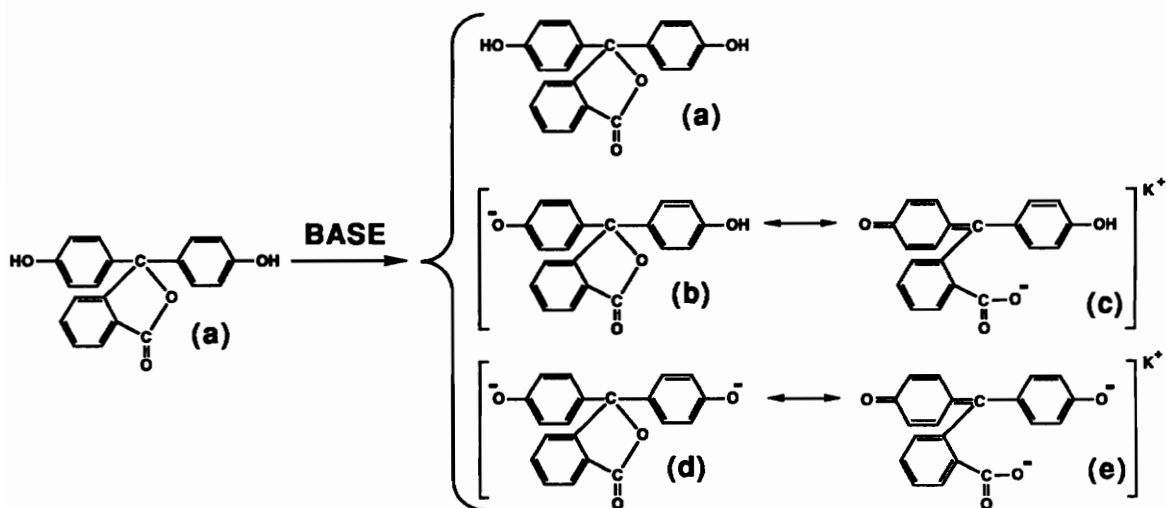


Figure 4.2.2.7 Kinetic plot comparing Di-PP formation in the condensation reaction under different basic conditions. (An overlay of the curves generated in Figures 4.2.2.2-4)

The difference between the Mono-PP plot (Figure 4.2.2.6) and the Mono-BIS A plots (Figure 4.2.1.7) will be discussed Section 4.2.3.

A comparison of the formation of Di-PP under different basic conditions is shown in Figure 4.2.2.7. With K_2CO_3 , the formation of Di-PP proceeds slowly during the first 4 h at 135 °C. Upon heating to 155 °C, the product rapidly approaches 100%. In comparison, it is seen that the KOH reactions follow the same initial trend in which the Di-PP is formed after the first 30 min. After heating to 155 °C at 240 min., the curves deviate from one another as the 2.0 mole KOH approaches 50% conversion and the 1.0 mole KOH staying at ~25% conversion. These low conversions suggest that about half of the KOH was consumed by solvent hydrolysis.

In proposing a hypothesized mechanism to explain the trends of the kinetic plots (Figures 4.2.2.2 and 4.2.2.3), the relative concentration of the ionic species of PP in each reaction will be considered. A representation of the proposed ionized forms of PP under basic conditions is shown in Scheme 4.2.2.3.



Scheme 4.2.2.3 Proposed derivatives of PP under different basic conditions.

The relative amounts of the proposed derivatives from Scheme 4.2.2.3 are given in Table 4.2.2.1.

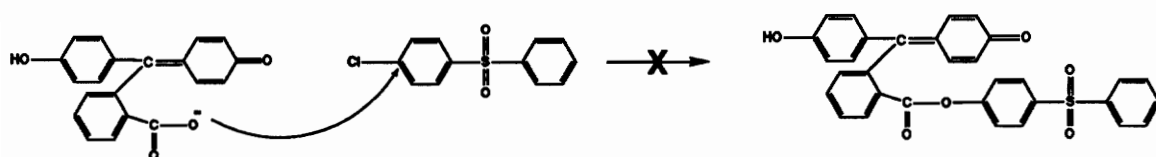
Table 4.2.2.1 Relative amounts of proposed PP derivatives under different basic conditions.

PP Isomer (from Scheme 4.2.2.3)	K ₂ CO ₃	1.0 mole KOH	2.0 mole KOH
(a)	Minor	Trace	Trace
(b) and (c)	Major	Major	Minor
(d) and (e)	Trace	Minor	Major

Since K₂CO₃ is such a weak base, it is most likely that the only mono-potassium salts are formed (Scheme 4.2.2.3b and c). With KOH however, di-potassium salts are formed (Scheme 4.2.2.3d and e). The ring-opened quinone dianion (Scheme 4.2.2.3e) is likely to be more stable than its ring-closed bisphenate isomer (Scheme 4.2.2.3d) due to the stability of the carboxylate anion. As a result, it seems likely that under strong base conditions, the equilibrium lies in favor of the ring-opened quinone (Scheme 4.2.2.3e). This may explain why PP reacts so differently with strong vs. weak bases in a condensation process.

With K₂CO₃ as the base, the reaction turns purple as the temperature reaches ~70 °C. This indicates the formation of the ring opened quinone isomer of PP as shown previously in Scheme 4.2.2.3c. Since the reaction kinetics under K₂CO₃ conditions show that this monomer reacts much the same way BIS A does (i.e. a mono adduct is formed and disappears as it is consumed to form a di adduct), it is logical to conclude that the PP

quinone must ring close before undergoing S_NAR with 4-CDPS. Evidence of this lies in the fact that the purple color of the reaction disappears by the end; therefore the Di-PP adduct must be in its ring closed form. The UV/vis spectra of all peaks formed during the HPLC analyses were examined. No absorbance >320 nm was observed. This indicates that no quinones were formed, suggesting that the carboxylate anions of the ring-opened forms (Scheme 4.2.2.3c and e) are not nucleophilic enough and/or are too sterically hindered to displace chlorine from 4-CDPS as shown in Scheme 4.2.2.4.



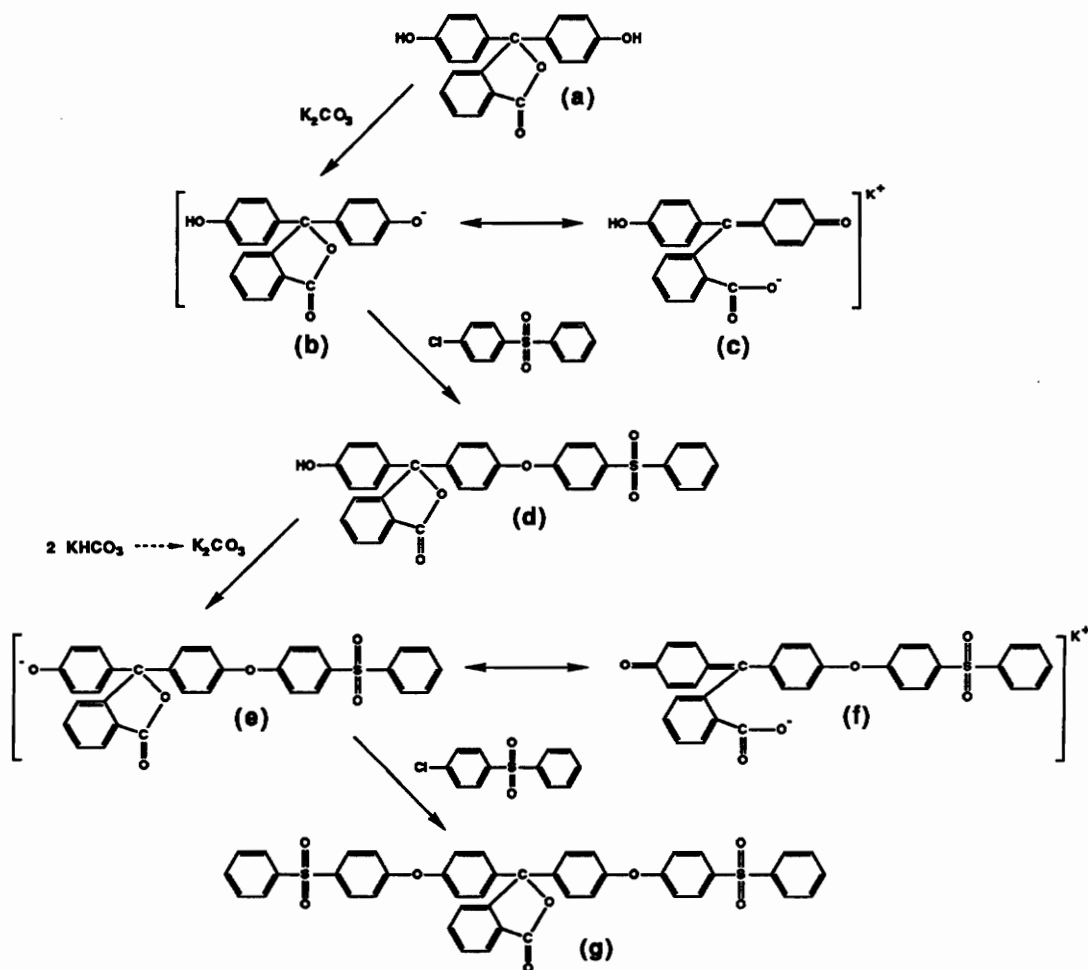
Scheme 4.2.2.4 Example of a the nucleophilic aromatic displacement reaction between the carboxylate anion of the quinone form of PP and an activated halide.

When phenolphthalein reacts with 4-CDPS and K_2CO_3 , two derivatives of the resulting anion are formed as shown in Scheme 4.2.2.5b and c. The ring closed derivative (Scheme 4.2.2.5b) can then react with 4-CDPS. Upon formation of the Mono-PP adduct (Scheme 4.2.2.5d), $KHCO_3$ is formed which later decomposes to form another mole of K_2CO_3 . This weak base is thus regenerated to further react with the mono adduct phenoxy, resulting in yet another phenate (Scheme 4.2.2.5e). This phenate can ring open once again to form the stable carboxylate anion (Scheme 4.2.2.5f), or can subsequently undergo condensation with 4-CDPS to form the Di-PP (Scheme 4.2.2.5g).

In the KOH model reactions, the solution turns a deep purple as the temperature approaches 70 °C. This again is consistent with quinone formation as shown previously in Scheme 4.2.2.3. It was previously shown in Figure 4.2.2.3b (and in Table 4.2.2.1) that

the Mono-PP forms faster with 1.0 mole KOH than with 2.0 mole KOH. This phenomena can possibly be explained by solubility. The insolubility of the PP dianion (Scheme 4.2.2.3 d and e) formed from 2.0 mole KOH results in a much lower concentration available for reaction. The PP monoanion formed with 1.0 mole KOH (Scheme 4.2.2.3 b and c) is soluble, resulting in a higher concentration of reactive species, therefore resulting in faster kinetics.

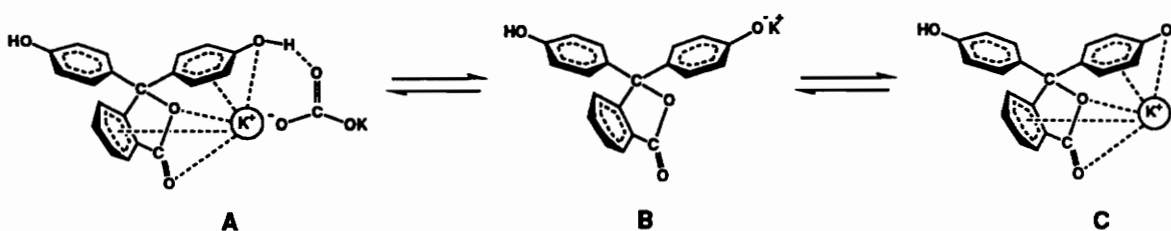
The proposed reaction mechanism based on the kinetic graphs and factors previously explained is shown in Scheme 4.2.2.5.



Scheme 4.2.2.5 Proposed reaction of PP with K_2CO_3 in an S_NAR process.

4.2.3 Comparison of Bisphenol A and Phenolphthalein Reactivities with 4-CDPS

It was the purpose of this comparison to either confirm or dispute the claim by Jin *et al.*⁴⁹⁹ that PP reacts faster than BIS A is a polycondensation process. They attribute the faster reactivity to an intramolecular autocatalytic effect on the polymerization; i.e. the heterocyclic lactone on phenolphthalein intramolecularly solvates the K^+ , thus making the phenate more nucleophilic as shown in Scheme 4.2.3.1.



Scheme 4.2.3.1 Proposed intracoordination of phenolphthalein with K_2CO_3 .⁴⁹⁹

Jin *et al.*⁴⁹⁹ have suggested that phenolphthalein can form a complex with K_2CO_3 . They further suggest that the pendant lactone is perpendicular to the two phenolic rings. The structure permits the π -electrons in the pendant benzene ring, the phenolic benzene, the oxygens in the lactone, and the phenoxy to complex with K_2CO_3 as shown in Scheme 4.2.3.1. Jin *et al.* have also suggested that this complex of phenolphthalein with K_2CO_3 results in several orders of magnitude faster polymerization as compared to BIS A.⁴⁹⁹ This is attributed to the potassium ion being intramolecularly solvated by the heterocyclic lactone, thus making the phenate more nucleophilic (Scheme 4.2.3.1c). This concept is investigated in the following model study comparisons for verification.

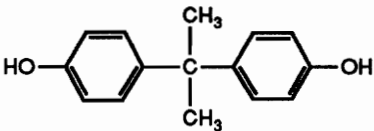
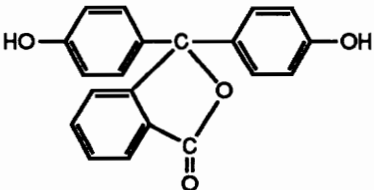
In comparing the relative reactivities of BIS A and PP many factors have to be considered. Factors that increase reaction rate are:

- 1) greater phenate nucleophilicity
- 2) greater phenate concentration
 - a) solubility of the phenate in the reaction medium
 - b) pK_a of the bisphenol

Generally, acidity and nucleophilicity of the same types of compounds are inversely proportional. Also, greater acidity typically results in a higher concentration of phenate in solution. All these factors contribute to the kinetics of the reaction.

The average pK_a values ($pK_1 + pK_2$) for BIS A⁵⁰⁰ and PP⁵⁰¹ are given in Table 4.2.3.1.

Table 4.2.3.1 Average pK_a values for BIS A⁵⁰⁰ and PP⁵⁰¹

Acronym	Structure	pK_a Average Value
BIS A		10.76
PP		9.95

The protons of PP are more acidic than the protons of BIS A, likely due to the stabilization of the anions by the resonance depicted previously in Scheme 4.2.2.3b and c.

The greater acidity of PP should result in a faster neutralization reaction upon contact with K_2CO_3 , when compared with BIS A. However, the same anion stabilization mechanism that causes PP to be more acidic, is also expected to make the PP phenate less nucleophilic as compared to the BIS A phenate.

In comparing the relative reactivities of BIS A and PP, two approaches were used. First, the reaction plots shown previously (Section 4.2.1 and 4.2.2) for each bisphenol were overlaid according to base; e.g. the BIS A K_2CO_3 plot (Figure 4.2.1.3) was overlaid with the PP K_2CO_3 plot (Figure 4.2.2.2). This approach will be referred to as the "Separate Reactions Overlaid". The second approach was to react both BIS A and PP in the same reaction vessel with 4-CDPS. This approach will be referred to as the "Mixed Reaction". Calculations were used (Section 3.4.3) to determine % conversion of all starting materials, intermediates, and products. To simplify, only the Mono and Di adducts for each bisphenol are plotted (Figures 4.2.3.1 - 4.2.3.6).

The amounts of each component for comparison of the two approaches are given in Table 4.2.3.2

Table 4.2.3.2 Amounts of starting materials for the Separate and Mixed Reaction.

Separate Reactions	Mixed Reaction
1.0 mole BIS A <u>or</u> 1.0 mole PP	0.5 mole BIS A <u>and</u> 0.5 mole PP
2.1 mole 4-CDPS	2.1 mole 4-CDPS
1.15 mole K_2CO_3 , <u>or</u> 1.0 mole KOH, <u>or</u> 2.0 mole KOH	1.15 mole K_2CO_3 , <u>or</u> 1.0 mole KOH, <u>or</u> 2.0 mole KOH

In Figure 4.2.3.1, the Separate Reactions of BIS A and PP were overlaid to compare relative reactivities under K_2CO_3 conditions. It is seen that both the Mono and Di adducts of BIS A are forming faster than the adducts of PP. This would seem to disprove the Jin *et al.* hypothesis mentioned previously in Scheme 4.2.3.1, that PP reacts faster with K_2CO_3 as the base. The Mixed Reaction, where both BIS A and PP were reacted in the same pot, is shown in Figure 4.2.3.2. In the Mixed Reaction, the Mono and Di adducts of PP form faster than the adducts of BIS A. This trend is exactly the opposite of what was seen for Figure 4.2.3.1 in the Separate Reactions Overlaid.

Because K_2CO_3 is not soluble in DMAc, it forms a heterogeneous suspension. Because of this, the K_2CO_3 does not initially (at time 0), totally convert the bisphenols to the monophenate (i.e. $K_2CO_3 + BIS\ A \Rightarrow KHCO_3 + BIS\ A + K^+BIS\ A^-$). The further the reaction is driven to form the mono-potassium phenate before the 4-CDPS is added, the faster the kinetics will be due to a higher concentration of mono-phenate. BIS A is faster in the Separate Reaction (Figure 4.2.3.1) likely due to the higher concentration of mono phenate that was formed at time 0. The amount of mono phenate formed at time 0 is not reproducible; therefore, more accurate kinetics would be achieved in the mixed system where both BIS A and PP have equal opportunity to react with K_2CO_3 to form their respective mono phenates. In this Mixed Reaction (Figure 4.2.3.2), the kinetics of both BIS A and PP are generated in the same run, thus eliminating run to run differences seen in overlaying the Separate Reactions.

Figure 4.2.3.2 indicates that PP is slightly more reactive than BIS A. This is likely due to more PP having been converted to mono potassium salt than BIS A. Because of the higher ratio of PP to base in the Mixed reaction, more PP is converted, since it is more acidic. This would result in a higher concentration of the lesser reactive PP mono phenate. As a result of the concentration increase, the kinetics are faster.

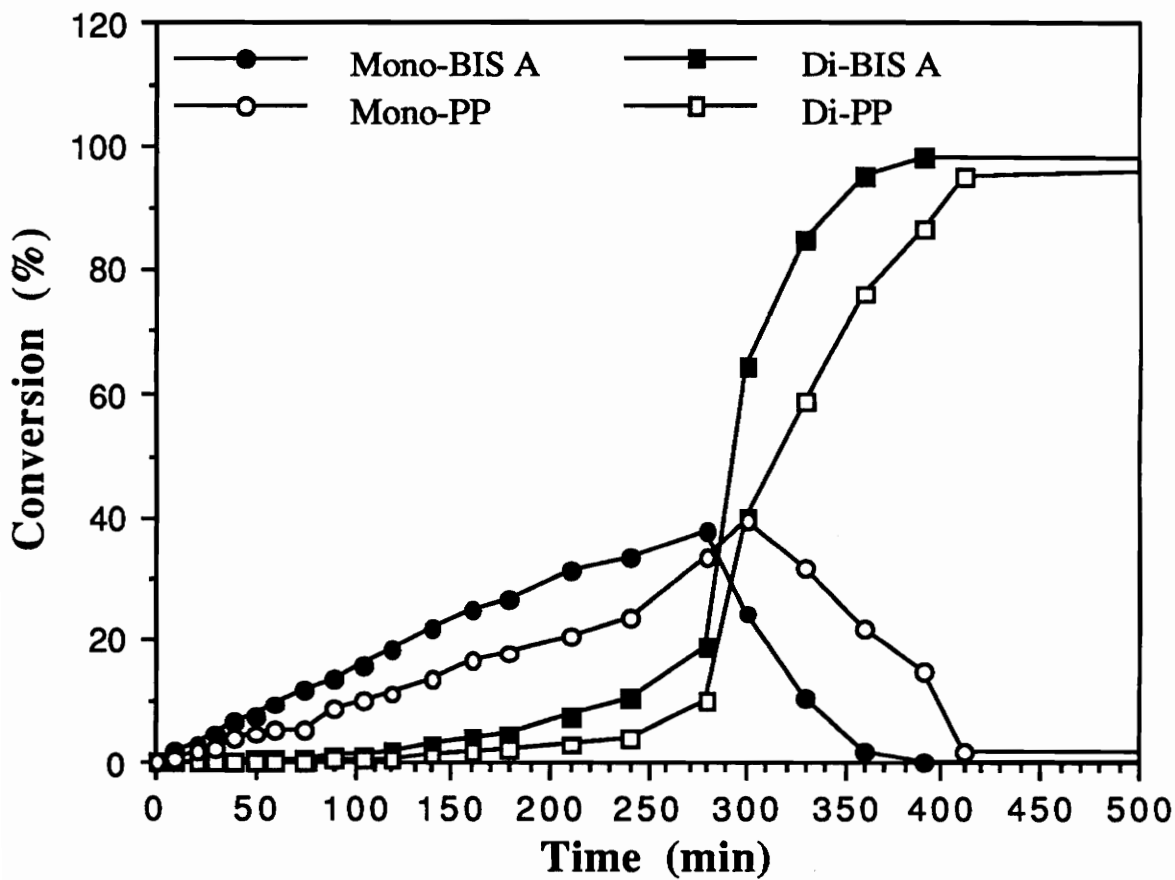


Figure 4.2.3.1 Relative formation of Mono and Di adducts for BIS A and PP with K_2CO_3 in Separate Reactions Overlaid.

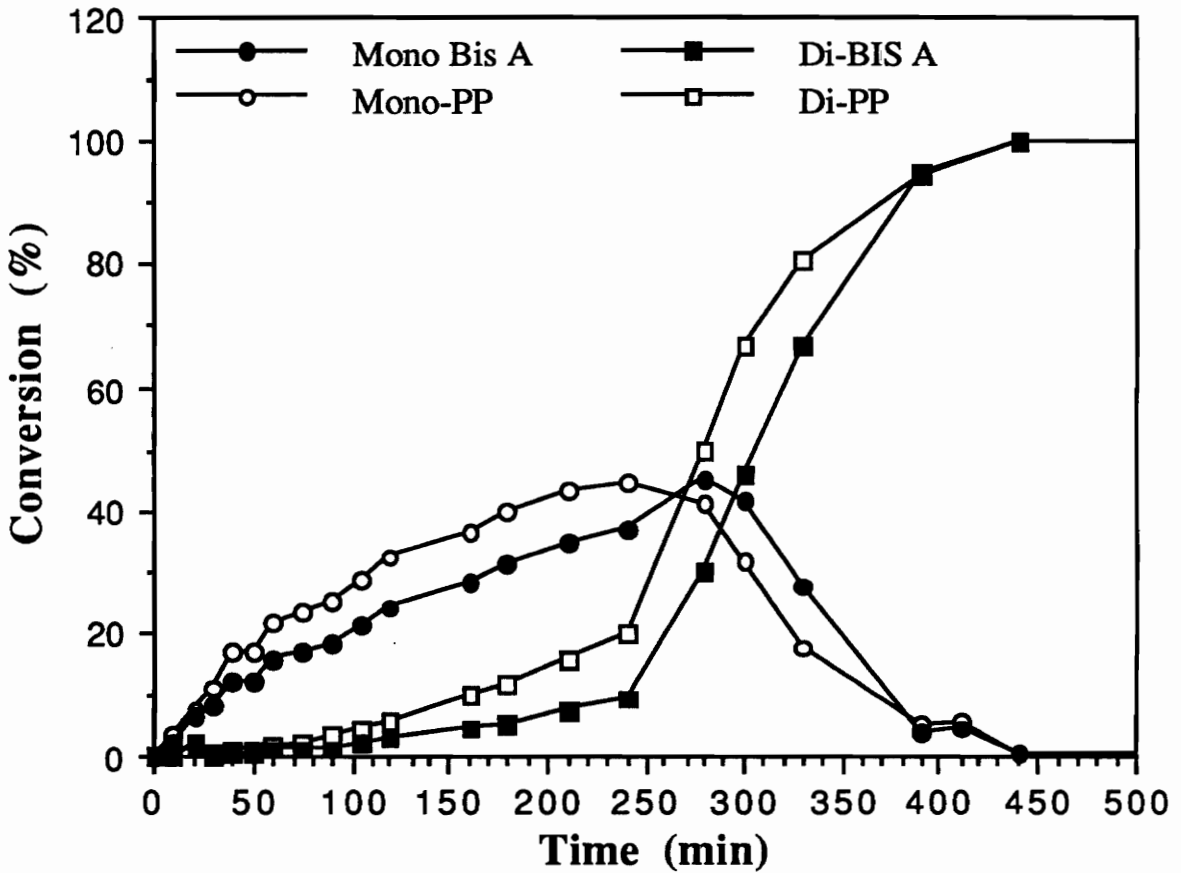
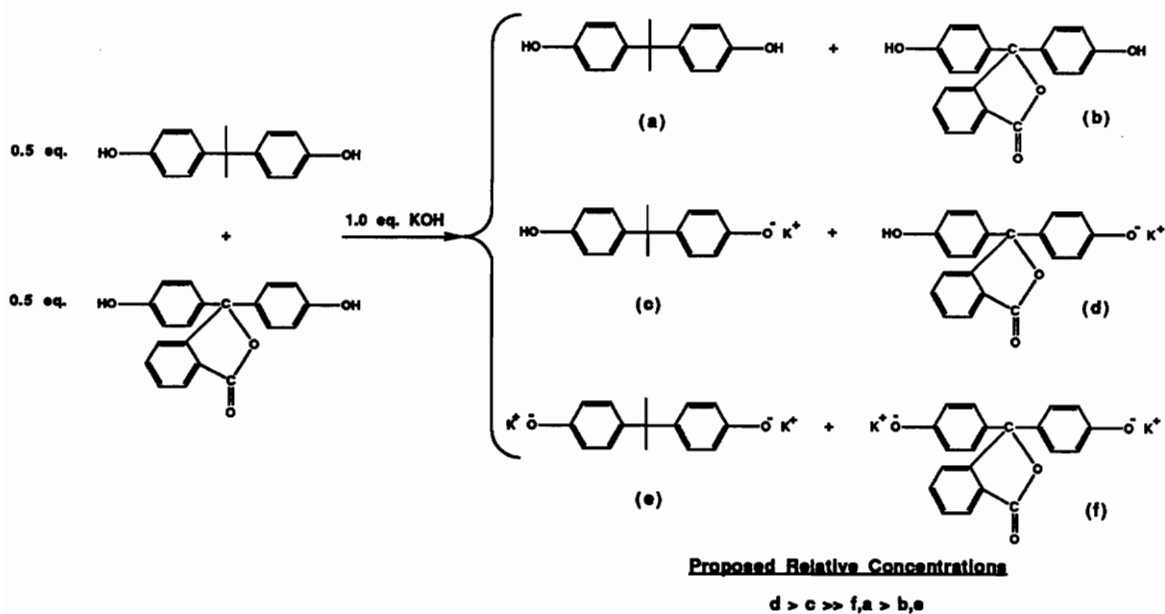


Figure 4.2.3.2 Relative formation of Mono and Di adducts for BIS A and PP with K_2CO_3 in a Mixed Reaction.

Figures 4.2.3.3-4 are plots to show the relative formation of the Mono and Di adducts of BIS A and PP under 1.0 mole KOH. For the Separate Reactions (Figure 4.2.3.3), the Mono and Di-BIS A adducts form faster than that of PP. In the Mixed Reaction (Figure 4.2.3.4), the Mono-BIS A forms faster than the Mono-PP, but the Di-PP

forms faster than the Di-BIS A. A possible explanation of this trend is as follows. While K_2CO_3 does not completely ionize the phenols, 1.0 mole KOH should mainly make the monophenolate of each species. Figures 4.2.3.3-4 indicate that the monophenolate of BIS A is more reactive than the monophenolate of PP. However, since PP is more acidic than BIS A, a higher concentration of PP diphenolate would be formed resulting in a faster formation of Di-PP.

Scheme 4.2.3.2 gives the proposed species in a Mixed Reaction of BIS A and PP under 1.0 mole KOH conditions. The relative initial concentrations of each are proposed to be $d > c \gg f, a > b, e$.



Scheme 4.2.3.2 Proposed relative initial concentrations of BIS A and PP derivatives in a Mixed Reaction with 1.0 mole KOH.

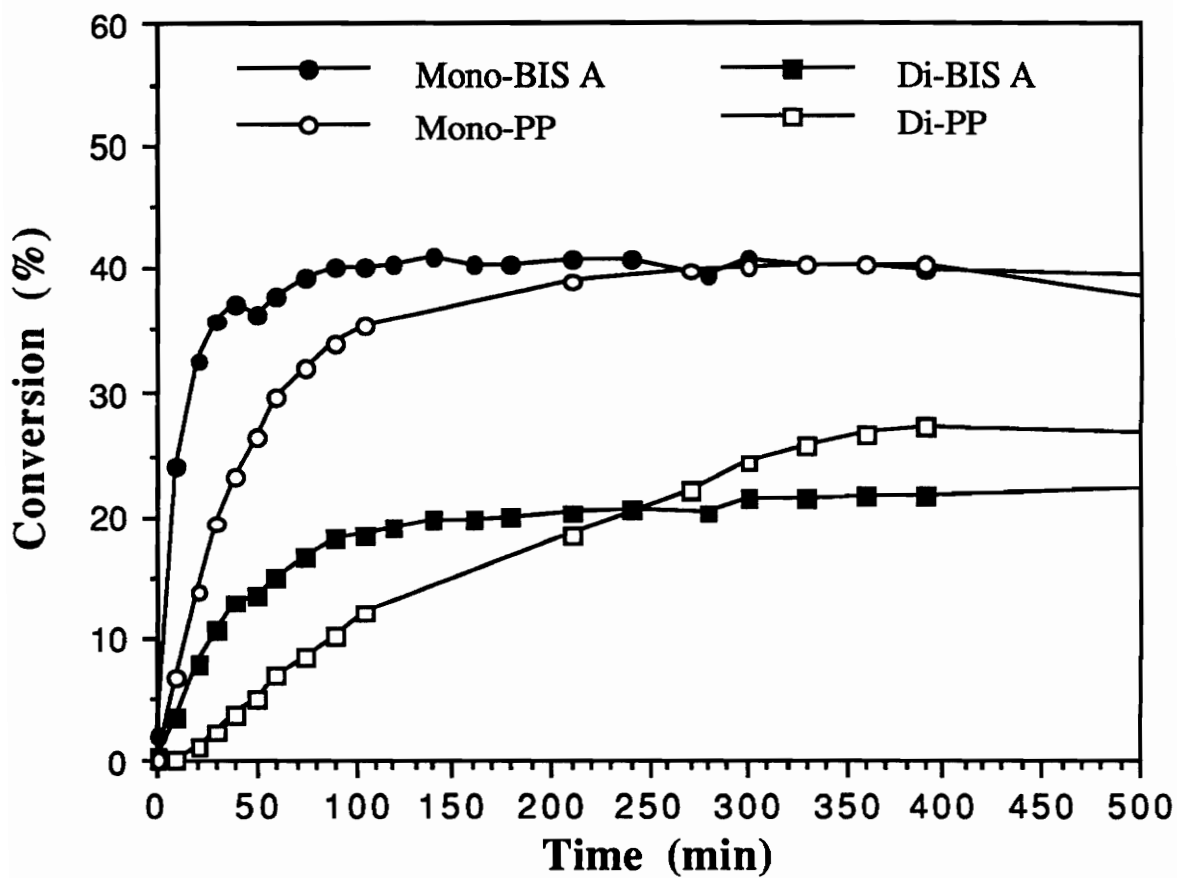


Figure 4.2.3.3 Relative formation of Mono and Di adducts for BIS A and PP with 1.0 mole KOH in Separate Reactions Overlaid.

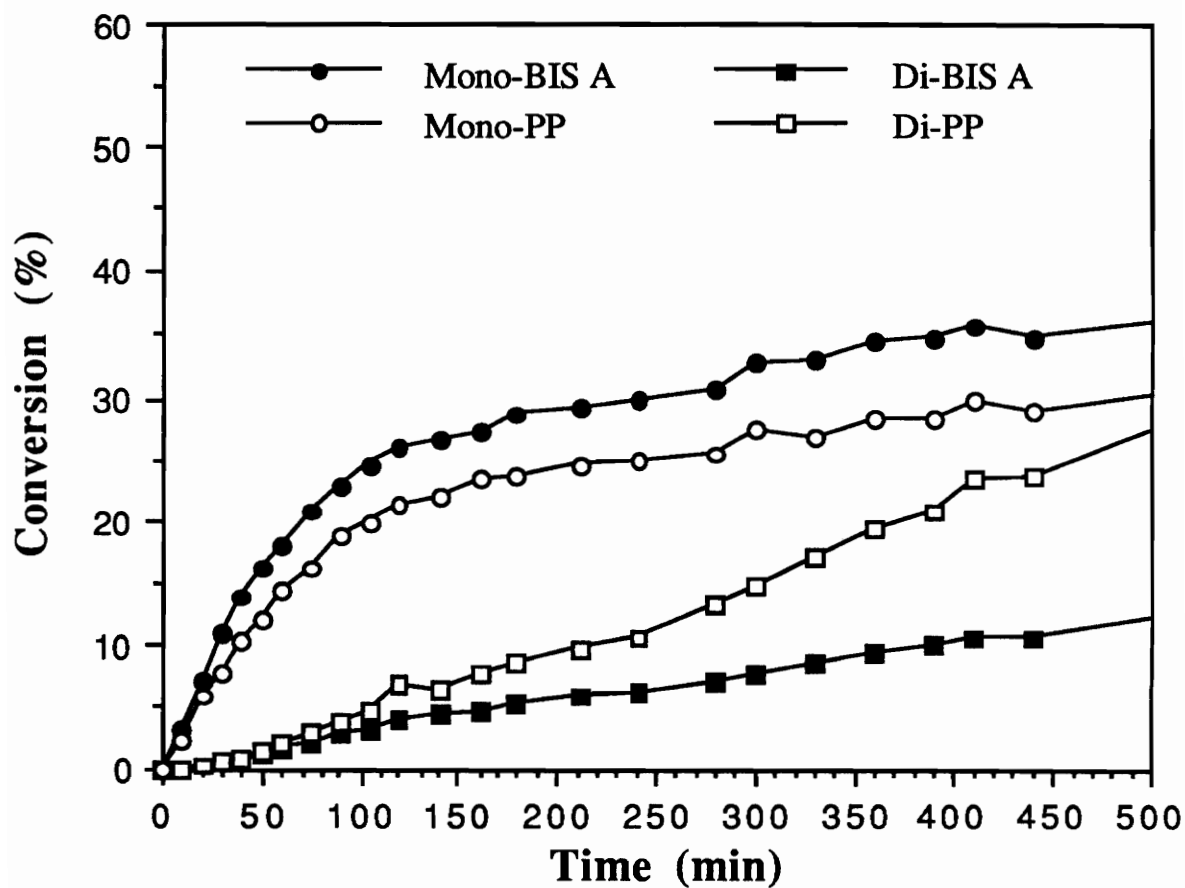


Figure 4.2.3.4 Relative formation of Mono and Di adducts for BIS A and PP with 1.0 mole KOH in a Mixed Reaction.

The same comparison as described previously in Figures 4.2.3.1-2 and 4.2.3.3-4 was also done using 2.0 mole KOH as the base. In the Separate Reaction (Figure 4.2.3.5), the Mono and Di-BIS A adducts form much faster than the Mono and Di-PP adducts. In the Mixed Reaction (Figure 4.2.3.6), the trend is reversed with the Mono-PP forming in higher concentrations as compared to the Mono-BIS A. The Mono and Di-PP have higher conversion at 1 h as compared in the Separate Reactions. The most striking difference is the > 100% increase of Mono-PP and > 800% increase of Di-PP in the Mixed Reaction.

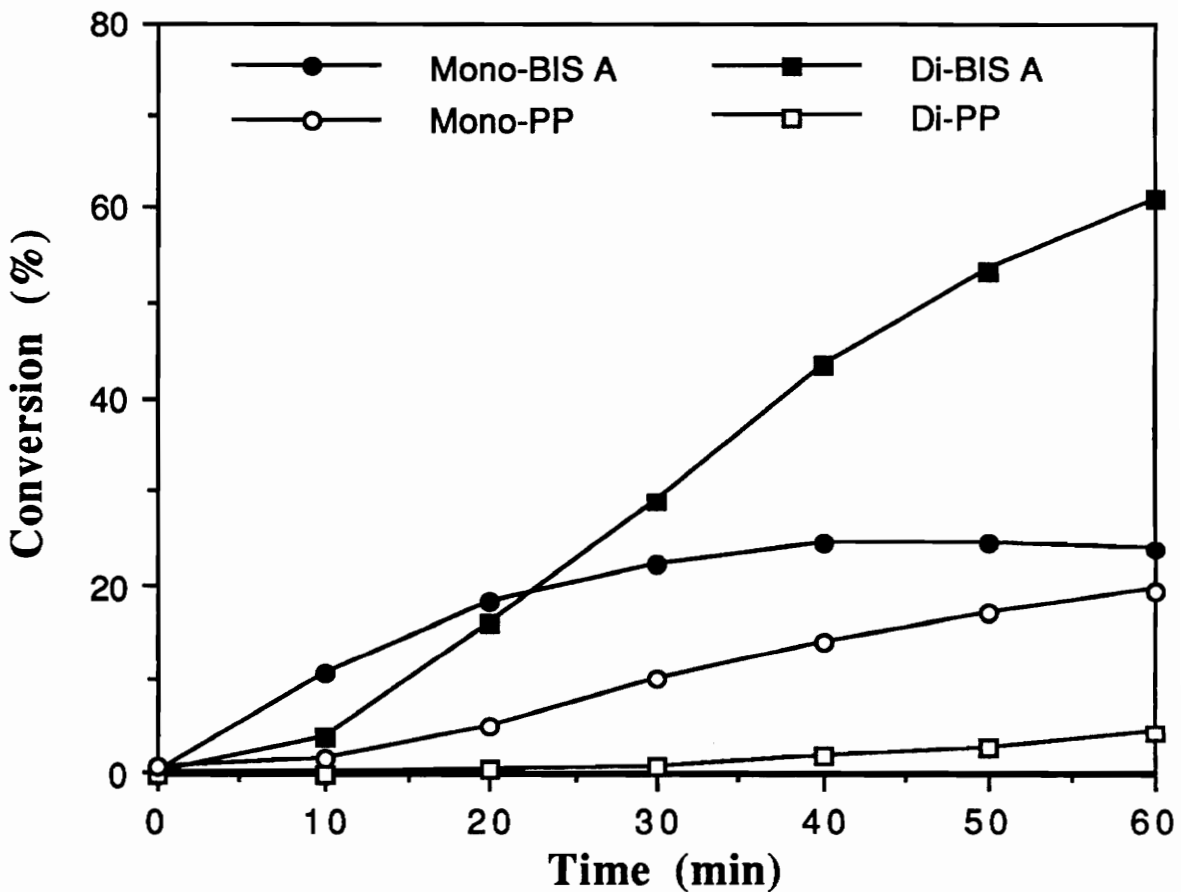


Figure 4.2.3.5 Relative formation of Mono and Di adducts for BIS A and PP with 2.0 mole KOH in Separate Reactions Overlaid.

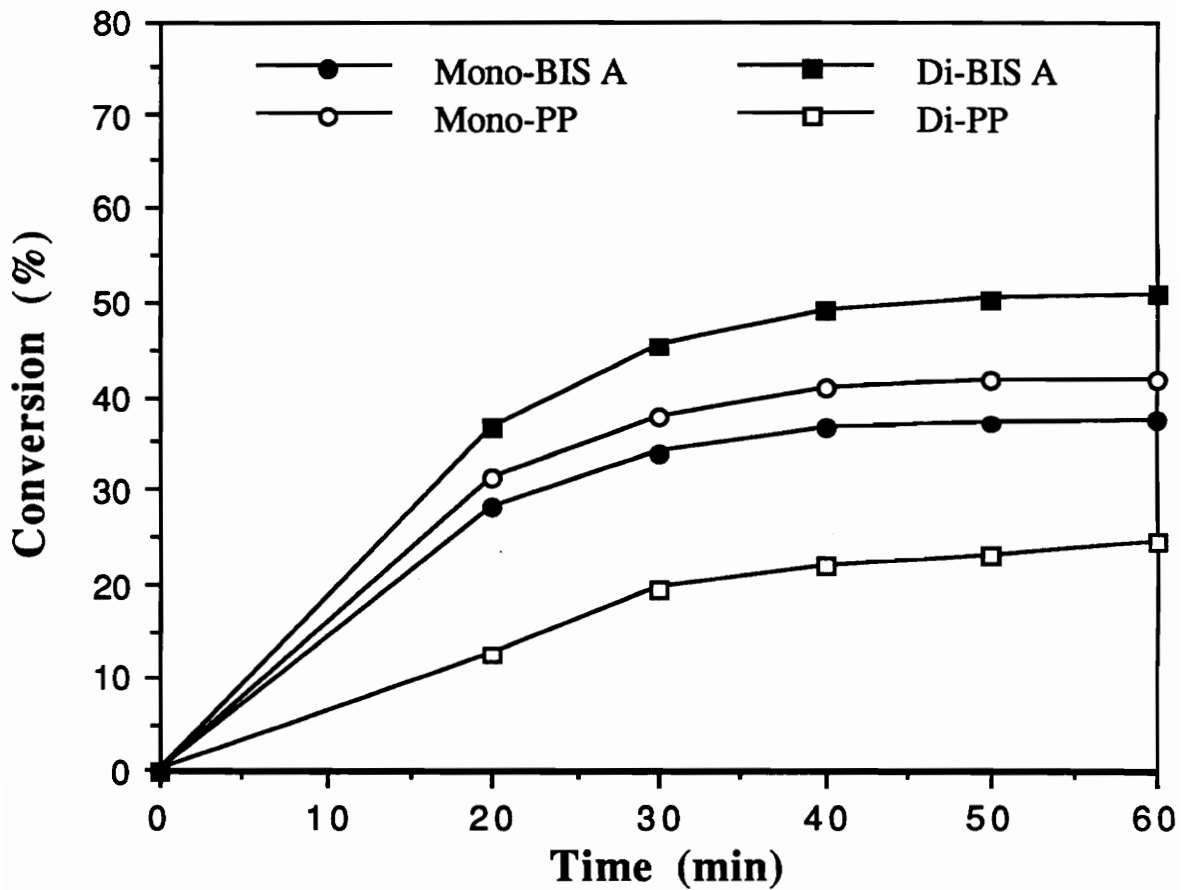


Figure 4.2.3.6 Relative formation of Mono and Di adducts for BIS A and PP with 2.0 mole KOH in a Mixed Reaction.

These trends may be explained as follows. With 2.0 mole KOH, the diphenates of both BIS A and PP are formed. However, PP can consume three moles of KOH to form a diphenate carboxylate shown in Figure 4.2.3.7. The formation of the diphenate carboxylate is unlikely in the Separate Reaction, but in the Mixed Reaction it is likely, since the molar ratio of KOH/PP = 4. The diphenate carboxylate of PP is expected to be more nucleophilic than all of the anion species shown previously in Scheme 4.2.2.3 because it is a trisanion.

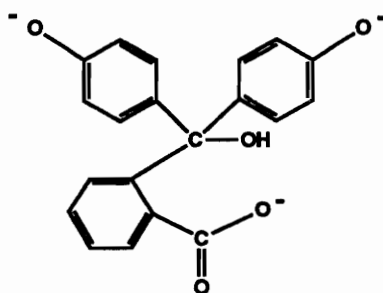


Figure 4.2.3.7 Structure of the phenate carboxylate anion of phenolphthalein.

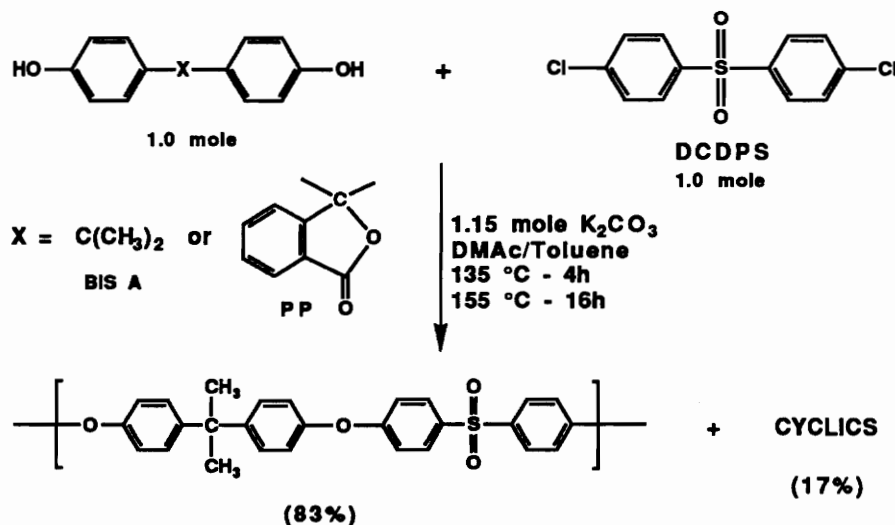
4.2.4 Model Compound Study Conclusions

The following conclusions are drawn from the model compound study:

- 1) The K_2CO_3 reaction is a slower step-wise process than the KOH reaction.
- 2) It is better to use K_2CO_3 as base than KOH, because KOH leads to hydrolytic side reactions, keeping conversion less than 100%.
- 3) The results of this study do not support the significantly faster reactivity of PP over BIS A as reported by Jin *et al.*⁴⁹⁹
- 4) No nucleophilic displacement by phenolphthalein carboxylate was observed.

4.2.5 Polymerization Kinetics

Model polymerizations were done in an effort to confirm the results of the model compound study which predict that the relative reactivities of BIS A and PP should be similar in nucleophilic aromatic poly(arylene ether) synthesis. Scheme 4.2.5.1 represents the conditions were used to prepare a high molecular weight poly(arylene ether)s.



Scheme 4.2.5.1 Polymerization conditions for K_2CO_3 model polymerization of BIS A or PP with DCDPS.

During the polymerization, kinetic step growth of the oligomers was followed by HPLC (Figure 4.2.5.1) and GPC (Figure 4.2.5.2) of aliquots taken at various time intervals. It was interesting to note that the last aliquot collected before the polymer was isolated by precipitation, contained a high amount of cyclooligomers (~17 area % of the final polymer in both PP and BIS A-PES). This level is surprising due to the relatively high concentrations of monomers used (~10 wt. %). Mullins *et al.* had to operate at very low dilution (continuous addition of monomers to K_2CO_3 /DMAC/toluene) and low temperatures (<140 °C) to obtain a high cyclic yield (~55%).^{46,80}

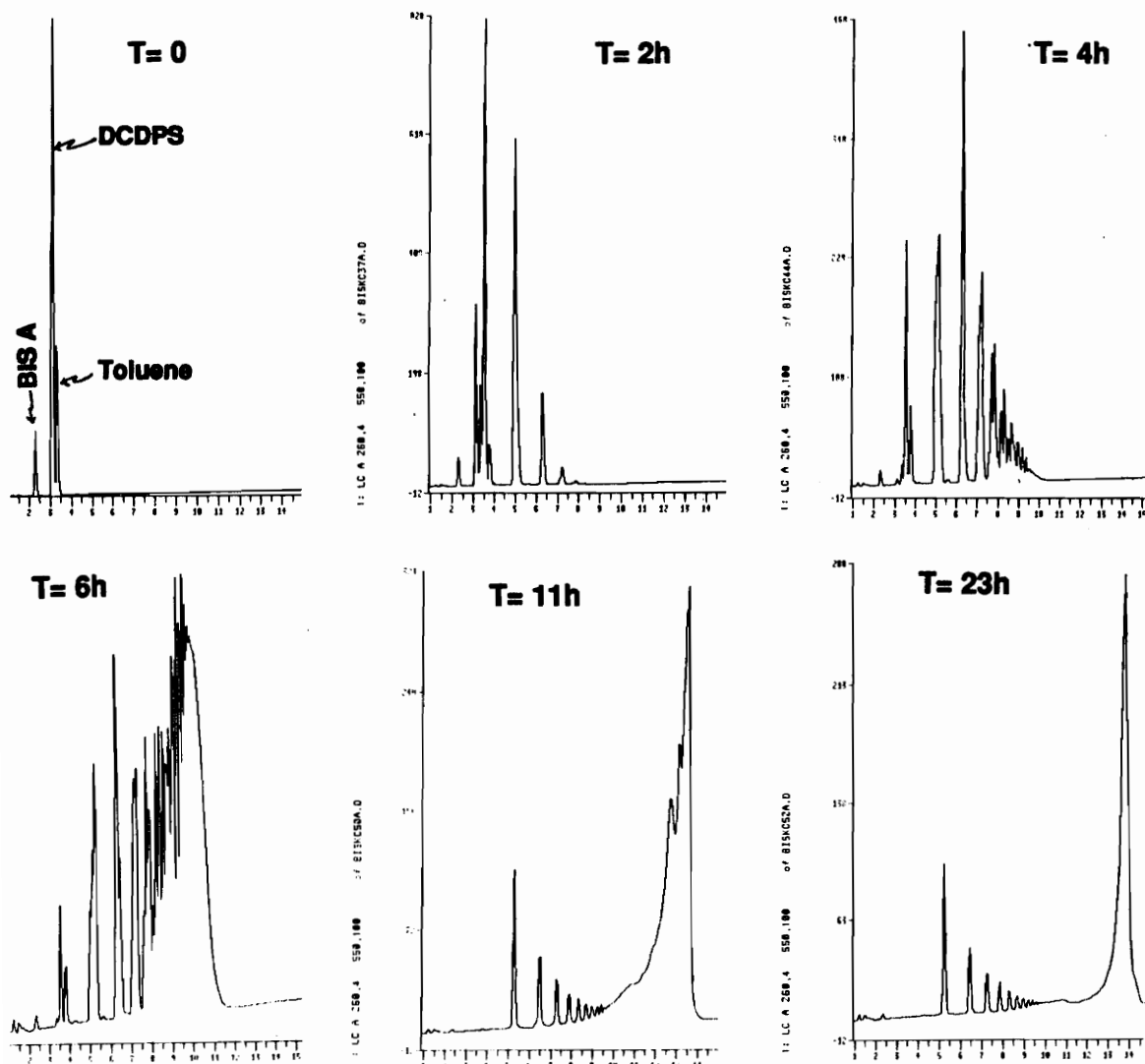


Figure 4.2.5.1 HPLC traces representing different stages of BIS A-PES formation

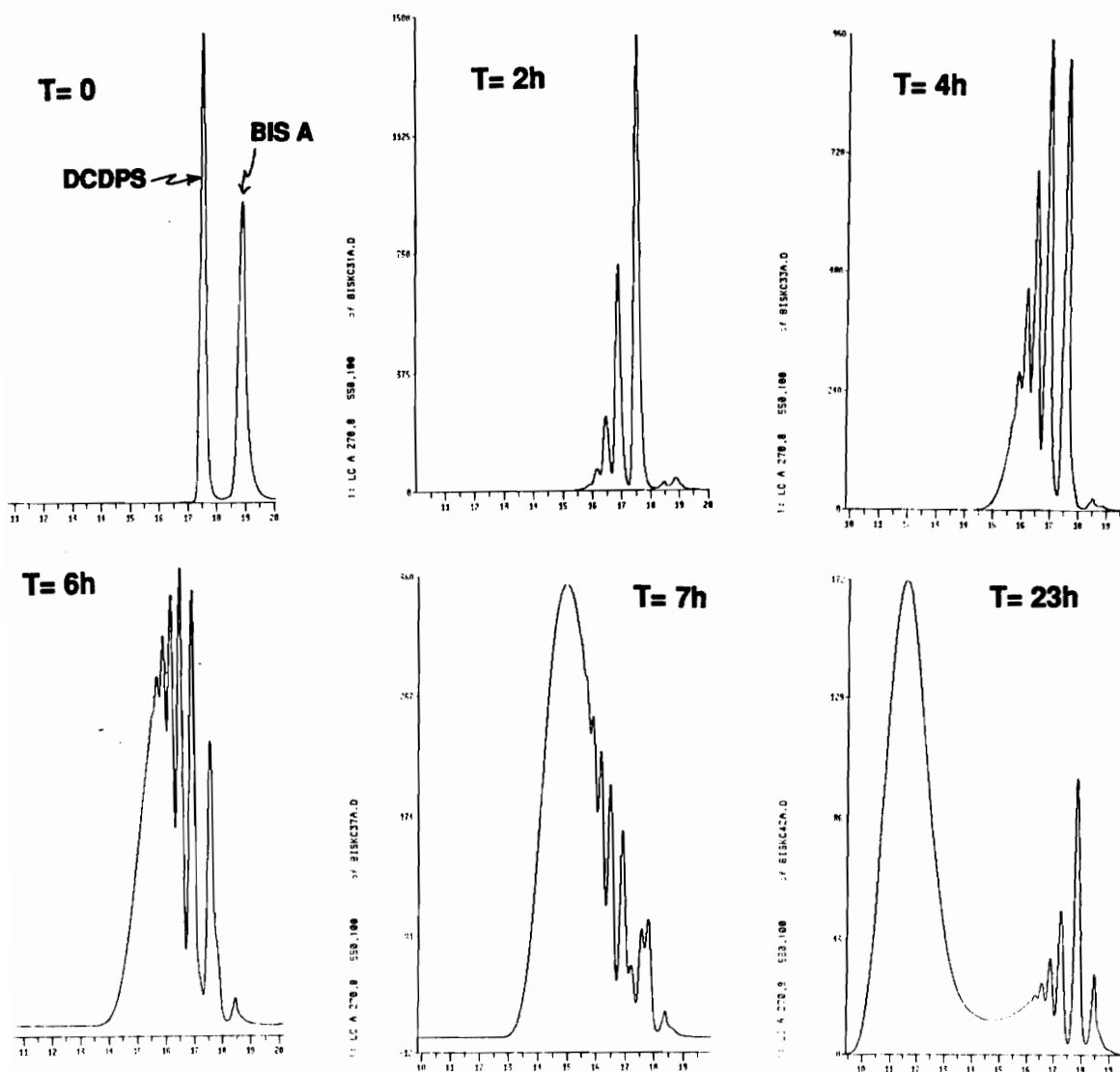


Figure 4.2.5.2 GPC traces representing different stages of BIS A-PES formation.

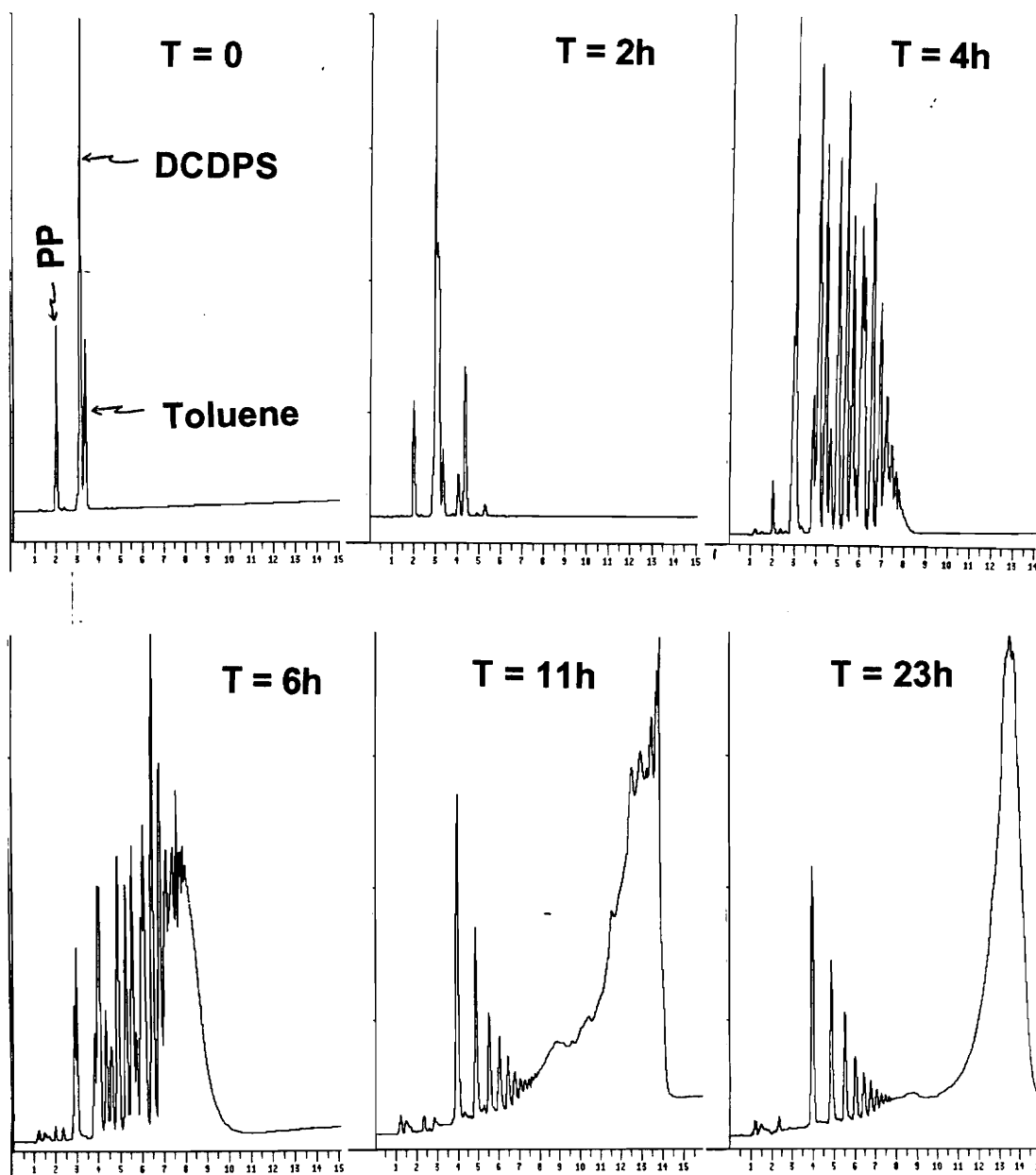


Figure 4.2.5.3 HPLC traces representing different stages of PP-PES formation.

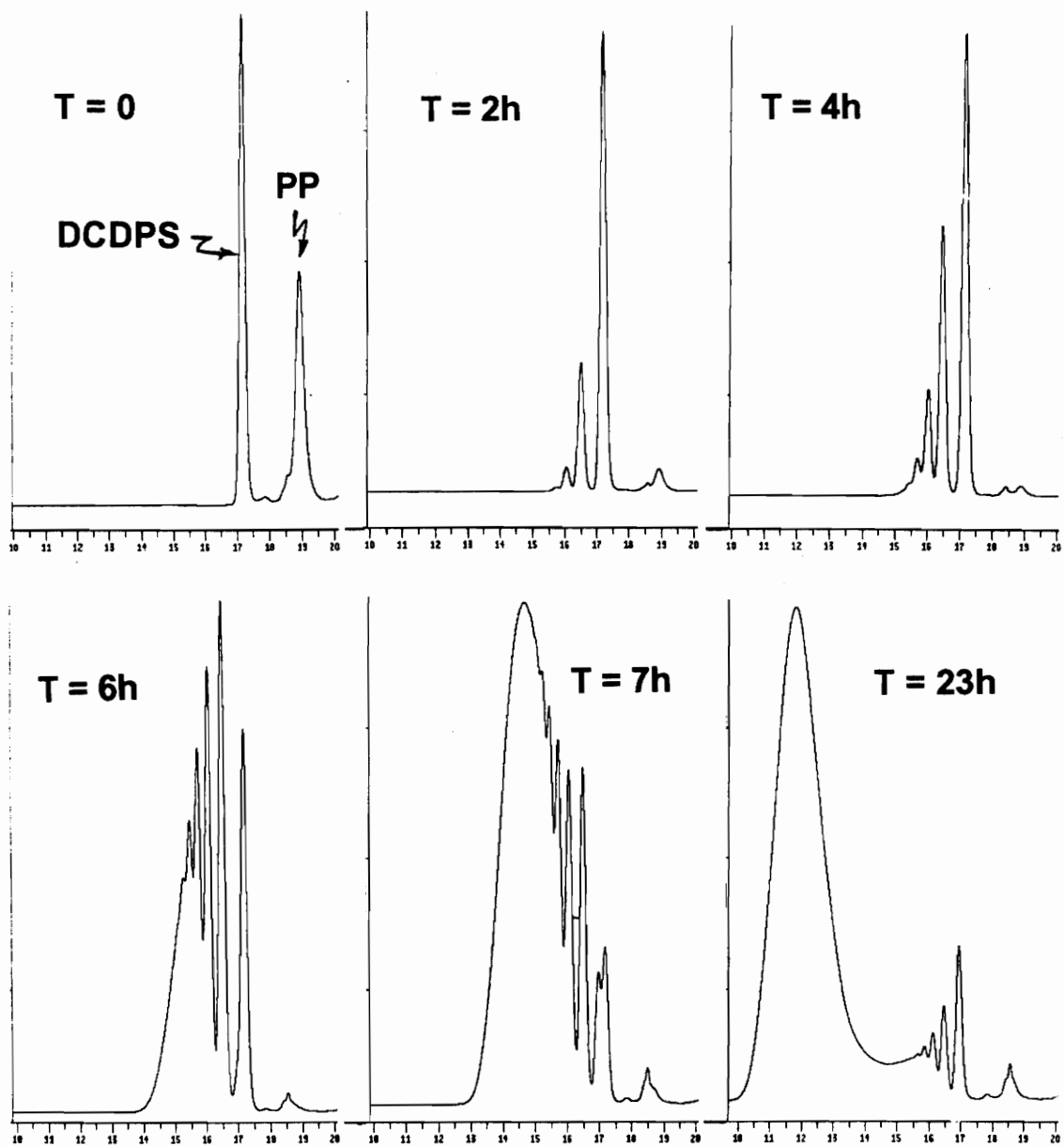


Figure 4.2.5.4 GPC traces representing different stages of PP-PES formation.

The results of the polymerization kinetic study confirm the conclusions of the model compound kinetic study (Section 4.2.1-4.2.4). The differences in the kinetics of oligomer growth in both the BIS A and PP polymerization were negligible. Furthermore, the level of cyclooligomers formed was identical (~17 area %) shown by the HPLC traces of the final BIS A-PES and PP-PES prior to precipitation (Figure 4.2.5.5a and b). It should be pointed out that precipitation of the polymer by pouring into MeOH/H₂O decreases the cyclooligomer level in the precipitated polymer by ~50%. Of course, the level of cyclooligomers in the precipitated polymer would be variable depending upon the solvent/nonsolvent ratio used during the precipitation.

Cyclooligomers of both BIS A and PP-PES were, obtained by redissolving the purified polymer in chloroform (~5 wt. %). The polymer was then reprecipitated by the addition of two volumes of methanol. The filtrate was evaporated to dryness yielding a white solid. HPLC analysis of the solid showed that it was a mixture of cyclooligomers. Analysis of the residue by fast atom bombardment mass spectroscopy (Figures 4.2.5.6 and 4.2.5.7) shows that the smallest cyclooligomers for BIS A and PP each have a degree of polymerization (DP) of two. The pure cyclic dimer of BIS A has been reported by Gibson *et al.*⁷⁹

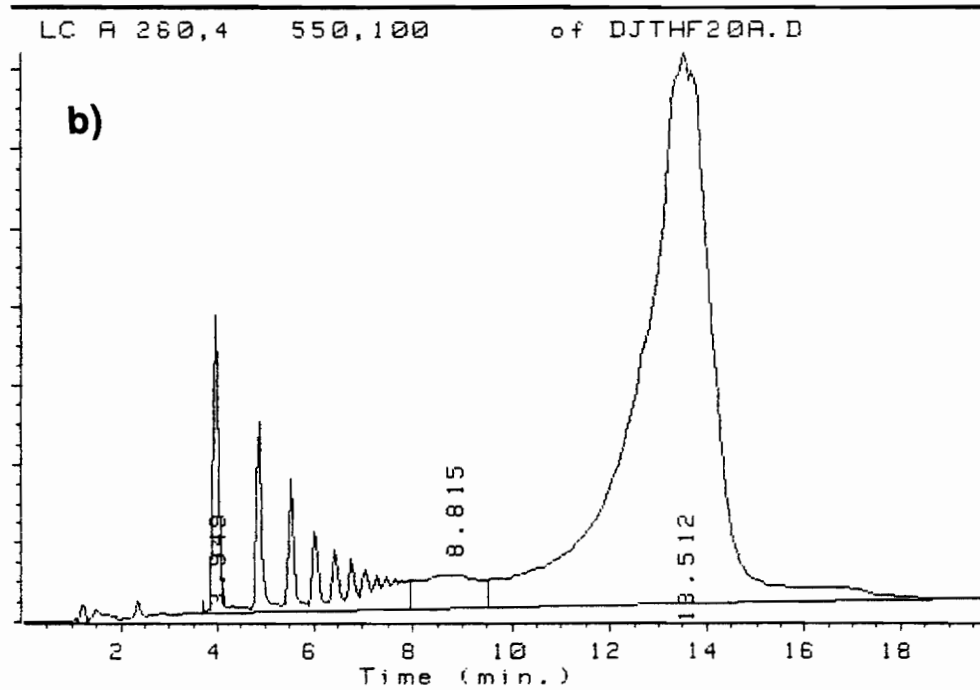
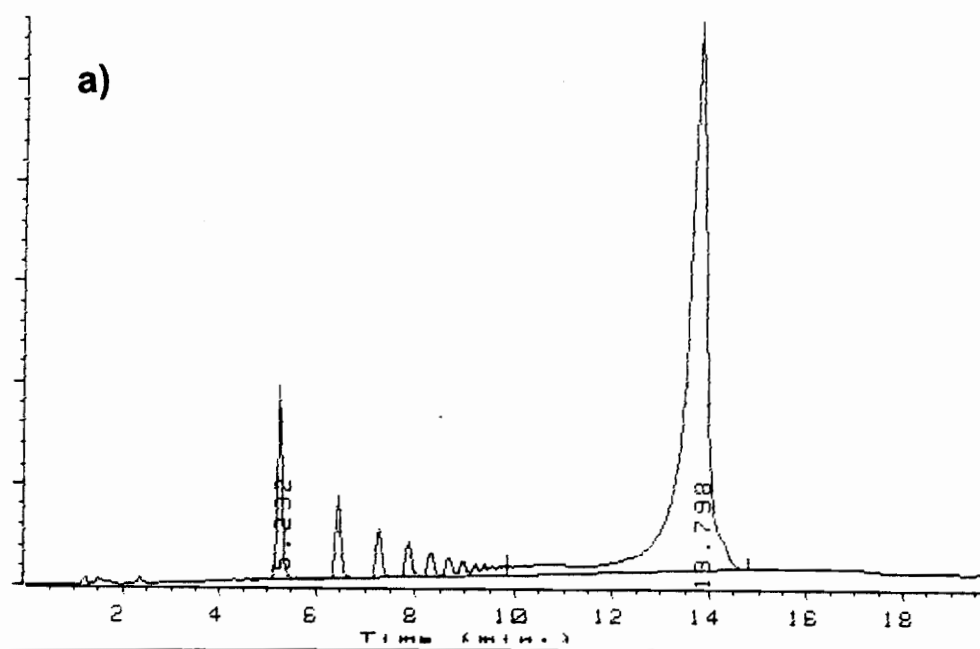


Figure 4.2.5.5 HPLC trace of a) final BIS A, and b) final PP-PES

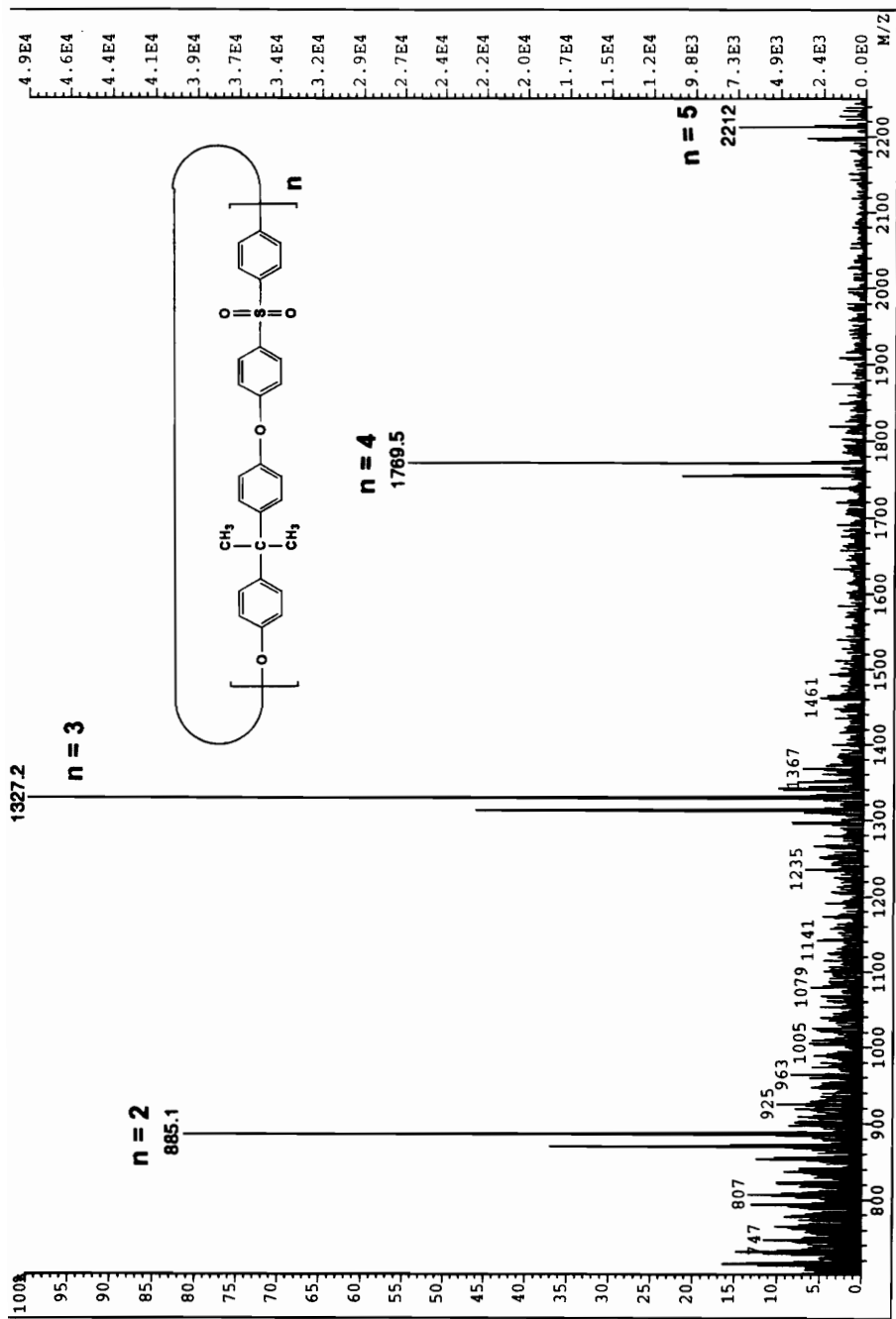


Figure 4.2.5.6 Mass spectrum of aryl ether sulfone cyclooligomers of BIS A

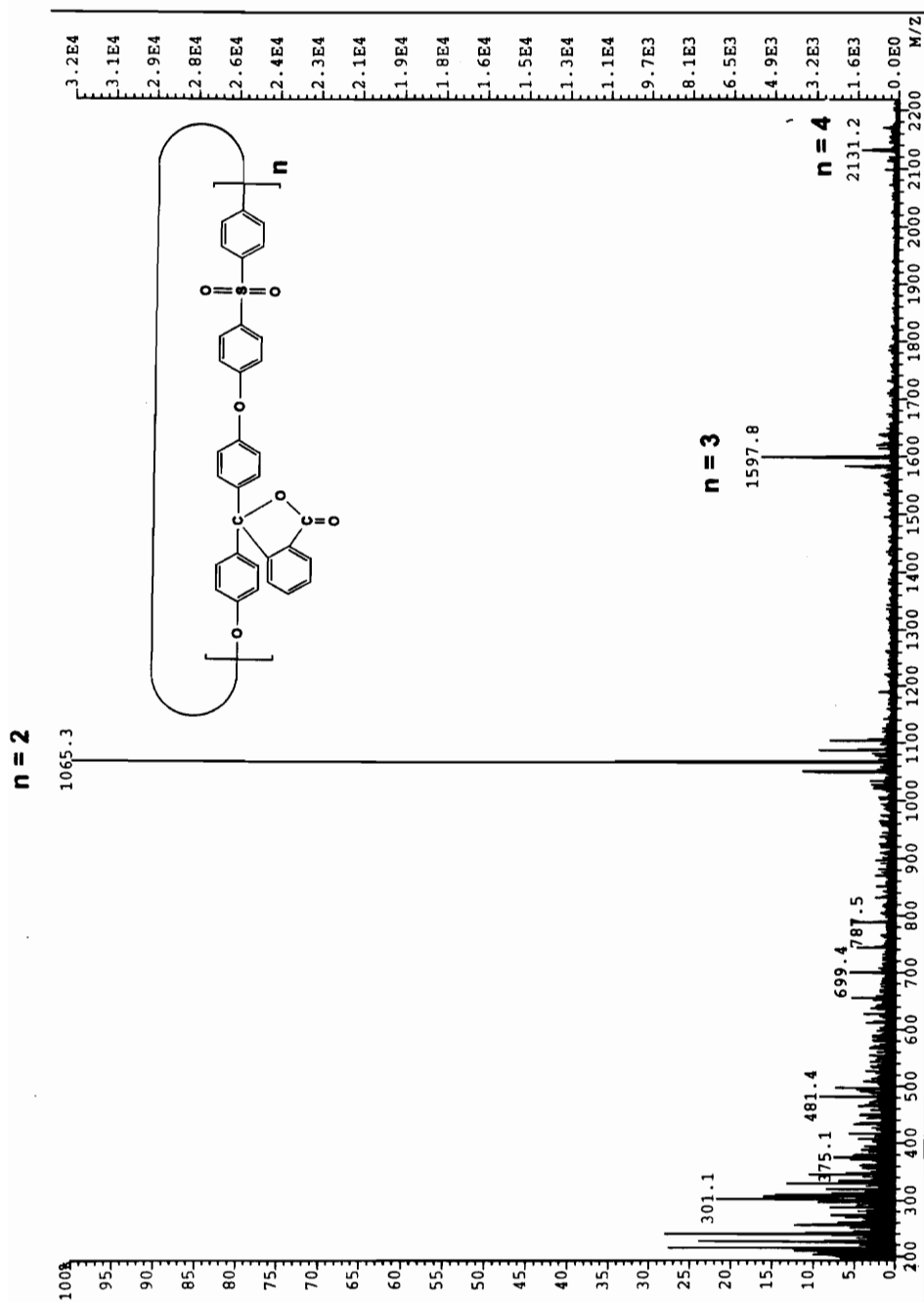


Figure 4.2.5.7 Mass spectrum of aryl ether sulfone cyclooligomers of PP.

It is interesting to note the systematic decrease in amount of each cyclic oligomer as the DP increases (Figure 4.2.5.8). This is likely due to the decreasing probability of cyclization vs. chain extension as chain length increases. In other words, as the chain ends get farther apart, the intramolecular cyclization reaction becomes less likely.

Suggestions for decreasing the formation of cyclics in poly(arylene ether) synthesis will be given in Section 5.0.

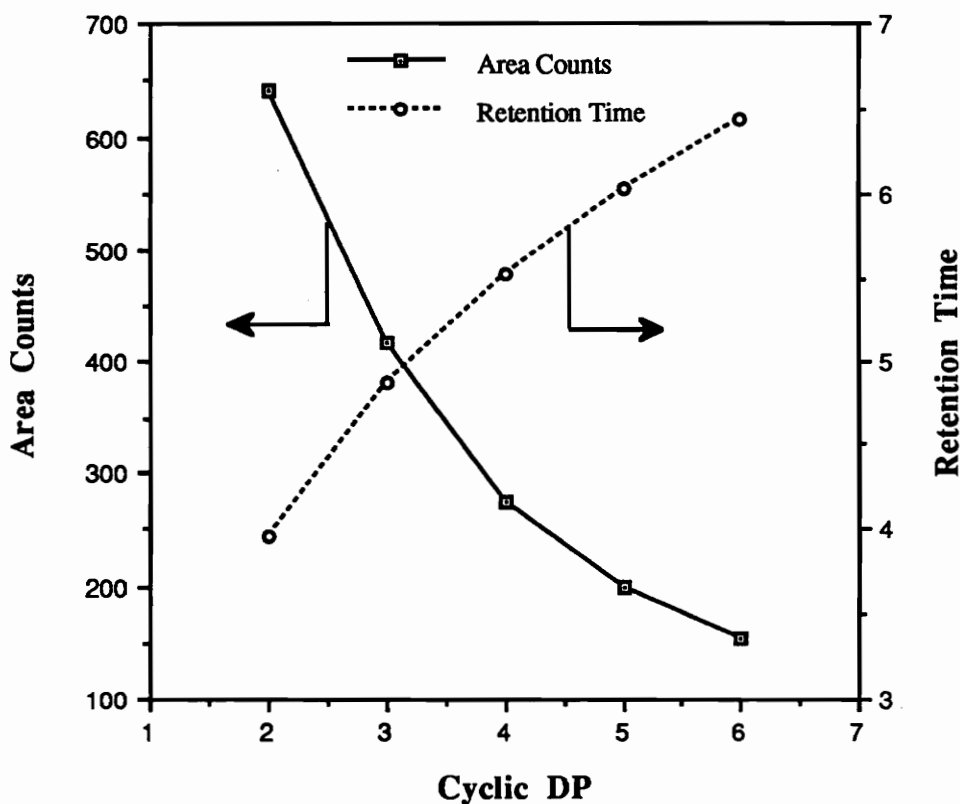


Figure 4.2.5.8 Plot of cyclooligomer ring size (DP) vs area counts and retention time. (taken from HPLC)

4.2.6 Model Polymerization Conclusions

The model polymerization study predicted the reaction rates of BIS A and PP with an activated halide would be about the same under K_2CO_3 conditions. When the model polymerizations were done, this trend held true. This study does not support the findings of Jin *et al.*⁴⁹⁹ hypothesis that PP forms an intermolecular complex with K_2CO_3 resulting in significantly increased reaction kinetics.

The following advantages were determined for the use of K_2CO_3 as the base in a polycondensation process. An exact equimolar amount of base is not needed because a weak base ensures no hydrolysis of the activated dihalide. As a result, all components of the reaction can be added to the flask initially. The weak base will not hydrolyze amide solvents, e.g. DMAc, so many polar aprotic solvents can be used.

As a result of this model study, the following disadvantages were determined for the use of KOH in poly(arylene ether) synthesis. An exact equimolar stoichiometry of base is required to ensure that the bisphenol consumes all the base and is converted to a bisphenate. If strong base is not consumed by the bisphenol, the activated dihalide is subject to hydrolysis. As a result, this reaction must be carried out in two steps: 1) addition of the bisphenol and base, dehydrate, then 2) add in the activated dihalide. A polar aprotic solvent must be used that will not undergo hydrolysis e.g. DMSO. Amide solvents should not be used due to the hydrolysis problem.

HPLC-UV/vis of aliquots collected during polymerization is an excellent tool for analysis of polymerization kinetics in poly(arylene ether)s. Further confirmation was collected to support the hypothesized mechanism for K_2CO_3 interaction in poly(arylene ether) synthesis. Mechanisms are proposed for the interaction of phenolphthalein with K_2CO_3 and KOH suggesting polycondensation through a quinone intermediate.

4.3 Unique Characteristics of Poly(arylene ether)s

4.3.1 Metal Complexing in PAE's

This study was performed to determine the extent of complexation of a metal halide, cobalt chloride (CoCl_2), with different poly(arylene ether)s. Previously in our laboratories, some initial work had been done to study the complexation of different metal halides with PAE's that containing phosphorus.^{209,311} This study has not only further investigated this phenomena, but also the possibility that the phenolphthalein moiety may also complex with metals as shown in Figure 4.3.1.1. The preparation of the metal containing polymer films is discussed in Section 3.5. The structures and acronyms for the polymers studied is shown in Table 4.3.1.1.

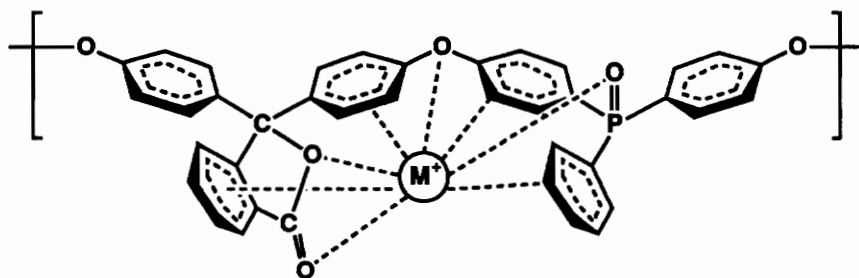


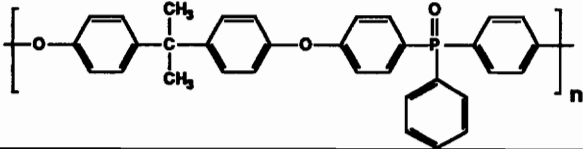
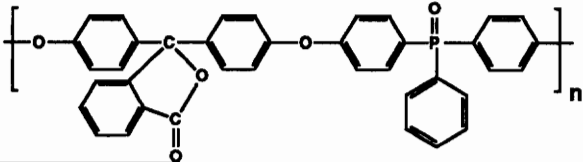
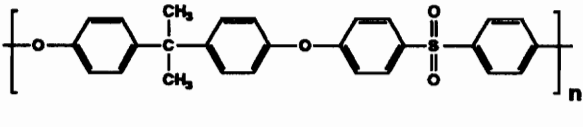
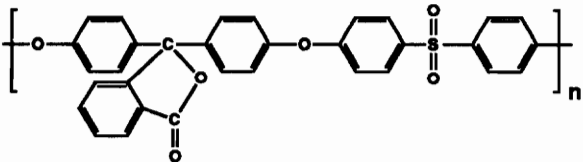
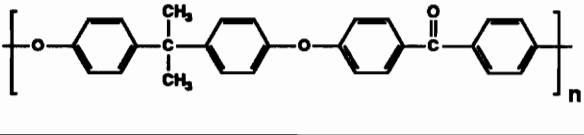
Figure 4.3.1.1 Hypothesized structure of PP-PEPO complexing with a metal.

The metal halide, CoCl_2 , was chosen because Bonaplata *et al.* showed that it had the greatest complexing ability with phosphorus-containing PAE's.²⁰⁹ As a result, only CoCl_2 was used with five different PAE's. All PAE's were controlled to have an Mn of 20 kg/mol. Polymers containing either phosphorus or phenolphthalein (e.g. BIS A-PEPO, PP-PEPO, PP-PES) resulted in optically clear, homogenous blue films. Polymers without these moieties (e.g. BIS A-PES, BIS A-PEK) resulted in films in which the metal salt precipitated. As a result, these films were brittle and opaque.

The drying temperature of the metal salt-containing films is extremely important, as even small traces of solvent (DMAc) can interfere with polymer complexation. Drying temperatures were chosen to be ~10-20 °C below T_g of the polymeric systems with no metal. As a result, the final drying conditions of 12 h under vacuum were used: PP-PEPO and PP-PES = 240 °C; BIS A-PEPO and BIS A-PES = 175 °C; BIS A-PEK = 150 °C.

The PP-PES film containing CoCl_2 was optically clear before drying but turned slightly opaque after drying at 240 °C for 12 h. This may be due to the sample being dried too close to the depressed T_g (240 °C), possibly resulting in oxidation of the metal salt.

Table 4.3.1.1. Poly(arylene ether)s used in metal complexation studies.

Acronym	Polymer Repeat Unit Structure
BIS A - PEPO	
PP - PEPO	
BIS A - PES	
PP - PES	
BIS A - PEK	

4.3.1.1 Thermal Analysis (TGA, DSC)

Thermal analysis was done on the five PAE samples with no metal halide and on those with 20 mole % CoCl_2 . These results can be seen in Tables 4.3.1.1.1 and 4.3.1.1.2. DSC analysis of the metal containing films showed an increase in T_g for the BIS A-PEPO and PP-PEPO, whereas a decrease was seen in PP-PES, BIS A-PES, and BIS A-PEK. The samples in which an increase in T_g was seen were the same samples which gave optically clear, homogeneous, tough films. This T_g increase may be due to the formation of an ionic network.

Since the PP-PES sample contains no phosphorus, it was of great interest to see whether the phenolphthalein might also complex metal. The initial optical clarity of the film before drying gave some indication that there was complexation between the metal and the phenolphthalein in the polymer backbone. However, once dried at $240\text{ }^\circ\text{C}$ the PP-PES film turned slightly opaque, which may be due to oxidation of the metal salt as mentioned earlier. As a result, a decrease in T_g was seen in the PP-PES film. To verify if there is truly metal complexation occurring, the PP-PES film should be dried at $210\text{--}220\text{ }^\circ\text{C}$, not $240\text{ }^\circ\text{C}$. It is suggested that the drying temperature of the PP-PES was too close to T_g , thus interfering with the results.

The other polymers in which the metal precipitated (BIS A-PES and BIS A-PEK) resulted in brittle, opaque films. Conceivably, the decrease in T_g may be due to the metal salt acting as a plasticizer, resulting in a depressed T_g .

Upon examination of the TGA traces for these PAE's, the same samples with depressed T_g 's (PP-PES, BIS A-PES, and BIS A-PEK) were also the only samples with significant decrease in 5% weight loss temperature. In PP-PES, the temperature at 5% weight loss only decreased $\sim 60\text{ }^\circ\text{C}$ as compared to BIS A-PES and BIS A-PEK which had a more significant decrease of $230\text{ }^\circ\text{C}$ and $290\text{ }^\circ\text{C}$, respectively. The phosphorus

containing polymers showing high complexation (BIS A-PEPO, PP-PEPO) did not lose a significant amount of thermal stability (~ 20 °C).

Table 4.3.1.1.1 Glass transitions of 20,000 g/mole poly(arylene ether)s containing 20 mole % CoCl₂.

Polymer Acronym (Mn = 20 kg/mole)	Tg (°C) of Base Polymer*	Tg (°C) of Polymer with 20 mole % CoCl ₂ *
BIS A-PEPO	198	231
PP-PEPO	261	288
BIS A-PES	188	171
PP-PES	255	240
BIS A-PEK	154	136

* Determined with DSC at 10 °C/min.

Table 4.3.1.1.2 TGA 5% wt. loss of poly(arylene ether)s containing 20 mole % CoCl₂.

Polymer Acronym (Mn = 20 kg/mole)	TGA (°C)* 5% wt. loss in air	
	Base Polymer	Polymer with 20 mole % CoCl ₂
BIS A-PEPO	523	504
PP-PEPO	519	501
BIS A-PES	521	295
PP-PES	507	451
BIS A-PEK	532	245

* Scan at 10 °C/min.

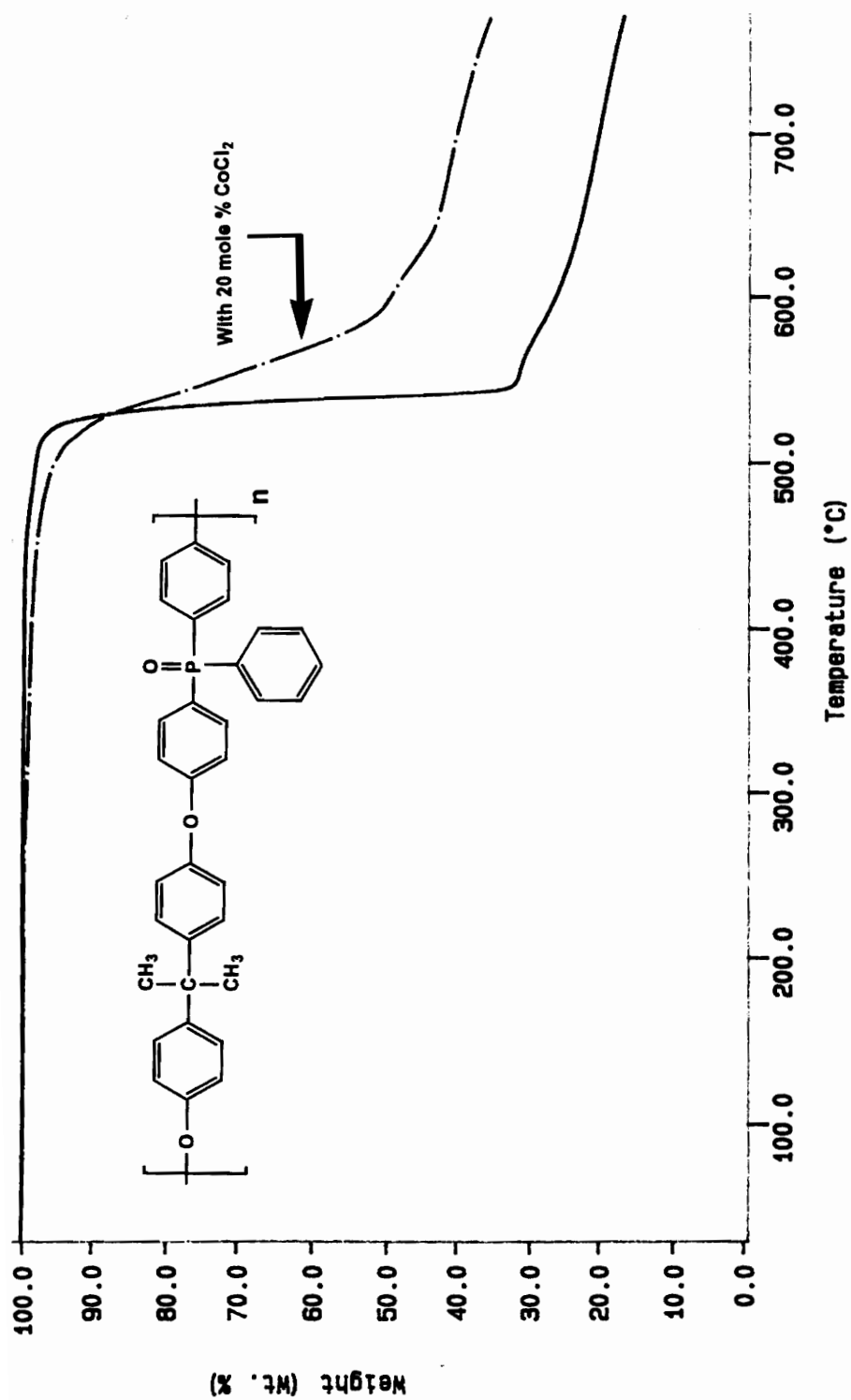


Figure 4.3.1.1.1 TGA traces of BIS A-PEPO with and without 20 mole % CoCl_2 ($10^\circ\text{C}/\text{min.}$ in air)

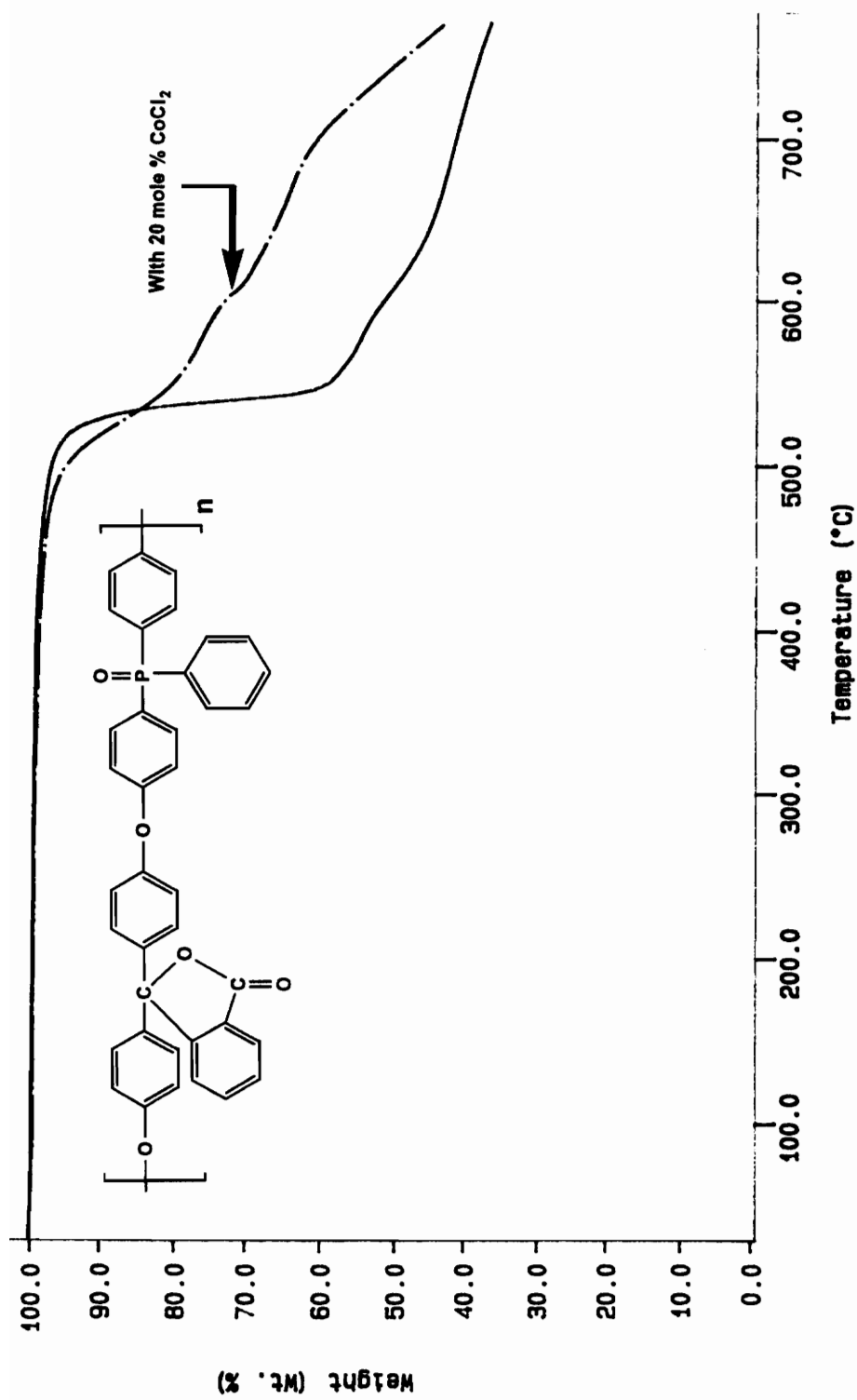


Figure 4.3.1.1.2 TGA traces of PP-PEPO with and without 20 mole % CoCl_2 ($10^\circ\text{C}/\text{min}$. in air)

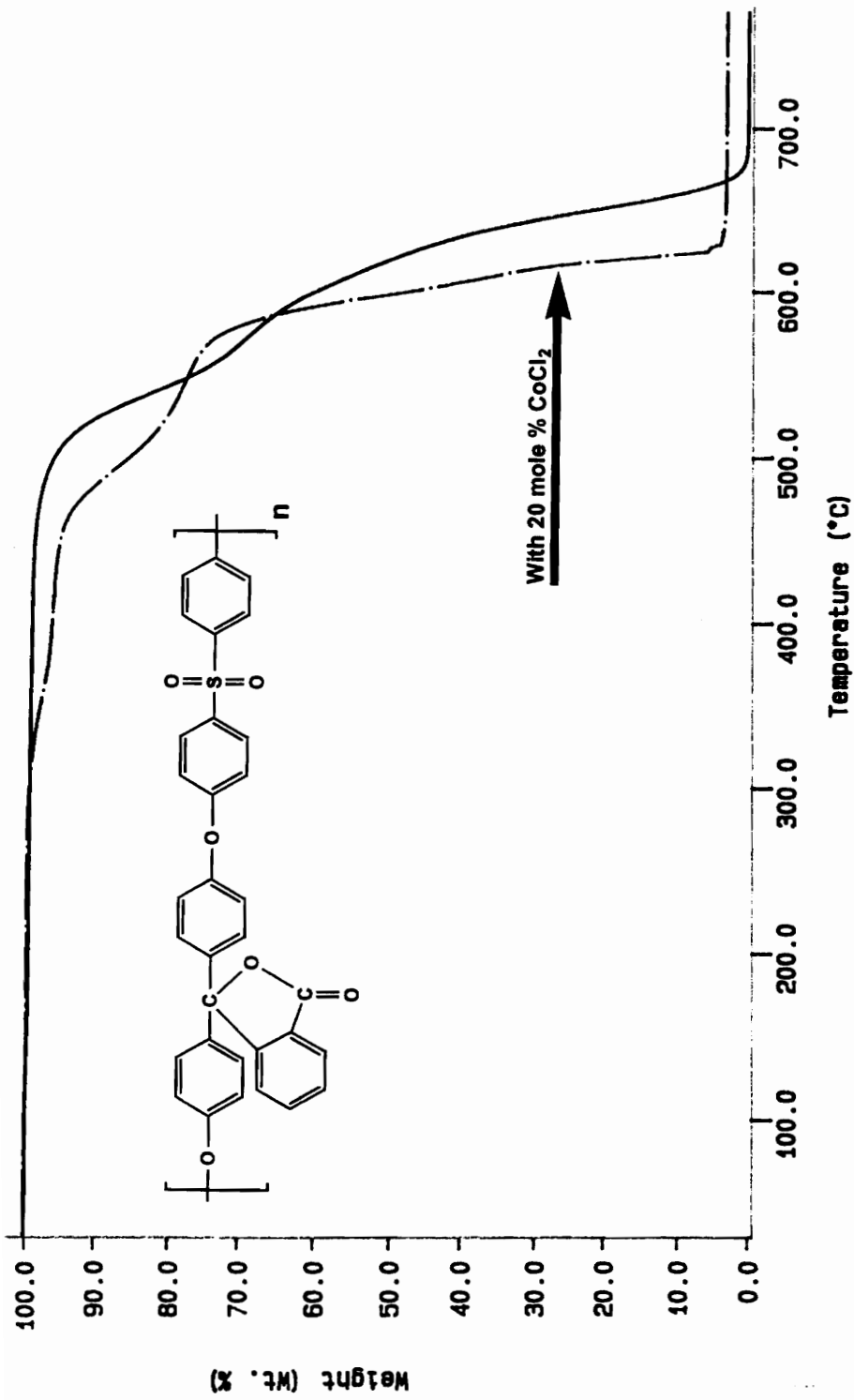


Figure 4.3.1.1.3 TGA traces of PP-PES with and without 20 mole % CoCl₂ (10 °C/min. in air)

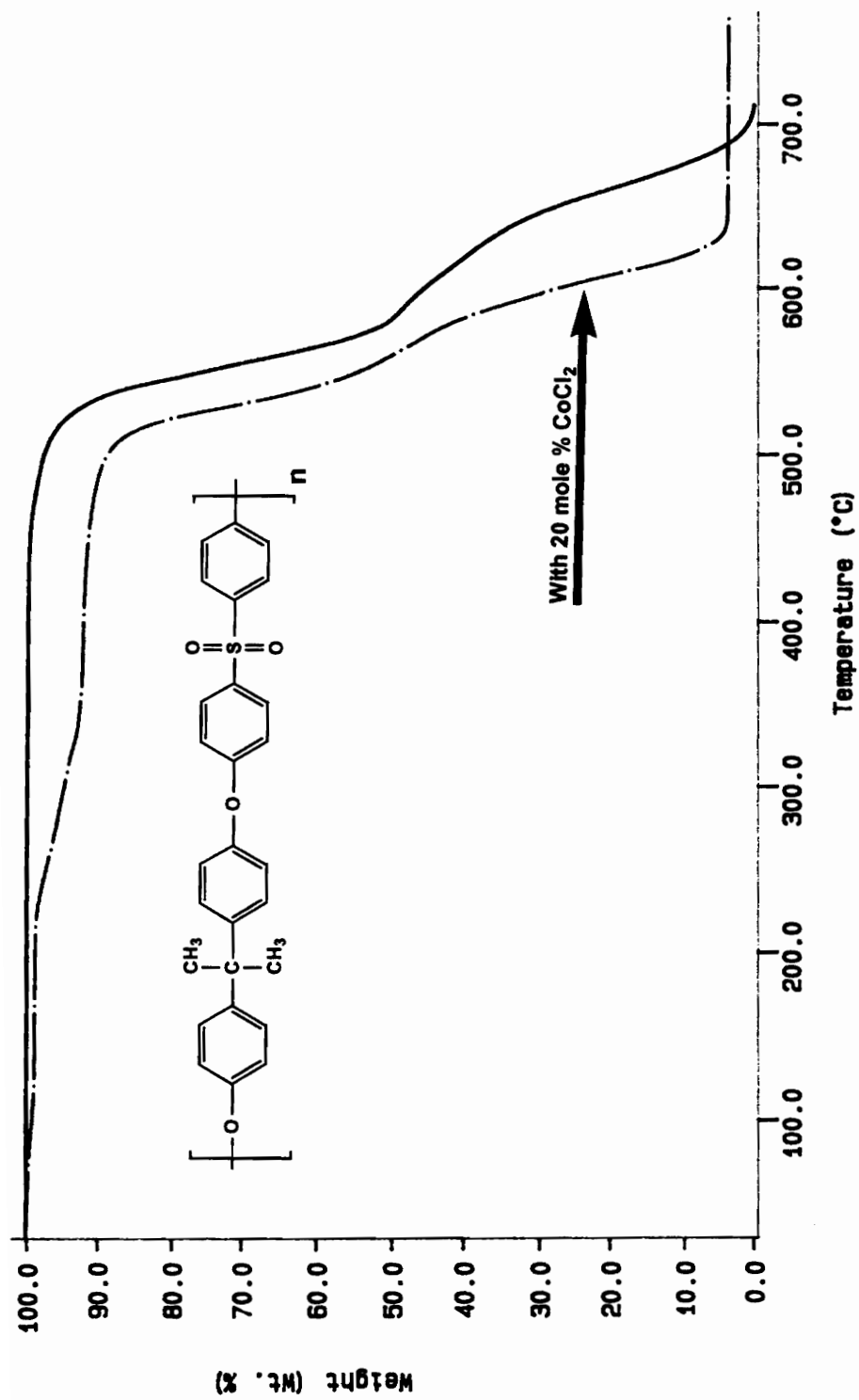


Figure 4.3.1.1.4 TGA traces of BIS A-PES with and without 20 mole % CoCl₂ (10 °C/min. in air)

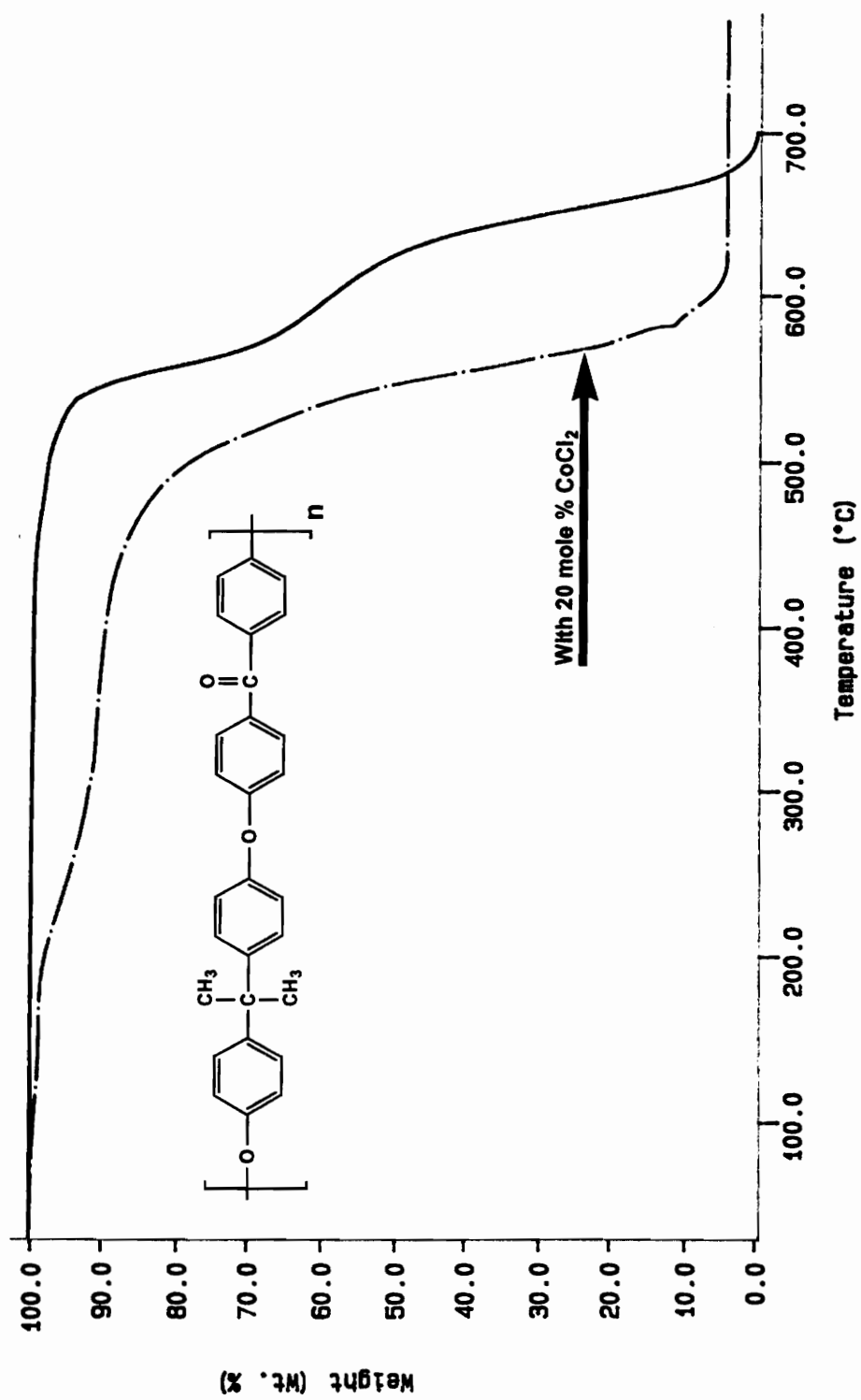
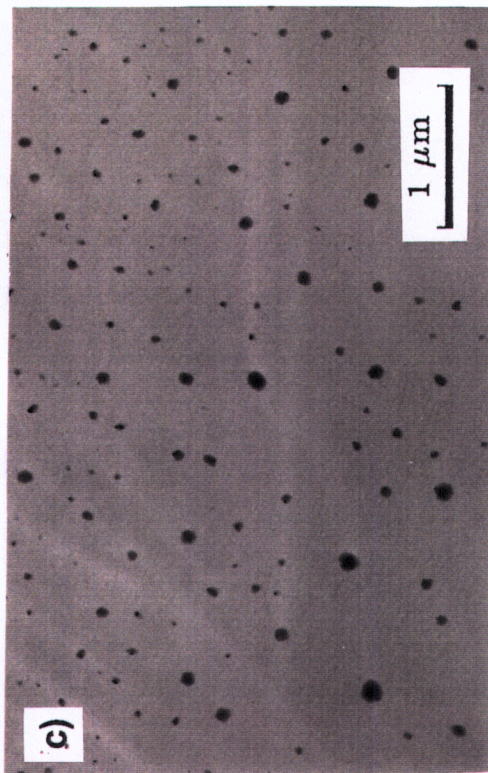
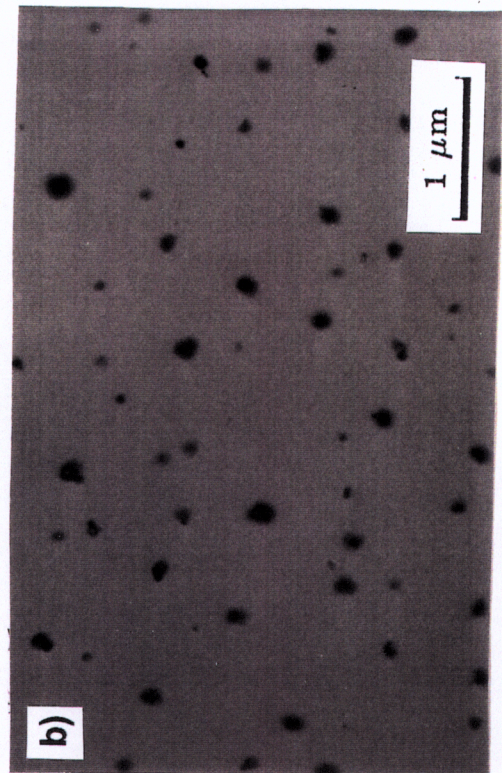


Figure 4.3.1.1.5 TGA traces of BIS A-PEK with and without 20 mole % CoCl_2 ($10^\circ\text{C}/\text{min}$. in air)

4.3.1.2 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) was utilized to determine if the metal salt domains within the polymeric matrix could be seen. Figure 4.3.1.2.1 shows TEM for the BIS A-PEPO, PP-PEPO, and PP-PES samples. At high magnification (18,750x), the domains of metal salt can be seen (black spots). There is very little metal salt that appears in the BIS A-PEPO, as compared to a much more significant amount that appears in the PP-PEPO and PP-PES films.

Figure 4.3.1.2.2 shows the TEM for the BIS A-PES and BIS A-PEK. These two samples exemplify what occurs when no metal complexation takes place. The films are brittle, and contain holes (white spots) due to the large metal salt clusters falling out.



(mag = 18,750x)

Figure 4.3.1.2.1 TEM of PAE's containing 20 mole % CoCl_2 : a) BIS A-PEPO, b) PP-PEPO, and c) PP-PES

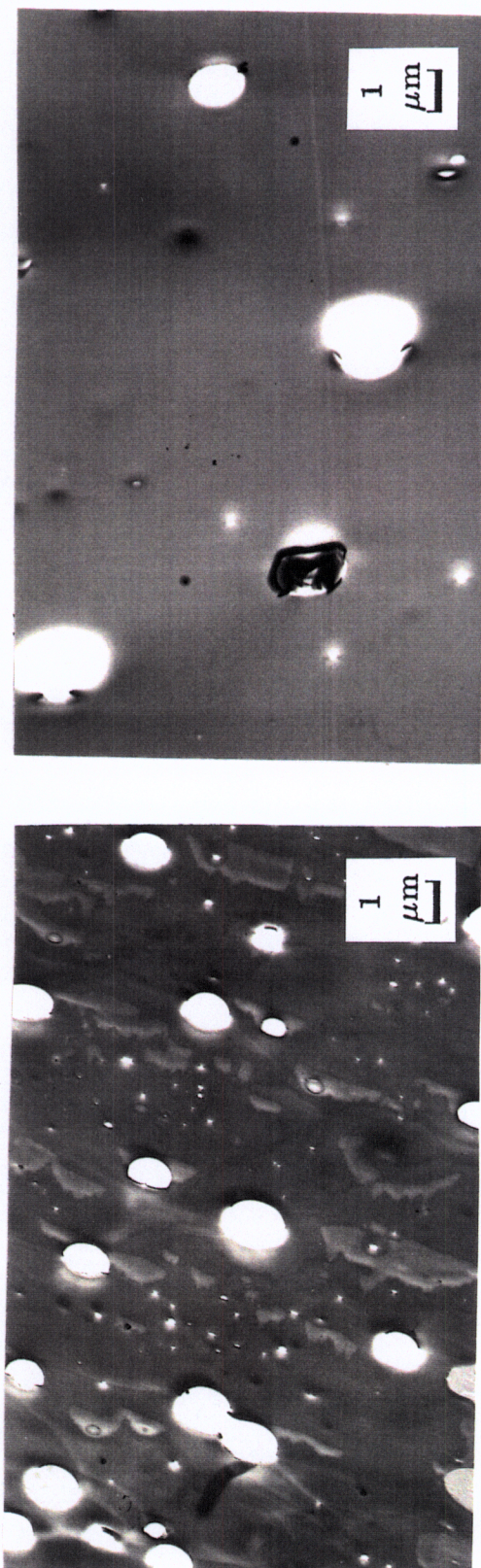


Figure 4.3.1.2.2 TEM of PAE's containing 20 mole % CoCl₂: a) BIS A-PES, and b) BIS A-PEK (mag = 5,900x)

In conclusion, the results of this study suggest that the phenolphthalein moiety complexes with metal salts, although not to the extent that the phosphine oxide does. This conclusion can be supported by the optically clear film that was obtained by adding 20 mole % of CoCl_2 to a PP-PES sample. Also a TEM analysis of the PP-PES film showed that there was an even distribution of metal salt within the polymer matrix. Evidence that phenolphthalein is less effective at metal salt complexing than phosphorus is the fact that with PP-PES the T_g was depressed ($\sim 15^\circ\text{C}$) and there was a decrease in 5% wt. loss ($\sim 60^\circ\text{C}$), although not to the extent that was seen for the truly non-complexed polymeric systems (BIS A-PES and BIS A-PEK).

In comparing the BIS A-PEPO and PP-PEPO systems, it was hoped that there would be evidence the phenolphthalein and phosphine oxide moiety would share the complexing with the CoCl_2 . More analysis on these systems will give a clearer defined picture of the role that phenolphthalein and phosphorus play in complexing with metal salts. Suggested future directions for this research will be discussed in Section 5.2.

4.3.2 Chemical Modification of Phenolphthalein-based Poly(arylene ether)s

An advantage in using phenolphthalein rather than bisphenol A in a polymer backbone, is it provides a reactive functionality for further chemical modification to enhance properties (e.g. raise T_g). The lactone ring is susceptible to insertion by nucleophiles. To demonstrate this concept, PP-PEPO was treated under both acid (*p*-toluene sulfonic acid) and base (potassium *t*-butoxide) catalysis with *p*-nitrophenylhydrazine (pNPH) in *o*-dichlorobenzene as a solvent. The experimental details are described previously in Section 3.6.2 and in Scheme 4.3.2.1.

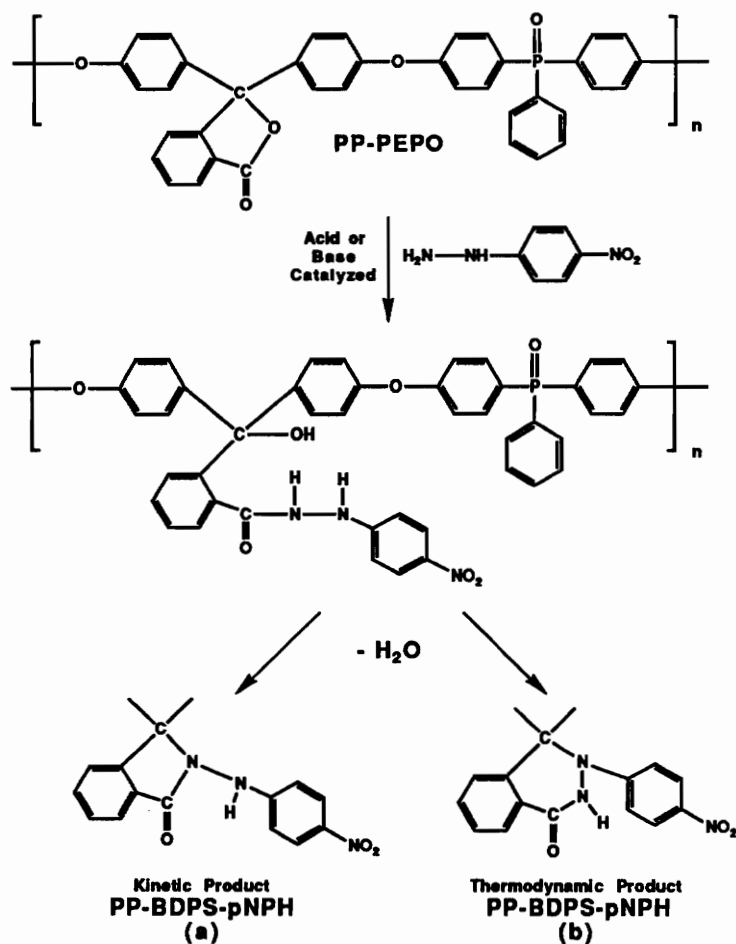
Under acid catalysis, the polymer remained in solution and was isolated by precipitation into methanol. To ensure complete removal of unreacted pNPH, the polymer was successively precipitated from chloroform/methanol until the filtrate was colorless.

Under base catalysis, the polymer precipitated from the reaction medium as a black sludge. After washing with methanol, the black solid was ground in a pestle and mortar to obtain a granular solid. The material was then extracted (Soxlet) with methanol for 2 days. The solid was not soluble in DMAc, DMSO, chloroform, *m*-cresol, or hexafluoroisopropanol.

Nitrogen analysis on the two polymers showed that the soluble polymer (acid catalysis) contained ~10 mole % pNPH. The insoluble polymer (base catalysis) contained ~25 mole % pNPH.

The two polymers were characterized by DSC and TGA. Only the 10 mole % derivatized polymer was characterized by IR (Figure 8.2.40), ^1H NMR (Figure 8.2.41), ^{13}C NMR (Figure 8.2.42), and GPC-UV/vis, due to the insolubility of the 25 mole % derivatized polymer.

DSC and TGA analysis of both polymers is shown in Table 4.3.2.1.



Scheme 4.3.2.1 Proposed structures of derivatized PP-PEPO.

Table 4.3.2.1 Characterization of derivatized 15 kg/mole PP-PEPO.

mole % Derivatized ^a (pNPH)	$[\eta]$ ^b	T_g (°C) ^c	TGA ^d
0	0.31	265	496
10	0.29	284	490
25	insoluble	296	485

^a Determined by elemental analysis - nitrogen content

^b Analyzed in chloroform at 25 °C

^c Determined with DSC at 10 °C/min.

^d 5% wt. loss in air at 10 °C/min.

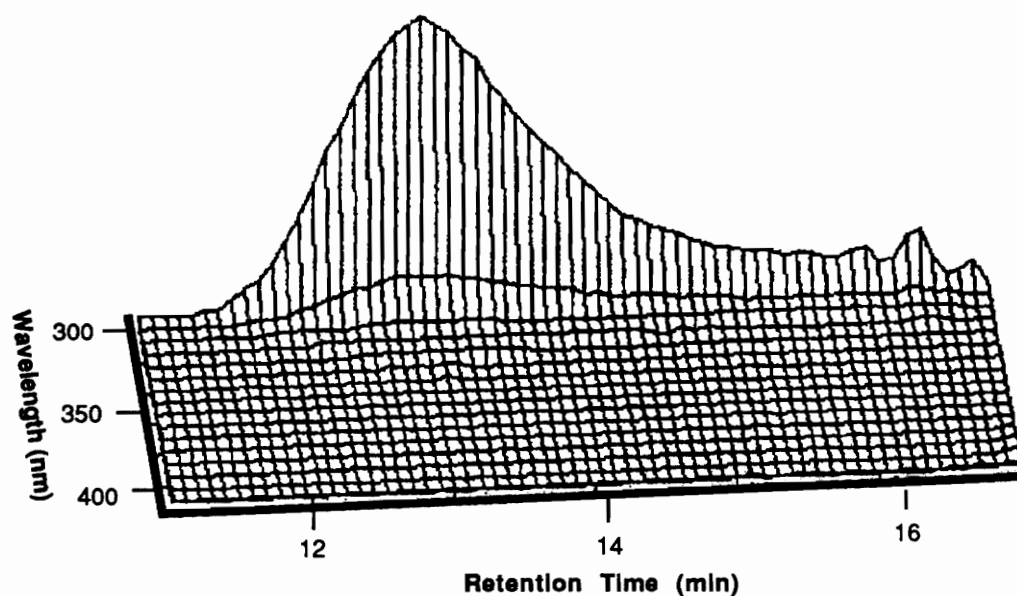
It should be pointed out that pNPH has two possible modes of insertion into the lactone ring resulting in the formation of a five or a six-membered lactam ring as shown previously in Scheme 4.3.2.1a and b.

The increase in T_g with incorporation of pNPH is likely due to both hydrogen bonding from the N-H as well as increased cohesive energy density due to the polar nitro group.

Intrinsic viscosity measurements on the underivatized and 10 mole % derivatized PP-PEPO samples indicate that the chemical modification had no effect on molecular weight. This observation was substantiated by GPC analysis. Since the GPC was equipped with a photo-diode array detector, multiple wavelength signals were collected during the analysis. Overlay of the signals collected at 270 nm (backbone phenyl chromophores) and 400 nm (pNPH chromophore) showed no offset, confirming that the pNPH incorporation is random, and uniform in all chains⁵⁰² as shown in Figure 4.3.2.2.

Chemical modification of the PP-PES was also attempted. In an effort to go to higher % derivatization without precipitating the polymer from the reaction medium, DMSO was used as solvent under potassium *t*-butoxide catalysis. Indeed, no polymer precipitated, however, upon pouring the reaction mixture into methanol/water, a fine powder precipitate was formed. GPC-UV/vis analysis of this powder showed that it was very low molecular weight. Furthermore, overlay of the 270 and 400 nm signals indicate that the pNPH chromophore resides mainly on chain ends⁵⁰² as evidenced by the offset of the 400 nm signal to the low molecular weight side of the 270 nm signal as shown in Figure 4.3.2.3.

a)



b)

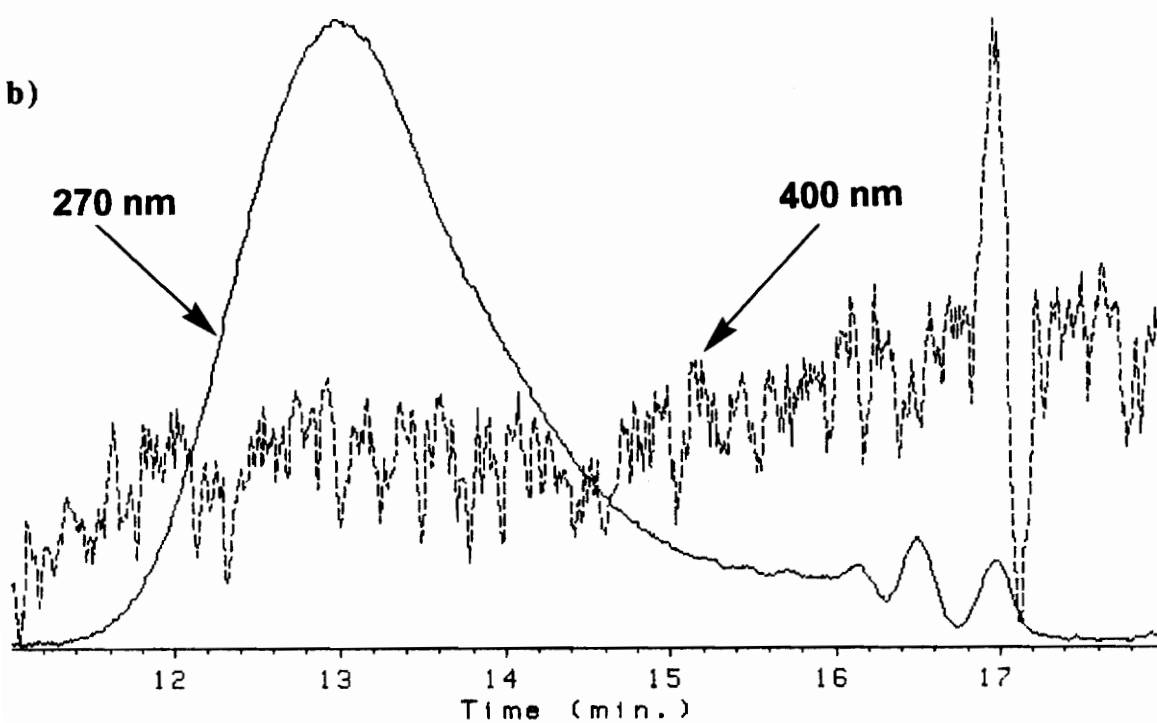
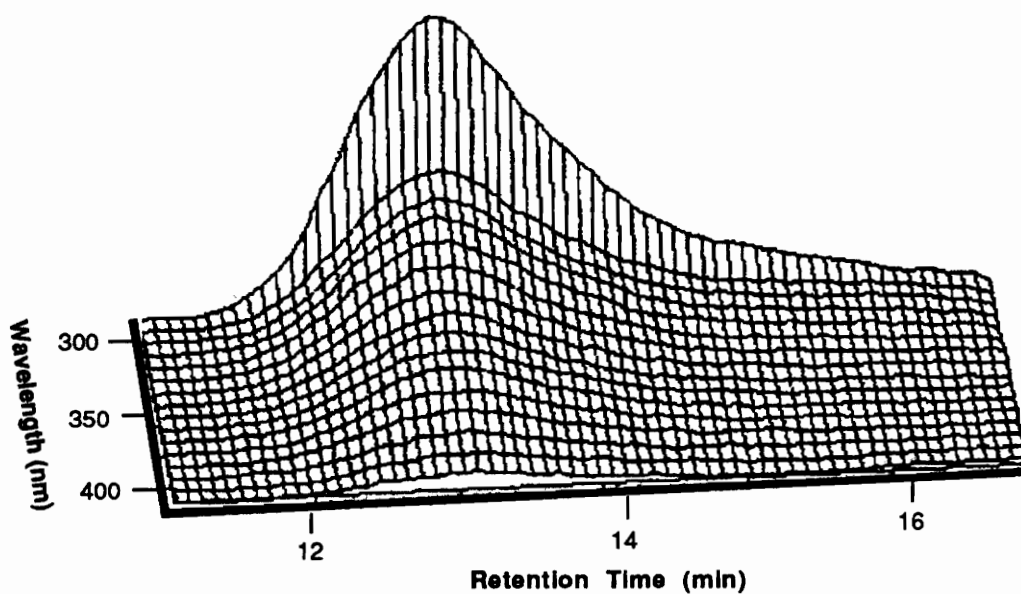


Figure 4.3.2.1 GPC-UV/vis of underivatized PP-PEPO: a) 3D plot of all wavelengths, and b) overlay of 270 and 400 nm.

a)



b)

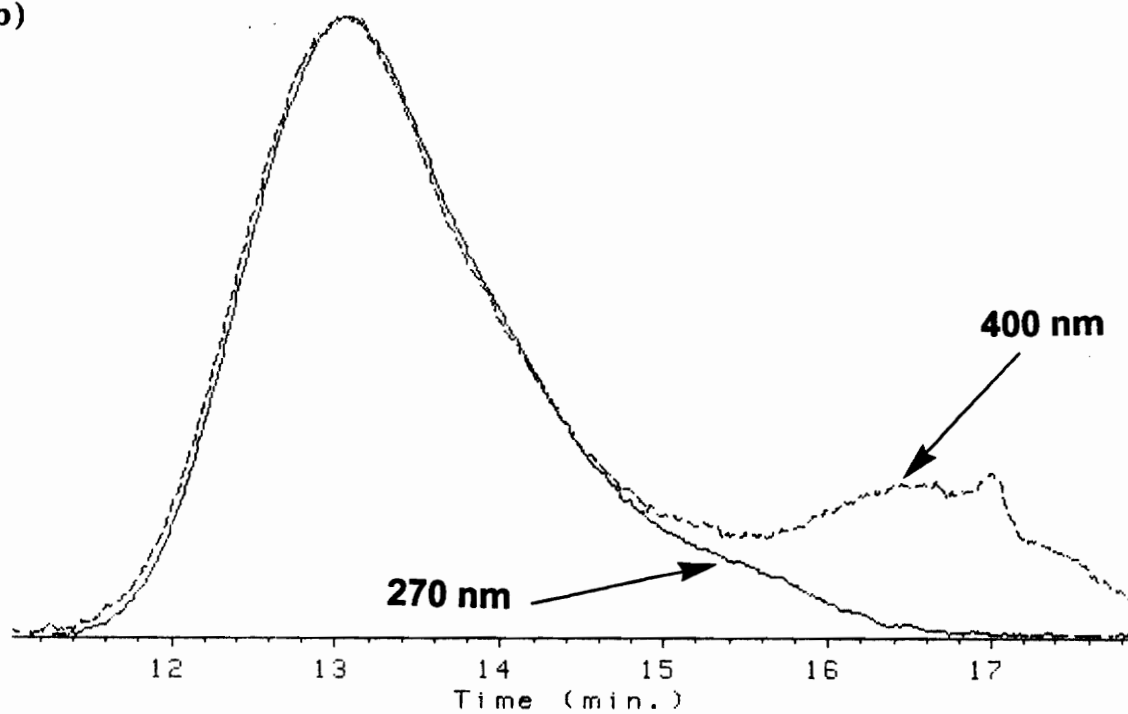
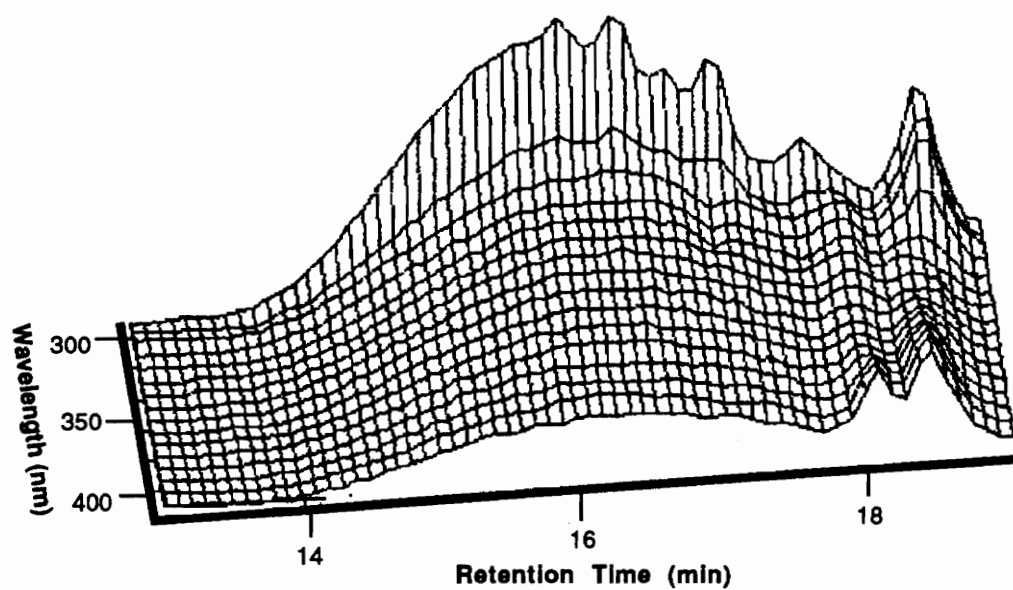


Figure 4.3.2.2 GPC-UV/vis of 10 mole % derivatized PP-PEPO: a) 3D plot of all wavelengths, and b) overlay of 270 and 400 nm.

a)



b)

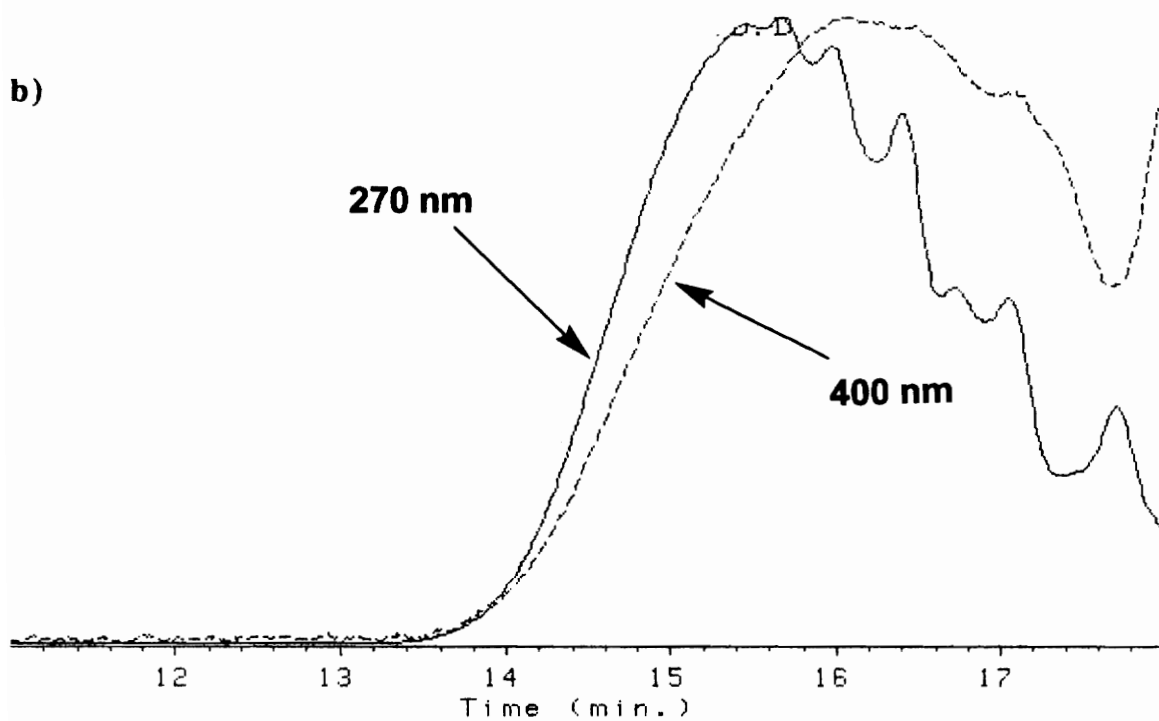
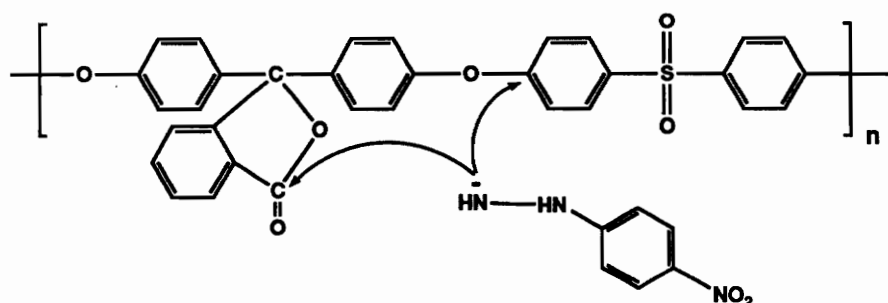


Figure 4.3.2.3 GPC overlays of derivatized PP-PES: a) 3D plot of all wavelengths, and b) overlay of 270 and 400 nm.

PP-PES was not successfully derivatized likely due to the solvent medium, DMSO. It is well known that with a strong base in DMSO, the ether link in PES can be cleaved.^{1,60,80,105} This is due to the sulfone being an excellent activating group within the polymer backbone, therefore activating the ether link towards nucleophilic displacement.



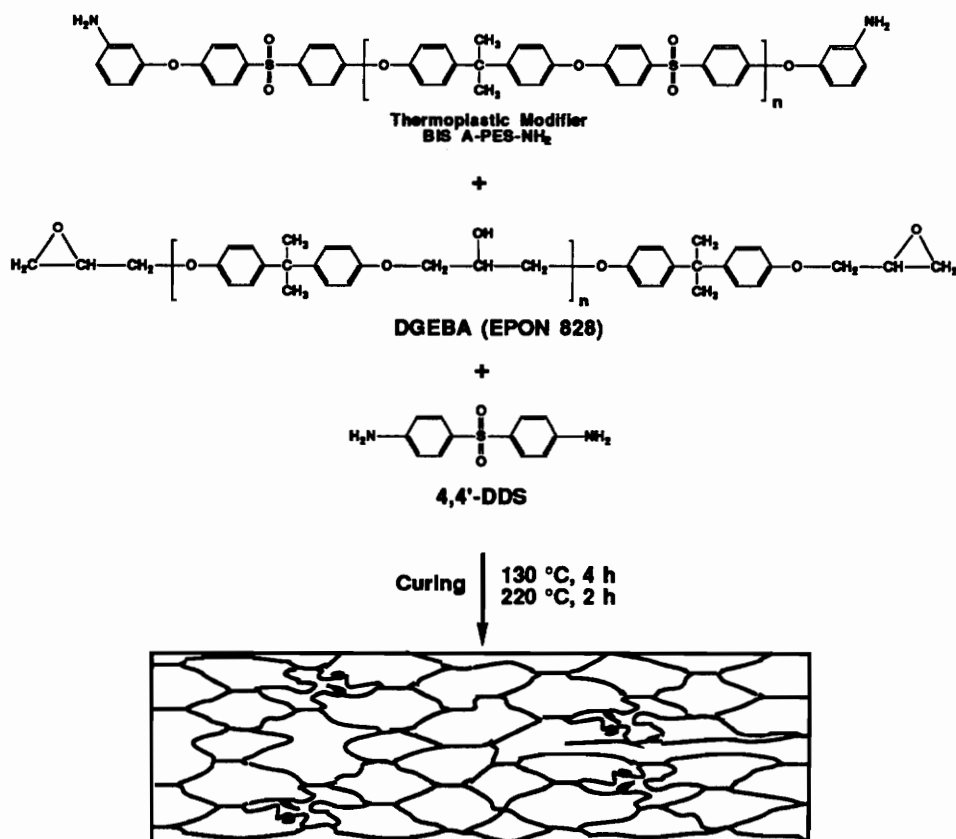
Scheme 4.3.2.2 Competing reaction between attack of the pendant lactone vs. cleaving the activated ether linkage during derivatization of PP-PES with pNPH.

As a result of this study, whenever opening a lactone under basic conditions, the cleavage of the activated ether link is a probable side reaction. The reaction under acidic conditions does not give evidence for any side reactions, yet these conditions do not allow for high conversion of derivatization.

4.3.3 Reactive Poly(arylene ether)s (PAE) as Tougheners in Epoxy and Cyanate Ester Blends

4.3.3.1 Reactive PAE Used in Epoxy Blends

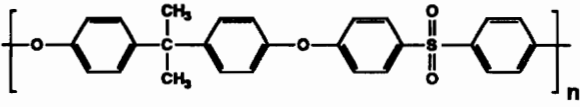
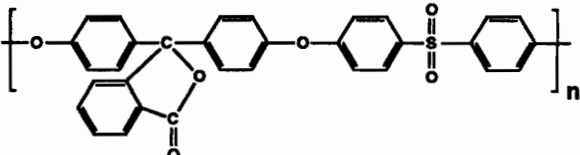
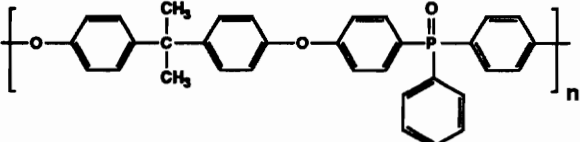
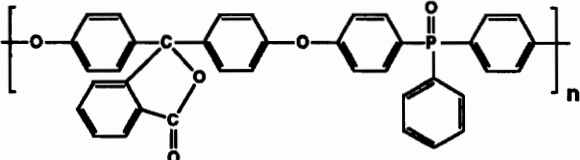
Poly(arylene ether)s can be used to act as thermoplastic modifiers for toughening epoxy resins.^{145,149,150,158,171,172,200,254,266,271,275,276,279,305,322,372,397,421,425,427,446,503} Many different amorphous poly(arylene ether)s were synthesized with varying molecular weights, structures, and end-groups. These polymers were synthesized according to the conditions discussed previously in Section 3.3. The blending conditions with epoxy were discussed previously in Section 3.7.1. Reaction conditions for functionalized PAE with an epoxy resin is shown in Scheme 4.3.3.1.1.³²²



Scheme 4.3.3.1.1 Example of a thermoplastic modifier toughened epoxy network.

A series of functionalized polymers containing chlorine, *t*-butyl, hydroxy, or amine end-groups were dissolved in epoxy resin and cured. The structures and acronyms for the polymers synthesized are shown in Table 4.3.3.1.1.

Table 4.3.3.1.1 Poly(arylene ether)s used tougheners in epoxy resins.

Acronym	Polymer Repeat Unit Structure
BIS A - PES	
PP - PES	
BIS A - PEPO	
PP - PEPO	

The polymers shown previously in Table 4.3.3.1.1 were controlled molecular weight systems with different reactive or non-reactive end-groups. The end-groups of these polymers are denoted by the following acronyms: reactive = amine (NH₂) and hydroxy (OH); non-reactive = chloro (Cl) and tertiary butyl (*t*-butyl). These polymers were characterized by intrinsic viscosity $[\eta]$, and polymers containing OH and NH₂ end-groups were also characterized by titration.

Table 4.3.3.1.2. Characterization of controlled molecular weight PAE's used as tougheners in epoxy resins.

Polymer Acronym/endgroup	Theoretical <Mn> (kg/mol)	Molar Ratio ^a Bisphenol/Endcap	[η] ^b dL/g	Titration <Mn> ^c (kg/mol)
BIS A-PES- <i>t</i> -butyl	10.0	10.76	0.24	n/a
BIS A-PES- <i>t</i> -butyl	15.0	16.44	0.30	n/a
BIS A-PES- <i>t</i> -butyl	20.0	22.04	0.33	n/a
BIS A-PES-Cl	5.0	n/a	0.16	n/a
BIS A-PES-Cl	15.0	n/a	0.31	n/a
BIS A-PES-NH ₂	15.0	16.44	0.29	17.5
BIS A-PES-NH ₂	25.0	27.75	0.37	26.7
BIS A-PES-OH	15.0	n/a	0.32	14.9
BIS A-PEPO-NH ₂	15.0	14.39	0.32	16.5
PP-PEPO-OH	20.0	n/a	0.34	19.9
PP-PES-NH ₂	15.0	13.60	0.25	17.0
PP-PES-Cl	15.0	n/a	0.25	n/a
PP-PES-OH	10.0	n/a	0.18	8.9
PP-PES-OH	15.0	n/a	0.26	15.5
PP-PES-OH	20.0	n/a	0.33	21.0

^a Determined by the Carother's Equation (appendix 8.1)

^b CHCl₃ at 25 °C

^c Titrated with 0.025N TMAH

The phase morphology of the modified epoxy was investigated by Yoon *et al.*³²² to determine the interaction of the thermoplastic modifier with epoxy network upon cure. With the NH_2 and OH end-groups, the PAE can cure in with the epoxy network, thereby forming covalent bonds between phases. With the reactive NH_2 end-groups, after mechanical deformation, the thermoplastic and epoxy phases remain bonded to each other, i.e. no delamination between phases occurs as shown in Figure 4.3.3.1.1a. In modified networks containing *t*-butyl end-groups on the thermoplastic modifiers, the ends are not reactive. As a result, holes form in the matrix after mechanical deformation as represented in Figure 4.3.3.1.1b. The illustration shown in Figure 4.3.3.1.1 is confirmed with TEM showing the same trend.³²²

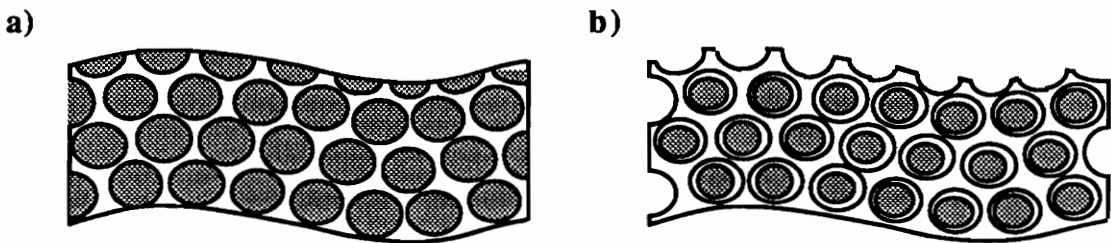


Figure 4.3.3.1.1 Representation of a PAE modified epoxy network after mechanical deformation: a) reactive NH_2 terminated PAE, and b) non-reactive *t*-butyl terminated PAE.

Fracture toughness studies were done to determine the overall effect of reactive (NH_2) versus nonreactive (*t*-butyl) end-groups on the toughened epoxy systems. A plot representing the two cases is shown in Figure 4.3.3.1.2.³²²

It can be seen in Figure 4.3.3.1.2 that with reactive end-groups on the thermoplastic modifier (BIS A-PES- NH_2), the fracture toughness continues to increase after phase inversion at 20 wt % when the thermoplastic becomes the continuous phase.

Conversely, when the nonreactive thermoplastic modifier (BIS A-PES-*t*-butyl) undergoes phase inversion, the fracture toughness decreases. The characterization of PAE toughened epoxy resins is discussed in much greater detail by Yoon *et al.*³²²

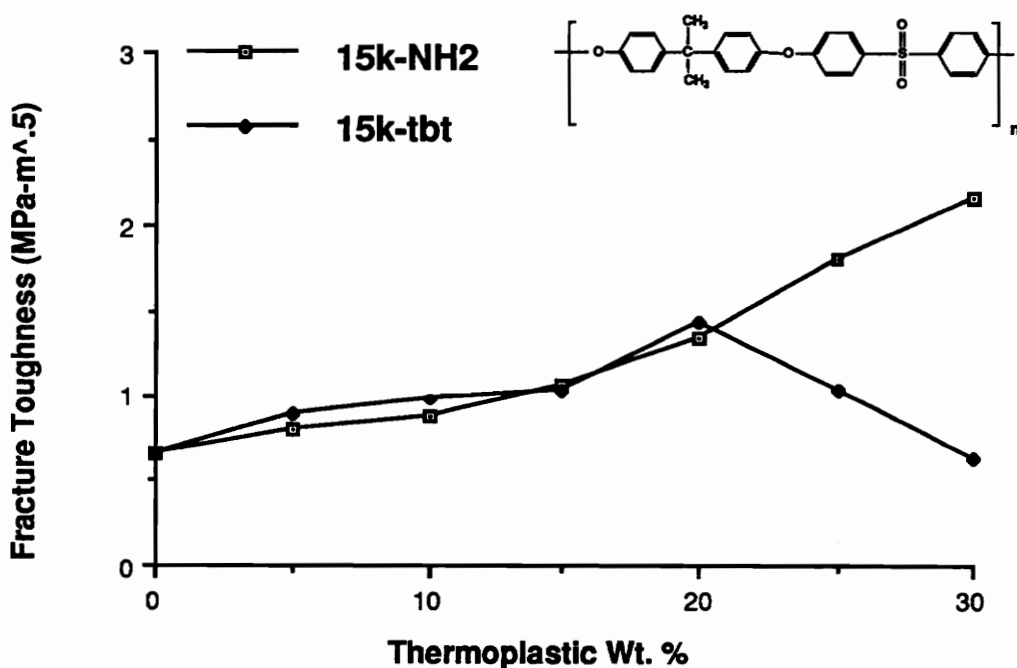


Figure 4.3.3.1.2 Fracture toughness plot of a modified epoxy network with a) reactive NH₂ terminated PAE, and b) nonreactive *t*-butyl terminated PAE.³²²

4.3.3.2 Reactive PAE Used in Cyanate Ester Blends

Poly(arylene ether)s (PAE) can also be used as toughness modifiers for cyanate ester networks.^{219,220} Specifically, PP based PAE's were utilized over the more typical BIS A-PAE's due to their increased thermal stability. The three PP systems studied are hydroxy functionalized phenolphthalein based poly(arylene ether ketone) (PP-PEK), poly(arylene ether sulfone) (PP-PES), and poly(arylene ether phosphine oxide) (PP-PEPO) as shown in Table 4.3.3.2.1.

Table 4.3.3.2.1 PP-PAE's used as toughness modifiers in cyanate ester resins.

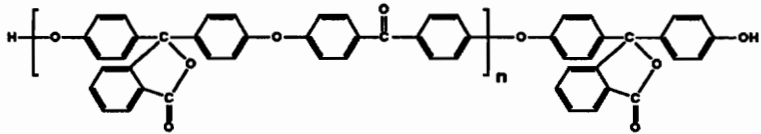
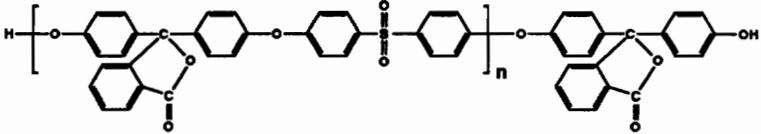
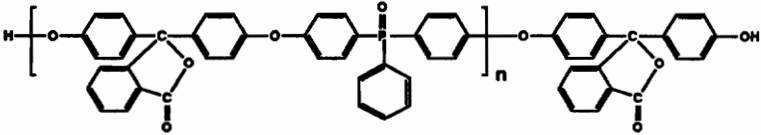
Acronym	Polymer Repeat Unit Structure
PP-PEK-OH	
PP-PES-OH	
PP-PEPO-OH	

Table 4.3.3.2.2 Characterization of PP-PAE's used as thermoplastic modifiers in cyanate ester resins.

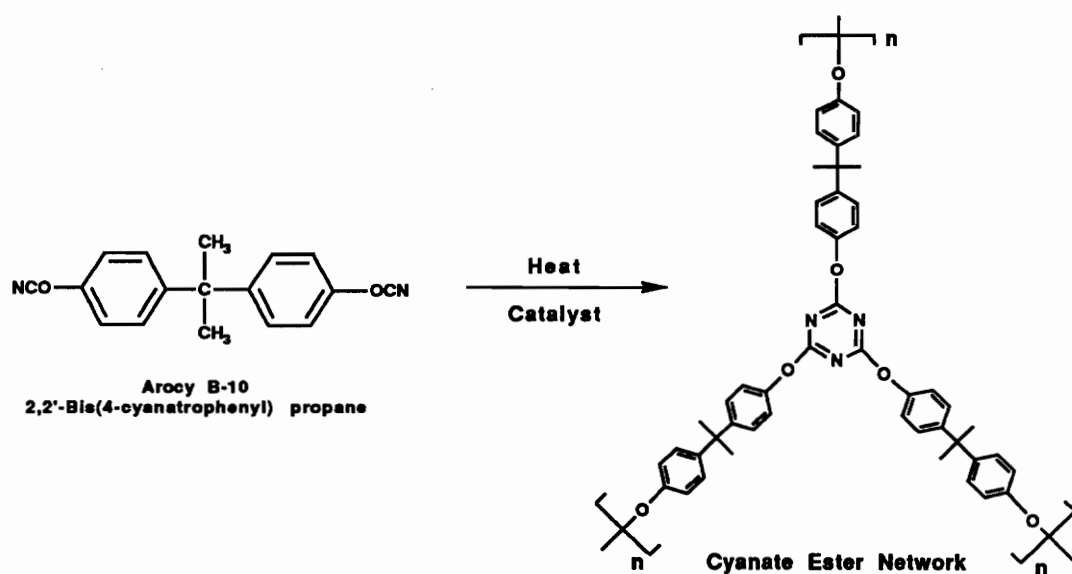
Polymer Acronym	Theoretical <Mn> (kg/mole)	$[\eta]^a$ (dL/g)	Titration $<Mn>^b$ (kg/mole)	Tg (°C) c
PP-PEK-OH	15.0	0.32	16.0	226
PP-PES-OH	10.0	0.18	8.9	252
	15.0	0.26	15.5	259
	20.0	0.33	21.0	262
PP-PEPO-OH	15.0	0.29	16.1	265

a CHCl₃ at 25 °C

b Titrated with 0.025N TMAH

c Determined with DSC at 10 °C/min.

These PP based PAE's were then blended with cyanate ester resin by Srinivasan^{219,220} and cured according to the process as described previously in Section 3.7.2. The proposed chemical process leading to three dimensional insoluble networks is shown in Scheme 4.3.3.2.1.⁵⁰⁴



Scheme 4.3.3.2.1 Cyclotrimerization of cyanate esters.⁵⁰⁴

5.0 SUGGESTED FUTURE DIRECTIONS

5.1 Model Polymerization (from Section 4.2.4)

Brunelle *et al.*⁵⁰⁵ determined that polycarbonate cyclooligomers could be made in high yield. Mullins *et al.*^{46,80} and Gibson *et al.*⁷⁹ determined that the same could be done in poly(arylene ether) systems. Each used extremely low concentrations of monomers when forming exclusively cyclooligomers. Using this information, increasing the % solids in the reaction should decrease the amount of cyclooligomer formation.

An interesting study would be to determine the role that % solids has on cyclooligomer formation in poly(arylene ether)s. A plot of cyclooligomer formation vs. % solids would be of a valuable resource, since cyclics significantly effect the overall properties of a polymer.

Another way to decrease cyclooligomer content is to decrease the ratio of toluene to DMAc to increase pot temperature >140 °C. It has been shown by Mullins *et al.*⁸⁰ that cyclooligomer formation is significantly decreased at temperatures > 140 °C. Typically, in our laboratories, the poly(arylene ether) reactions are azeotroped at 130-135 °C for 4 h. It is during this time that the cyclics are forming. By using less toluene, and raising the reflux temperature of the reaction to > 140 °C, the amount of cyclics may decrease.

Lastly, a plot of intrinsic viscosity vs. conversion in poly(arylene ether) formation (theoretical vs. actual) would show how much hydrolysis takes place with KOH vs. K₂CO₃.

5.2 Metal-complexing in Phenolphthalein Poly(arylene ether)s (from Section 4.3.1)

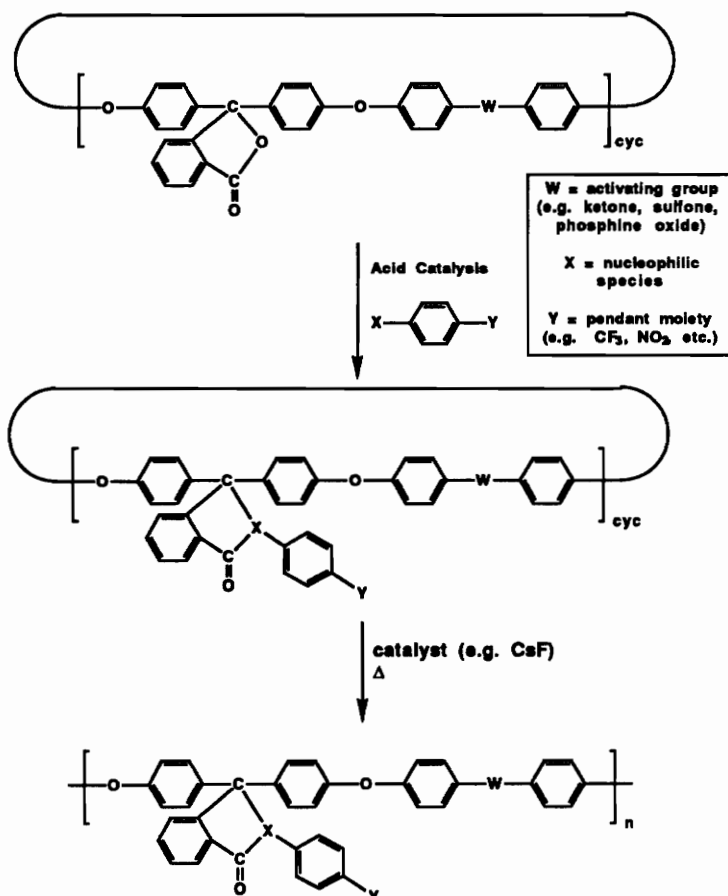
Techniques such as solid state ^{13}C and ^{31}P NMR can be used to determine the extent of complexation of either the carbonyl carbon on phenolphthalein or the phosphorus in the phosphine oxide. With the combination of these two techniques, it may be possible to determine more conclusively the role that phenolphthalein plays in metal complexing.

In addition, dynamic mechanical analysis (DMA) has proven to be an effective tool in analyzing these metal-complexed polymers.²⁰⁹ With a comparison of PP-PEPO, BIS-A PEPO, and PP-PES, this technique may provide interesting insight into the effect that metal complexation has on mechanical properties.

The drying temperature of metal-complexed films is crucial to the outcome of properties. Any residual solvent will plasticize the polymer, thus decreasing the overall properties. Drying the films at too high temperature will oxidize the metal which will also effect the properties. It has been determined that the optimal drying temperature of a metal containing film is $\sim 15\text{-}20$ °C below its new T_g (not the T_g of the polymer with no metal). Thus, the PP-PES film should be dried at $210\text{-}220$ °C and re-evaluated (e.g. DSC, TGA) to effectively compare this system to the others that were discussed in Section 4.3.1.

5.3 Chemical Modification of Poly(arylene ether)s (from Section 4.3.2)

To increase the amount of incorporation of the derivatizing species in the phenolphthalein backbone, other techniques may be employed. This may be accomplished by synthesizing phenolphthalein PAE cyclics by the Gibson *et al.* method⁷⁹ or the Mullins *et al.* method,⁸⁰ derivatize them with a nucleophilic small molecule, then ring open to build high MW. In this way, there would be a higher incorporation of the desired small molecule into each repeat unit.



Scheme 5.3.1 Proposed derivatization of phenolphthalein-containing cyclooligomers.

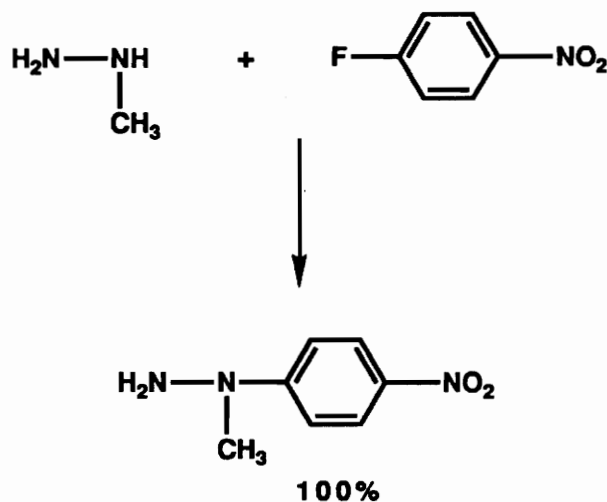
In this research, the chemical modifications were done on phenolphthalein-poly(arylene ether phosphine oxide) (PP-PEPO) systems. Another approach to verify the derivatization chemistry is to study a phenolphthalein-poly(arylene ether sulfone) (PP-PES) system. This polymer needs to be run under the same conditions that were used to make 25% derivatized PP-PEPO (i.e. potassium *t*-butoxide, *o*-dichlorobenzene). As a result, this new derivatized sulfone may further verify the technique. The labile ether linkage in the sulfone polymer may present problems under these strong base conditions.

5.4 Proposed Novel Monomers

5.4.1 Novel Phosphorus-containing Diamine

Polyimides are an important class of high performance polymers, mostly due to the rigid imide link within the backbone which lends itself to increased thermal and mechanical properties. Incorporating phosphorus into the polyimide backbone can achieve a material with increased high performance properties. The following proposal will discuss a new method for incorporating phosphorus into the polyimide backbone.

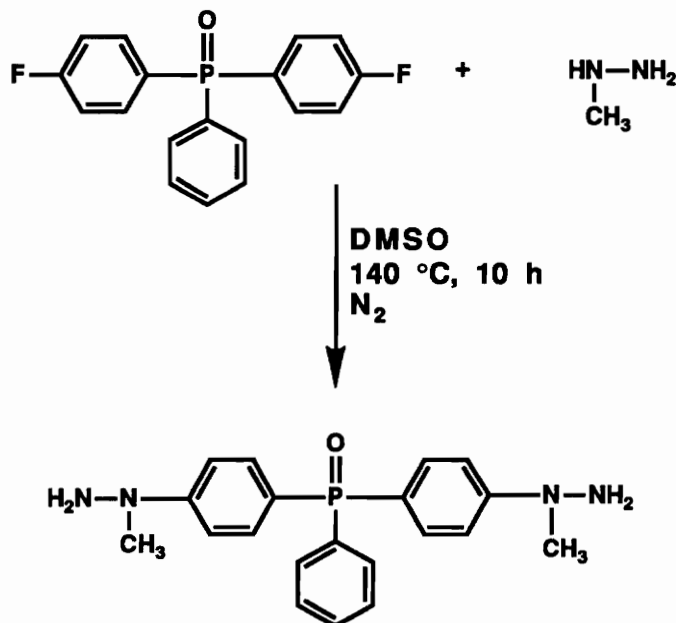
German researchers have found that when methylhydrazine is reacted with 4-fluoronitrobenzene, only one species is formed as shown in Scheme 5.1.1.⁵⁰⁶ Normally, one would expect a mixture of products resulting from the attack of the amine β to the methyl group. This derivative was not observed.⁵⁰⁶



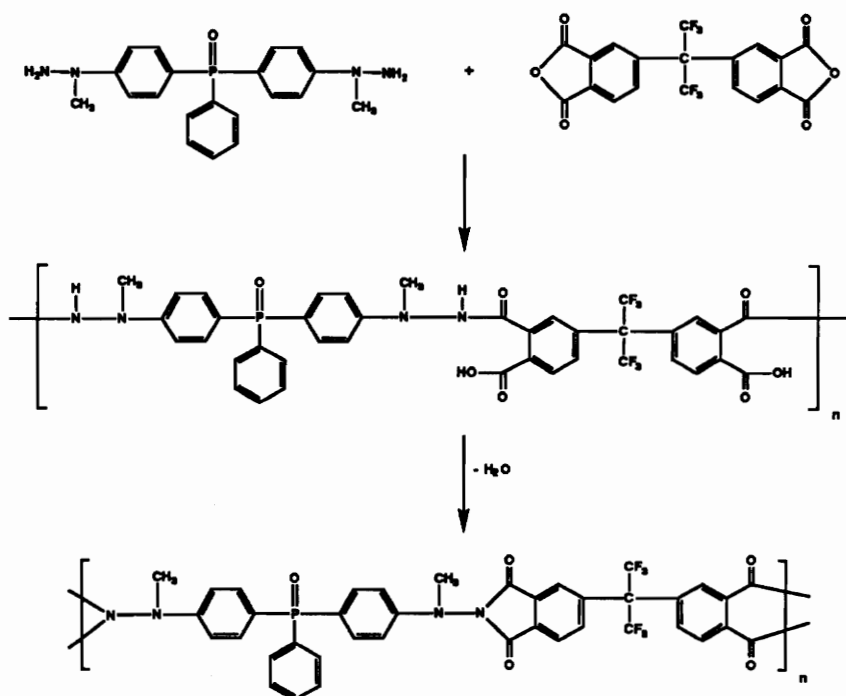
Scheme 5.4.1.1 Reaction of methylhydrazine with 4-fluoronitrobenzene.⁵⁰⁶

It has been the desire of our research group to make a phosphine oxide diamine using BFPPPO as an intermediate compound. Utilizing the concept as described previously in Scheme 5.4.1.1, analogous chemistry could be carried out on an activated dihalide (e.g. BFPPPO) as proposed in Scheme 5.1.2. As a result, a phosphine oxide containing diamine using BFPPPO as an intermediate may be possible.

This reaction as proposed in Scheme 5.1.2 was done as follows. A ten molar excess of methylhydrazine was added to the BFPPPO / DMSO solution. The colorless reaction was heated slowly to 140 °C. When the reaction reached a temperature of 135 °C, the reaction mixture turned yellow in color and a white precipitate formed. After 10 h, the reaction was cooled and the white precipitate filtered which, because of its solubility in water, was most likely the HF salt of methylhydrazine. The yellow homogeneous solution was then poured into water, and the yellow product isolated. Due to lack of time, this product was never characterized to determine if the novel amine as proposed in Scheme 5.1.2 was the true product. If this reaction proves to be successful, the following novel polyimide could be synthesized as shown in Scheme 5.1.3.



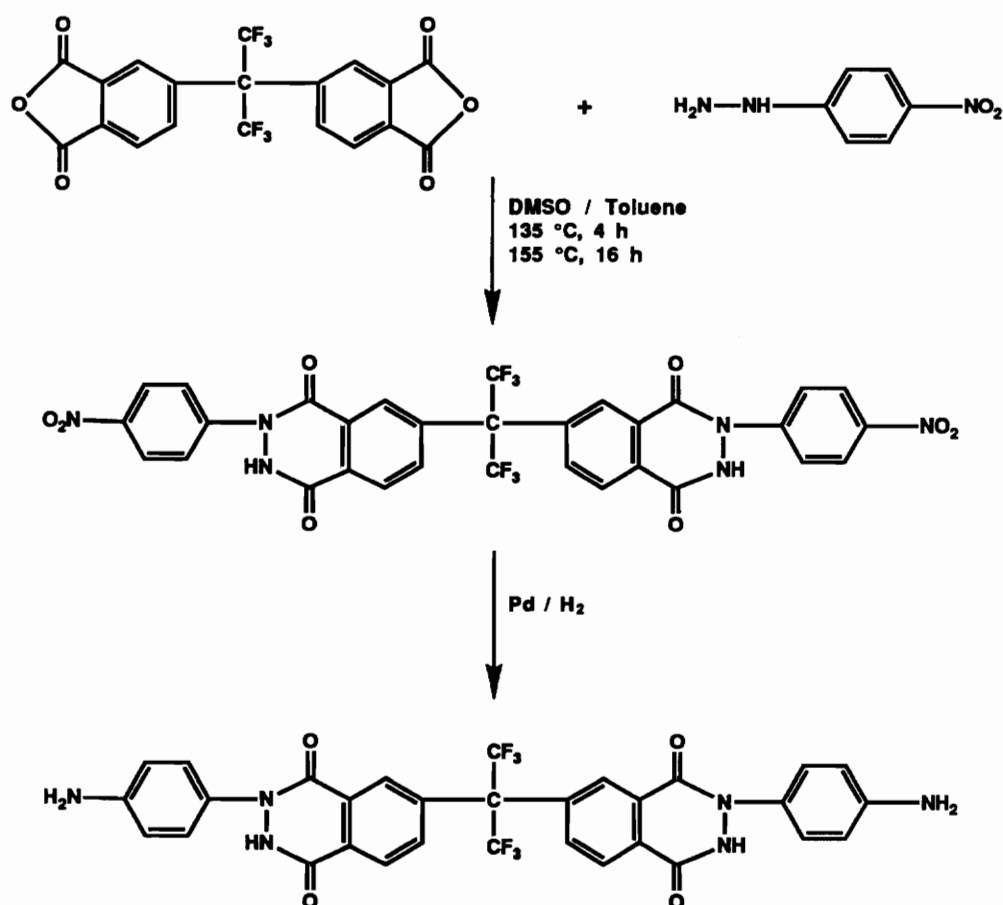
Scheme 5.4.1.2 Novel diamine proposed by the reaction of BFPPPO with methylhydrazine.



Scheme 5.4.1.3 Proposed synthesis of a novel phosphorus-containing polyimide.

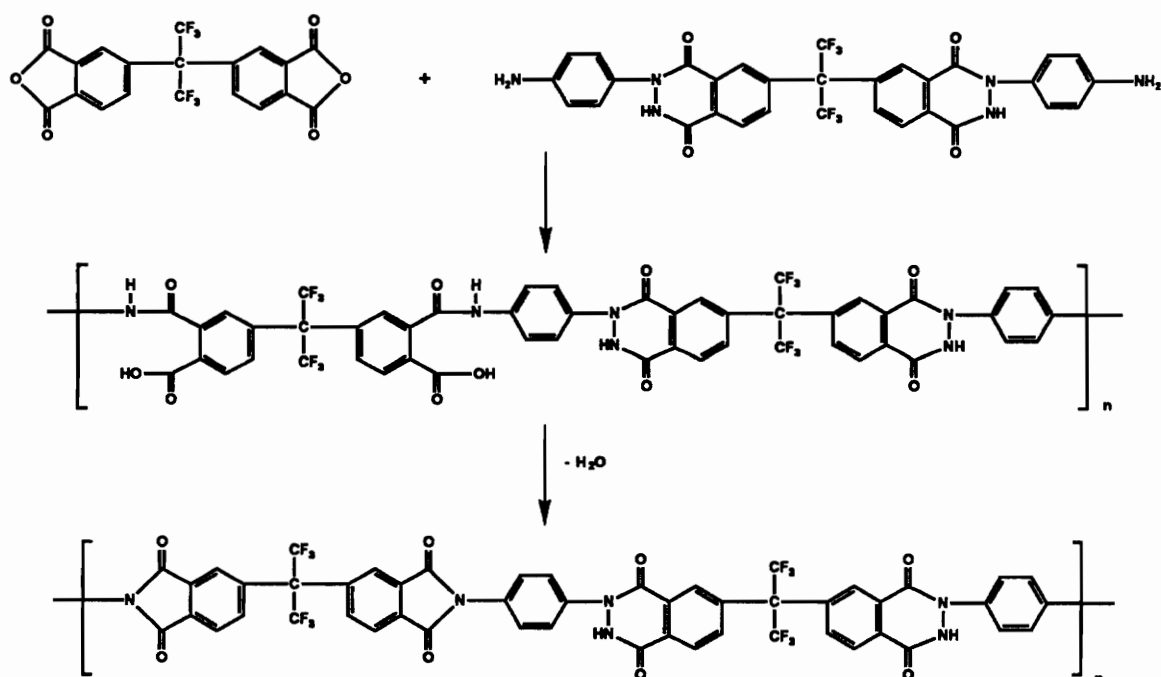
5.4.2 Novel Diamine Containing Phthalhydrazide Linkages

Polyimides typically contain a five-membered imide within the polymer backbone. By reacting an a dianhydride with *p*-nitrophenylhydrazine, a new series of diamines may be possible once the nitro group has been reduced from the intermediate species as shown in Scheme 5.4.2.1.



Scheme 5.4.2.1 Proposed synthesis of novel phthalhydrazide diamine by reacting a dianhydride with *p*-nitrophenylhydrazine.

In Scheme 5.4.2.1 only the thermodynamic six-membered ring is shown for simplicity. The five-membered kinetic product is also possible as discussed previously in Scheme 4.3.2.1. With the use of these new diamines, a new class of polyimides may be possible which contain phthalhydrazide linkages. The phthalhydrazide rings also contain a somewhat acidic amide proton which may contribute increased properties due to interchain cohesive forces. A proposed synthesis of novel phthalhydrazide polyimides utilizing these new diamines is shown in Scheme 5.4.2.2.

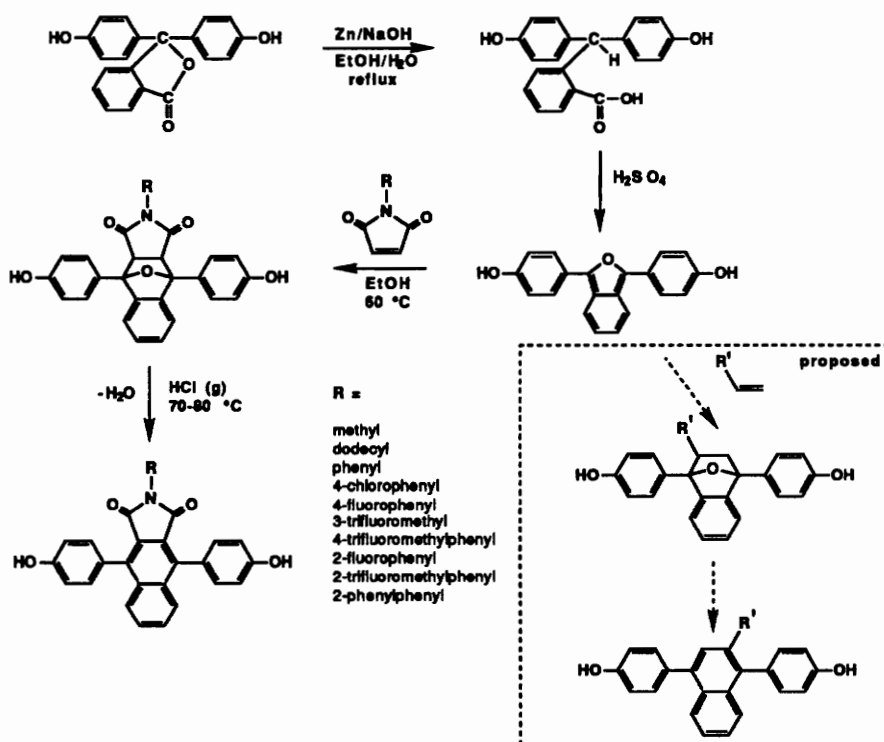


Scheme 5.4.2.2 Proposed synthesis of novel polyimides containing phthalhydrazide rings.

5.4.3 Novel Monomers from Phenolphthalein

Synthetic routes to several monomers using phenolphthalein as a starting material were shown previously in the Scheme 2.2.1.1. These monomers (i.e., phenolphthalein diamine, phenolphthalein dianhydride) may provide a means to incorporate the phenolphthalein moiety into other polymeric systems (i.e., polyimides). As a result, much of the derivatization chemistries may be utilized to attach small molecules onto a polyimide backbone containing phenolphthalein.

In addition, reaction of Strukelj and Hays³⁶⁶⁻³⁶⁸ new imidoaryl monomer with BFPPPO may provide an interesting combination. This synthetic approach also provides a variety of possibilities (e.g. R' = CF₃, etc.) to make new bisphenols using Diels-Alder chemistry as shown in Scheme 5.4.3.1 (dotted box).



Scheme 5.4.3.1 Proposed synthesis of novel bisphenols using Diels-Alder reaction on a phenolphthalein derivative.

6.0 SUMMARY

Poly(arylene ether phosphine oxide)s and poly(arylene ether sulfone)s were successfully synthesized by nucleophilic aromatic polycondensation. Aromatic bisphenols (e.g. phenolphthalein based derivatives) and activated dihalides (e.g. bis(4-fluorophenyl) phenyl phosphine oxide or 4,4'-dichlorodiphenylsulfone) were reacted in the presence of potassium carbonate and a polar aprotic solvent (e.g. DMAc).

Phenolphthalein based poly(arylene ether)s gave increased thermal and mechanical properties as compared to the more typical bisphenol A based systems. With the use of phenolphthalein, the pendant heterocyclic lactone on the resulting polymer was useful for chemical modification of the polymer and for complexation with metals.

Model studies were done to determine the role that potassium carbonate plays in a polycondensation process as compared to the stronger base conditions of potassium hydroxide. The bisphenol A and phenolphthalein monomers were also compared (using a model compound) for relative reaction rates under weak and strong base conditions. The results of the model compound study indicate that BIS and PP have approximately the same reactivity. Model polymerizations were carried out for kinetic comparison and confirmed these results. The extent of cyclooligomer formation of the step-growth polymeric system was found to be very significant.

Metal complexing studies were done on five different poly(arylene ether)s to determine the extent of complexation of both phosphorus and the lactone moiety of phenolphthalein. It was determined that both complex with metal halides, although phosphorus complexes to a larger degree.

The phenolphthalein-based poly(arylene ether phosphine oxide) was successfully derivatized with pNPH up to 25 mole %. The derivatized polymers showed an increased T_g .

A series of controlled molecular weight poly(arylene ether)s were synthesized with varying molecular weights, structures, and end-groups. These materials were used as tougheners in both cyanate and epoxy resins. Poly(arylene ether)s with reactive amine end-groups covalently cure in with the epoxy network, resulting in a modified network with increased fracture toughness as compared to non-reactive poly(arylene ether) thermoplastic modifiers.

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8.0 APPENDIX

8.1 *Controlling the Molecular Weight of Step Growth Polymers*

The Carother's Equation is a useful tool in determining the amounts of reagents for controlling the molecular weight in step-growth polymers. The following Figure 8.1.1 is a representation of some important terms and their definitions.

\overline{DP} = Degree of polymerization is the number of repeat units

$$\overline{DP} = \frac{\text{Molecular weight of polymer}}{\text{Molecular weight of repeat unit}}$$

\overline{Xn} = Number average degree of polymerization

$$\overline{Xn} = 2 \overline{DP}$$

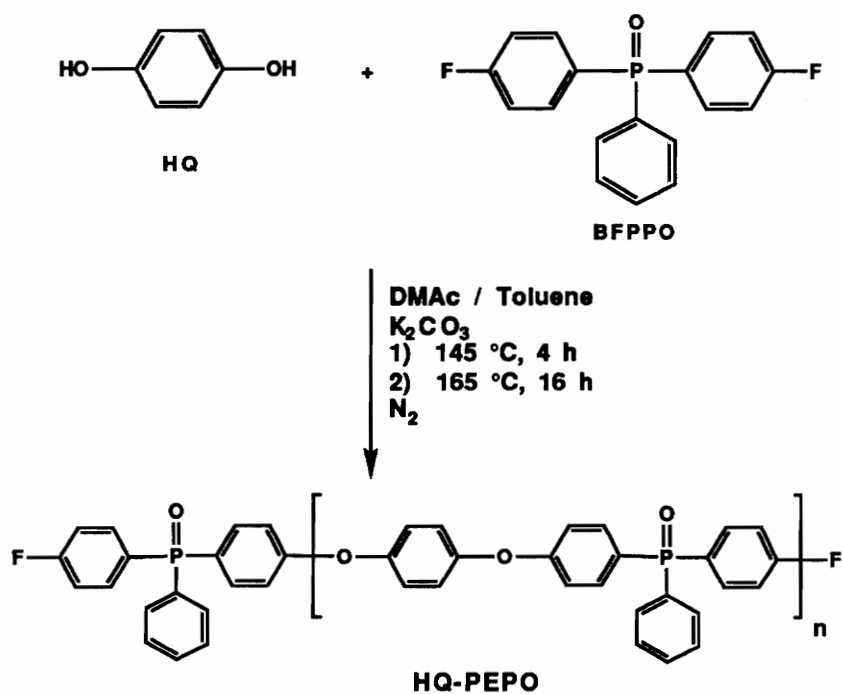
r = Stoichiometric imbalance

$$r = \frac{Xn - 1}{Xn + 1} = \frac{N_A}{N_B} \leq 1$$

where N = number of functional groups in a monomer

Figure 8.1.1 Definition of terms used in the Carother's Equation.

Controlling the molecular weight can be accomplished by two methods; a) using excess of one of the reagents, or b) using a monofunctional endcapper. Scheme 8.1.1 gives a synthetic representation of the components utilized in a reaction in which excess BFPPPO was used to control the molecular weight.



Scheme 8.1.1 Example of a controlled molecular weight synthesis of HQ-PEPO using stoichiometric imbalance.

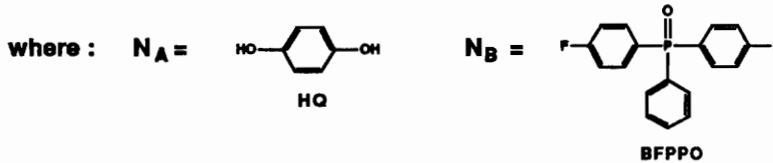
Figure 8.1.2 gives the calculations used to determine the amount of excess BFPPPO that is needed to control the molecular weight to 20 kg/mole.

$$\overline{DP} = \frac{\text{Molecular weight of polymer}}{\text{Molecular weight of repeat unit}} = \frac{20,000 \text{ g/mol}}{384.375 \text{ g/mol}} = 52.035$$

$$2 \overline{DP} = \overline{Xn}$$

$$\overline{Xn} = 2 * 52.0325 = 104.065$$

$$r = \frac{Xn - 1}{Xn + 1} = \frac{103.065}{105.065} = 0.9809 = \frac{N_A}{N_B}$$



$$r = \frac{N_A}{N_B} = 0.9809 = \frac{\text{mol HQ}}{\text{mol BFPPO}}$$

$$\text{mol HQ} = (\text{mol BFPPO}) \times r$$

Sample Calculation

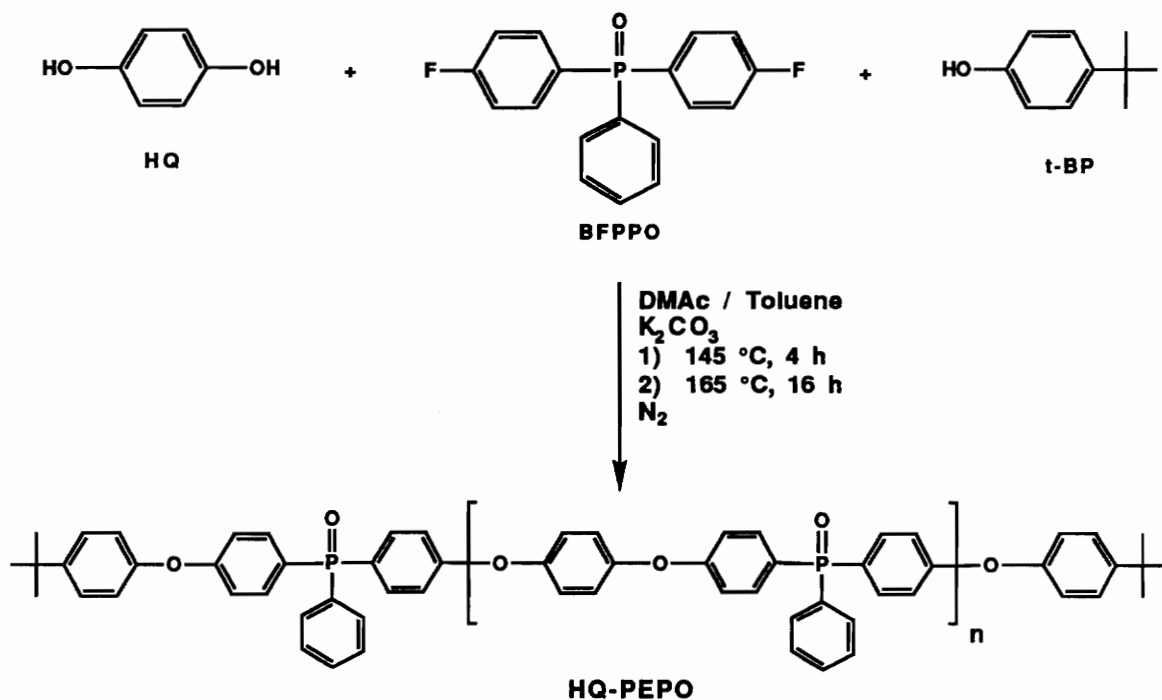
$$10 \text{ g BFPPO} = 0.0318 \text{ mol BFPPO}$$

$$\text{mol HQ} = 0.0318 \text{ mol BFPPO} \times 0.9809$$

$$= 0.0312 \text{ mol HQ} = 3.4369 \text{ g HQ}$$

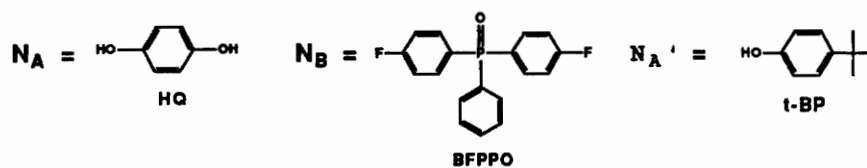
Figure 8.1.2 Sample calculation using the Carother's Equation for a 20 kg/mole HQ-PEPO with fluorine endgroups.

The second method that can be used to control the molecular weight is with the use of a monofunctional endcapper, e.g. *t*-butyl phenol (*t*-BP). The synthesis shown in Scheme 8.1.2 is an example of the components needed to control the molecular weight of HQ-PEPO by this method.



Scheme 8.1.2 Example of a controlled molecular weight synthesis of HQ-PEPO using a monofunctional endcapper (*t*-BP).

The calculations as shown previously in Figure 8.1.2 give the amounts of BFPEO and HQ that are needed. The amount of endcapper (*t*-BP) can be determined by the calculations as shown in Figure 8.1.3.



$$r = \frac{N_B}{N_A + 2 N_{A'}} = \frac{\text{mol BFPPPO}}{\text{mol HQ} + 2 \text{ mol t-BP}} = 0.9809$$

$$2 \text{ mol t-BP} = \frac{\text{mol BFPPPO} - r (\text{mol HQ})}{r}$$

$$2 \text{ mol t-BP} = \frac{(0.0318 \text{ mol BFPPPO}) - 0.9809 (0.0312 \text{ mol HQ})}{0.9809}$$

$$= 0.00124 \text{ mol t-BP}$$

$$= 0.1860 \text{ g t-BP}$$

Amounts for 20,000 g/mol endcapped polymer:

$$\text{BFPPPO} = 10.000 \text{ g}$$

$$\text{HQ} = 3.469 \text{ g}$$

$$\text{t-BP} = 0.186 \text{ g}$$

Figure 8.1.3 Sample calculation for using a monofunctional endcap to control molecular weight of HQ-PEPO.

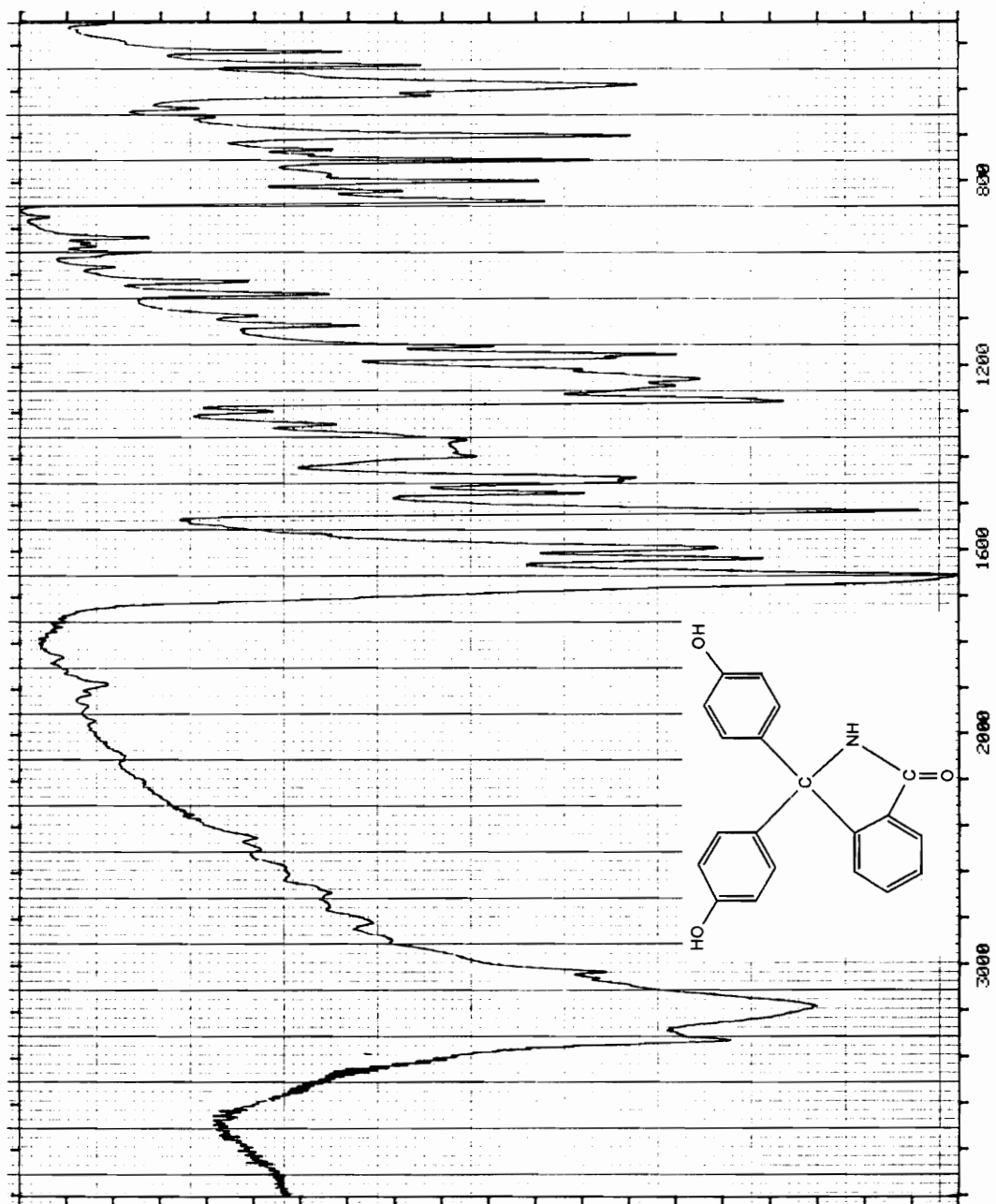


Figure 8.2.1 FTIR spectrum of PI.

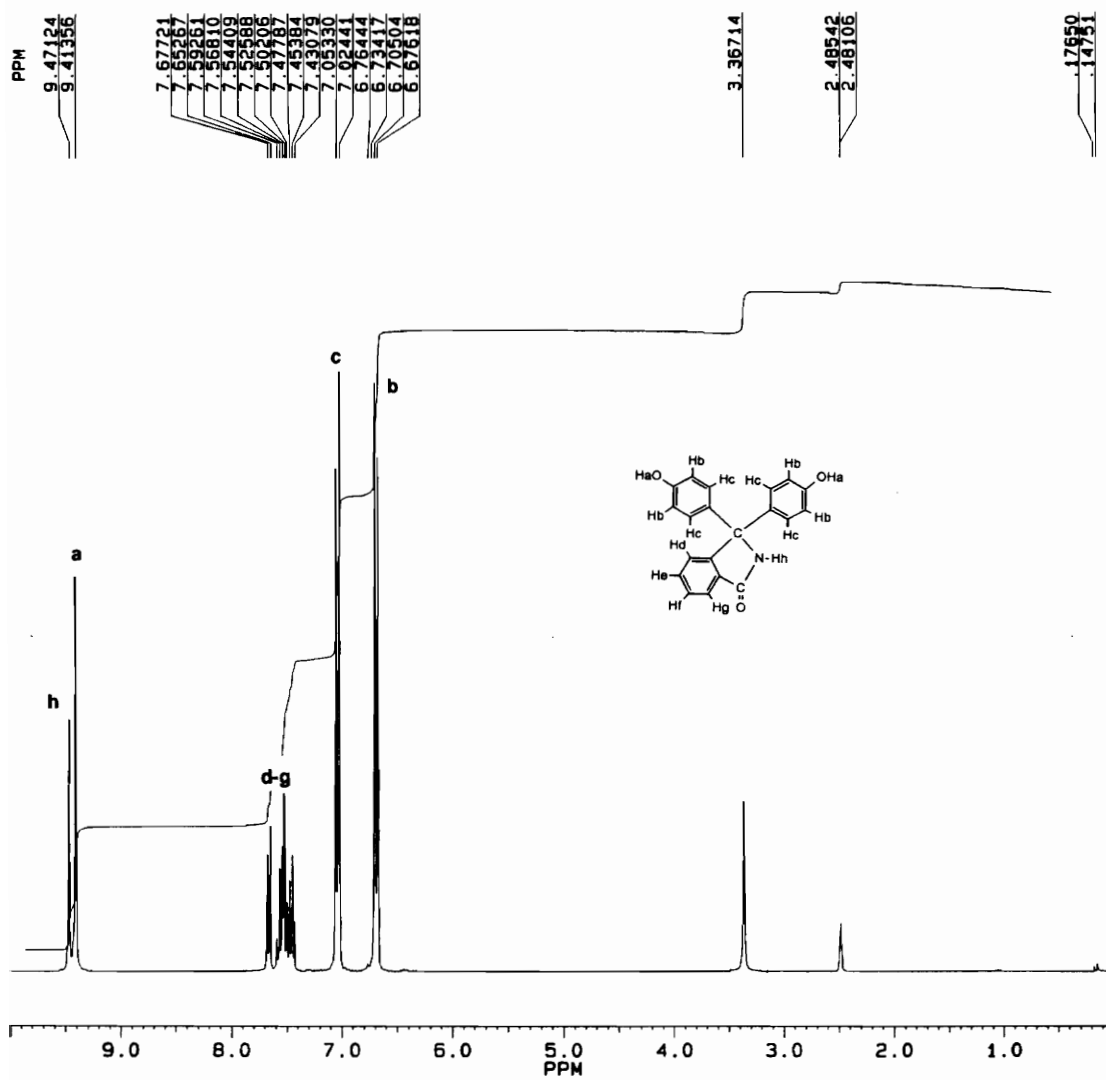


Figure 8.2.2 ^1H NMR spectrum of PI. (300 MHz, d_6 -DMSO)

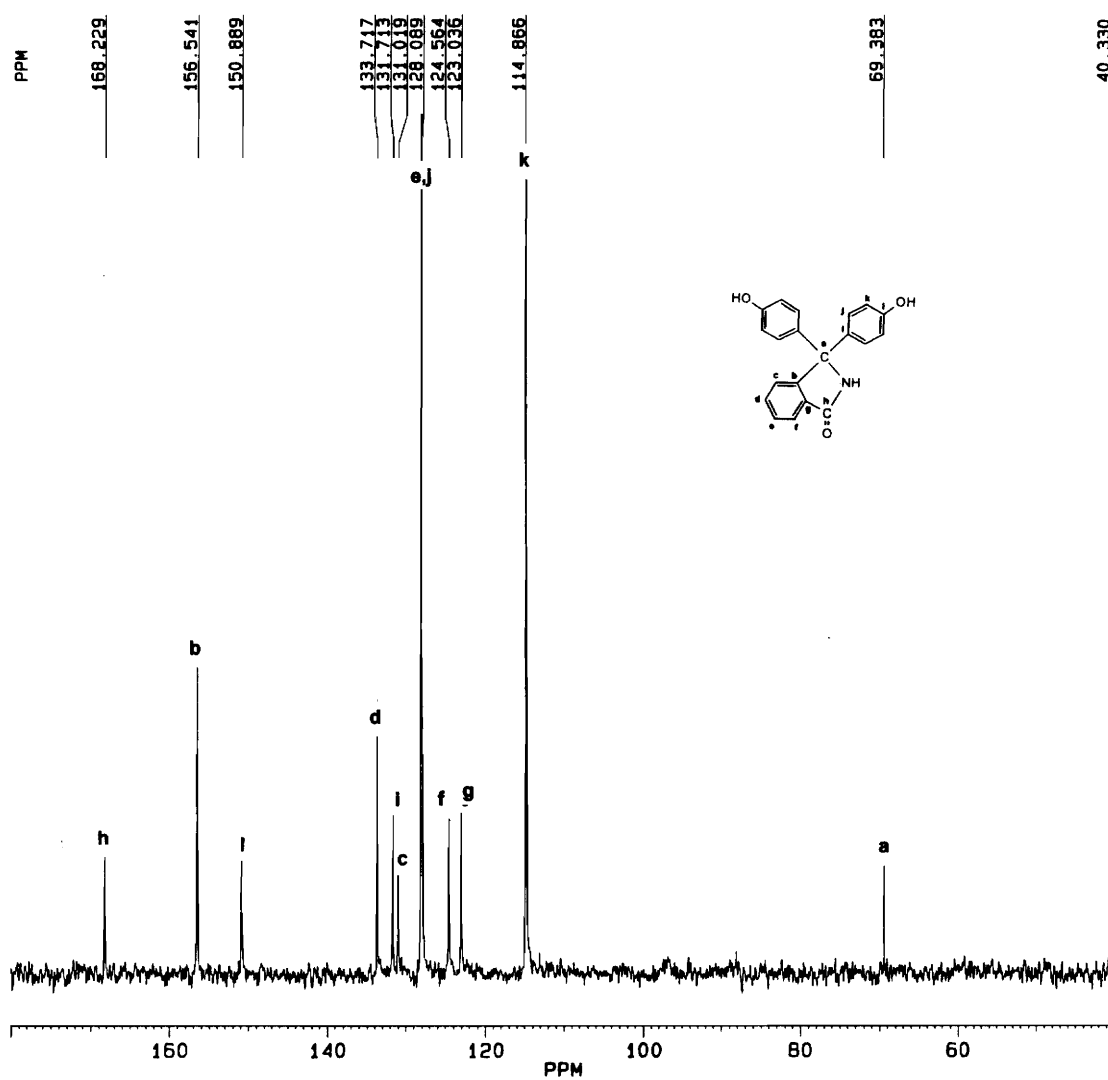


Figure 8.2.3 ^{13}C NMR spectrum of PI. (300 MHz, d_6 -DMSO)

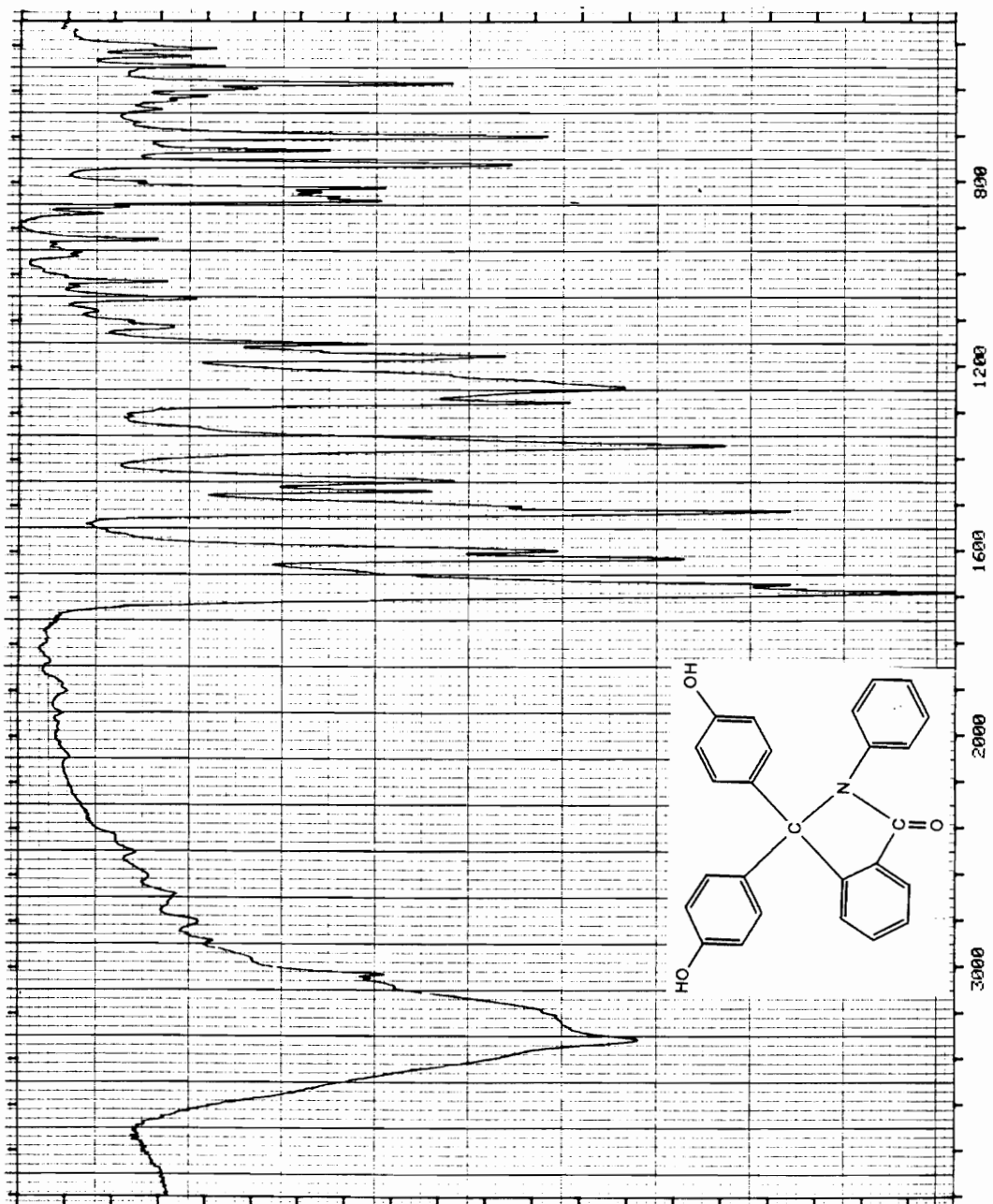


Figure 8.2.4 FTIR spectrum of PA.

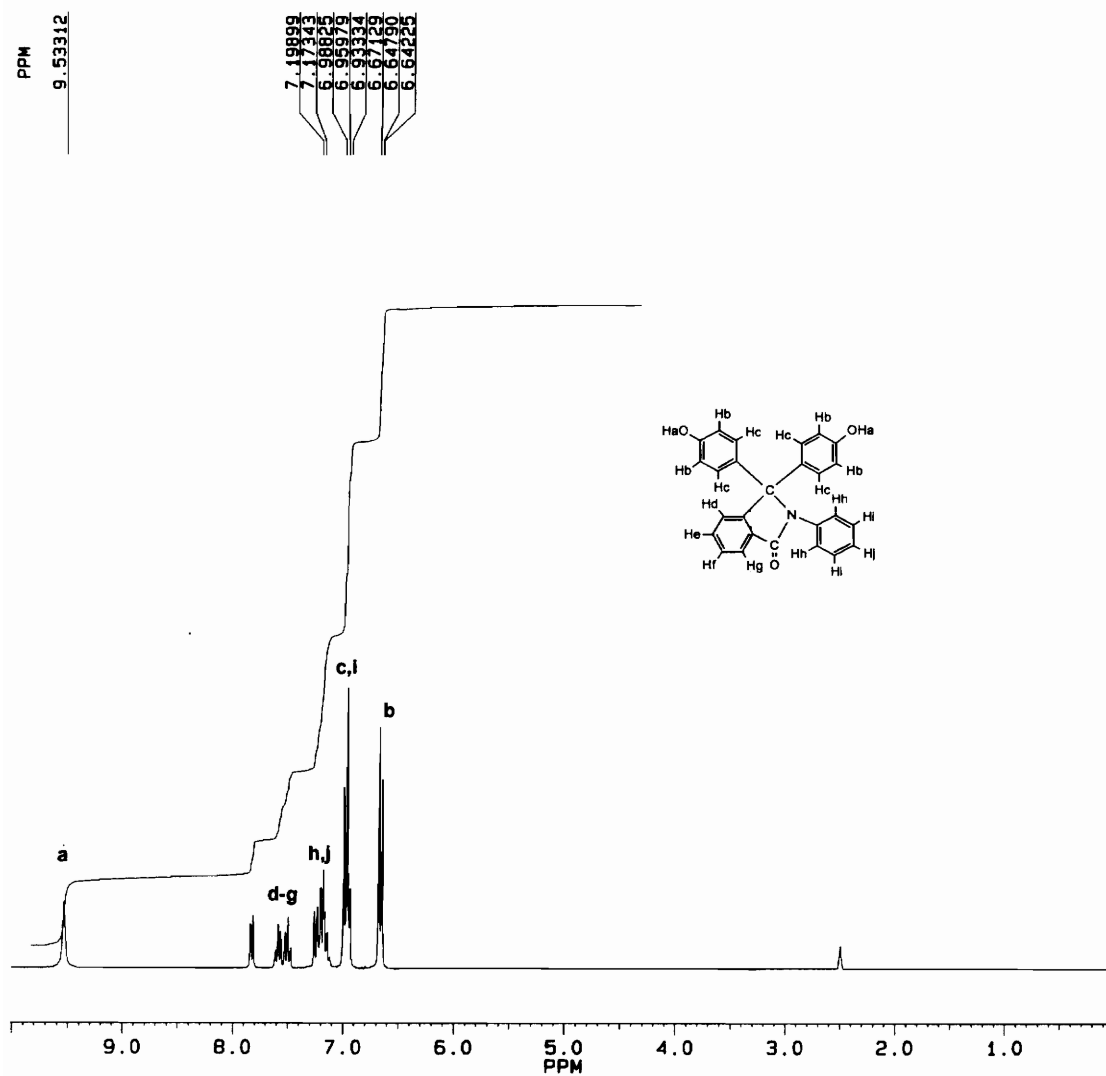


Figure 8.2.5 ¹H NMR spectrum of PA. (300 MHz, d₆-DMSO)

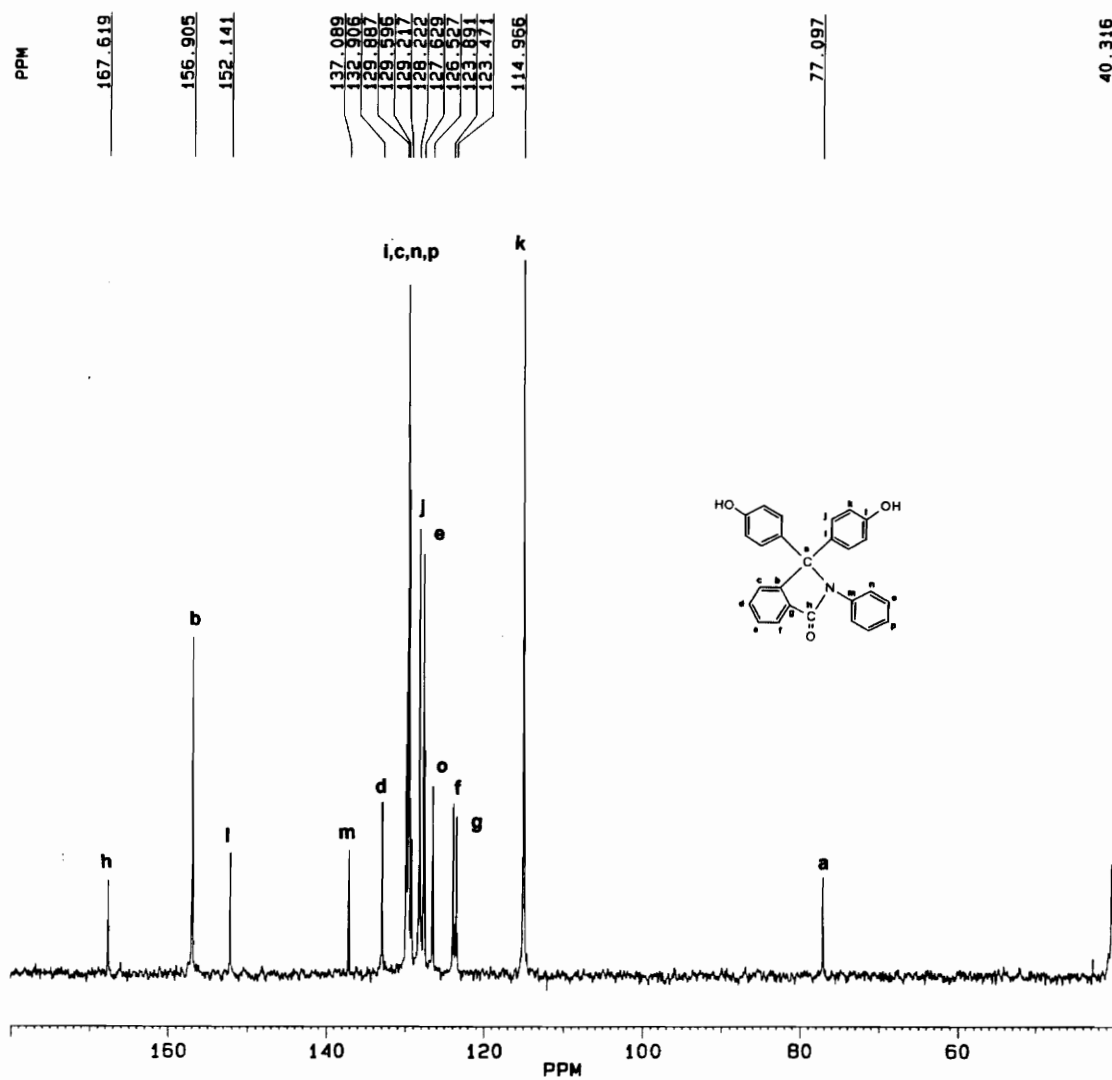


Figure 8.2.6 ^{13}C NMR spectrum of PA. (300 MHz, d_6 -DMSO)

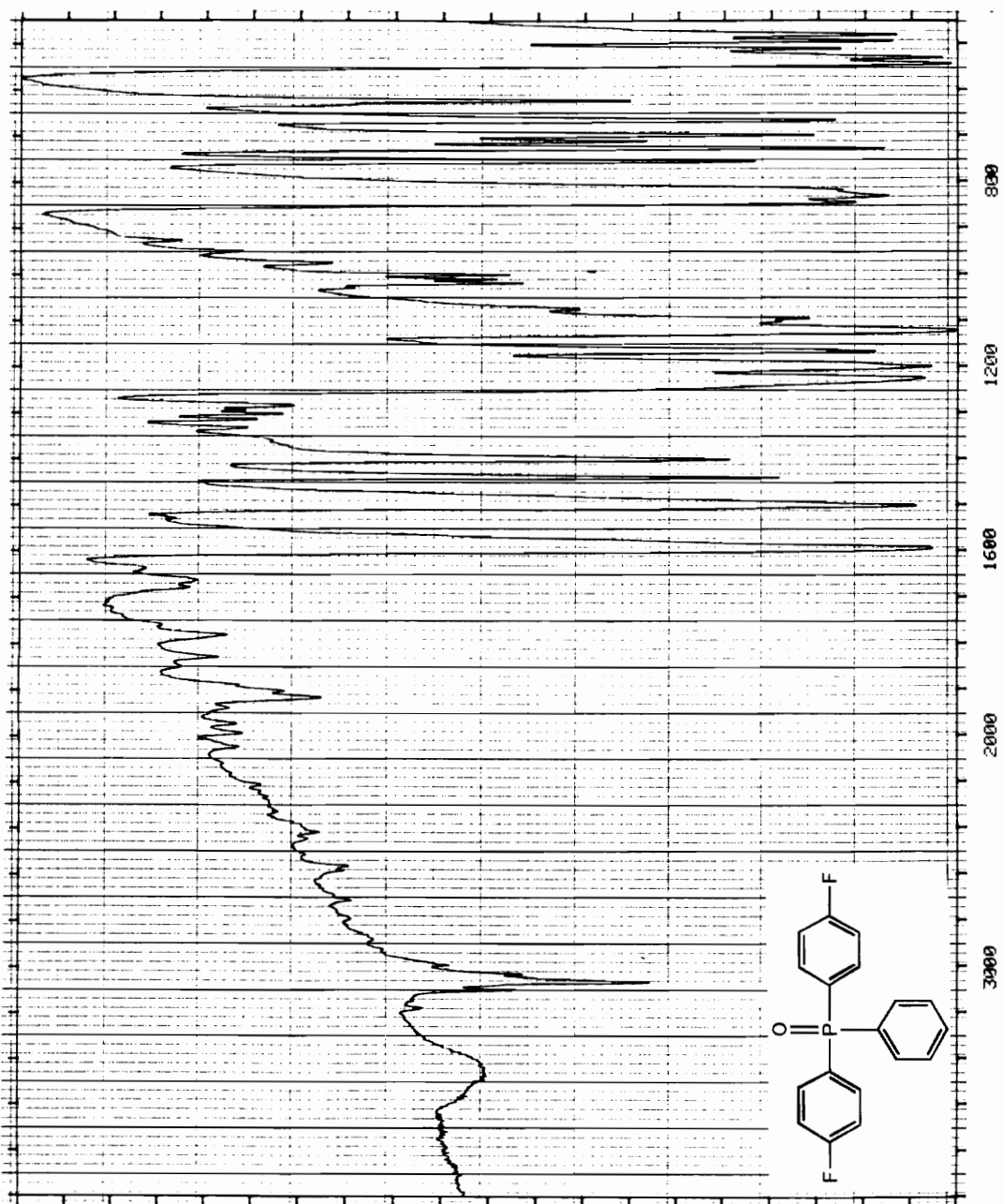


Figure 8.2.7 FTIR spectrum of BFPPO.

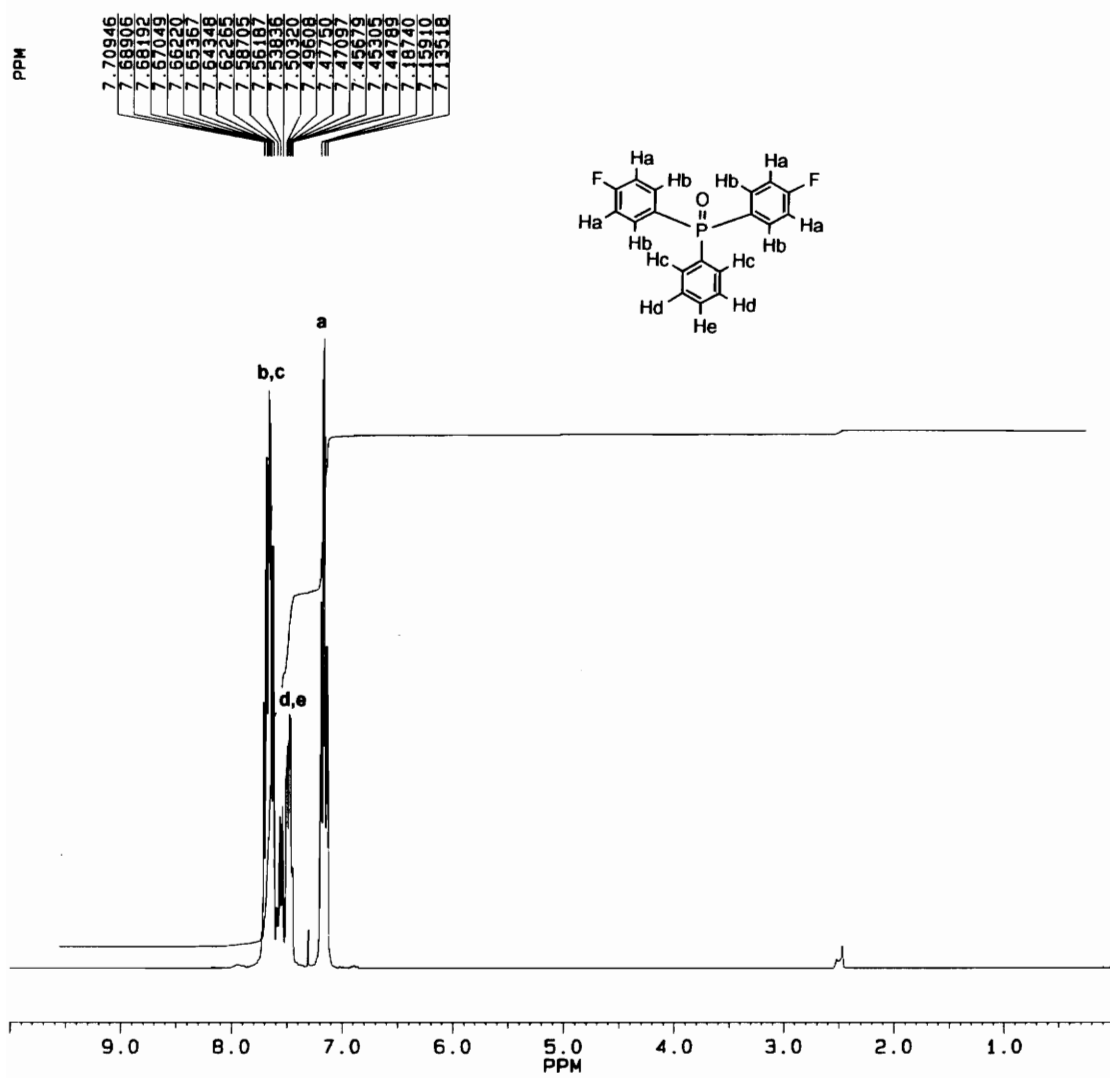


Figure 8.2.8 ^1H NMR spectrum of BFPPPO. (300 MHz, CDCl_3)

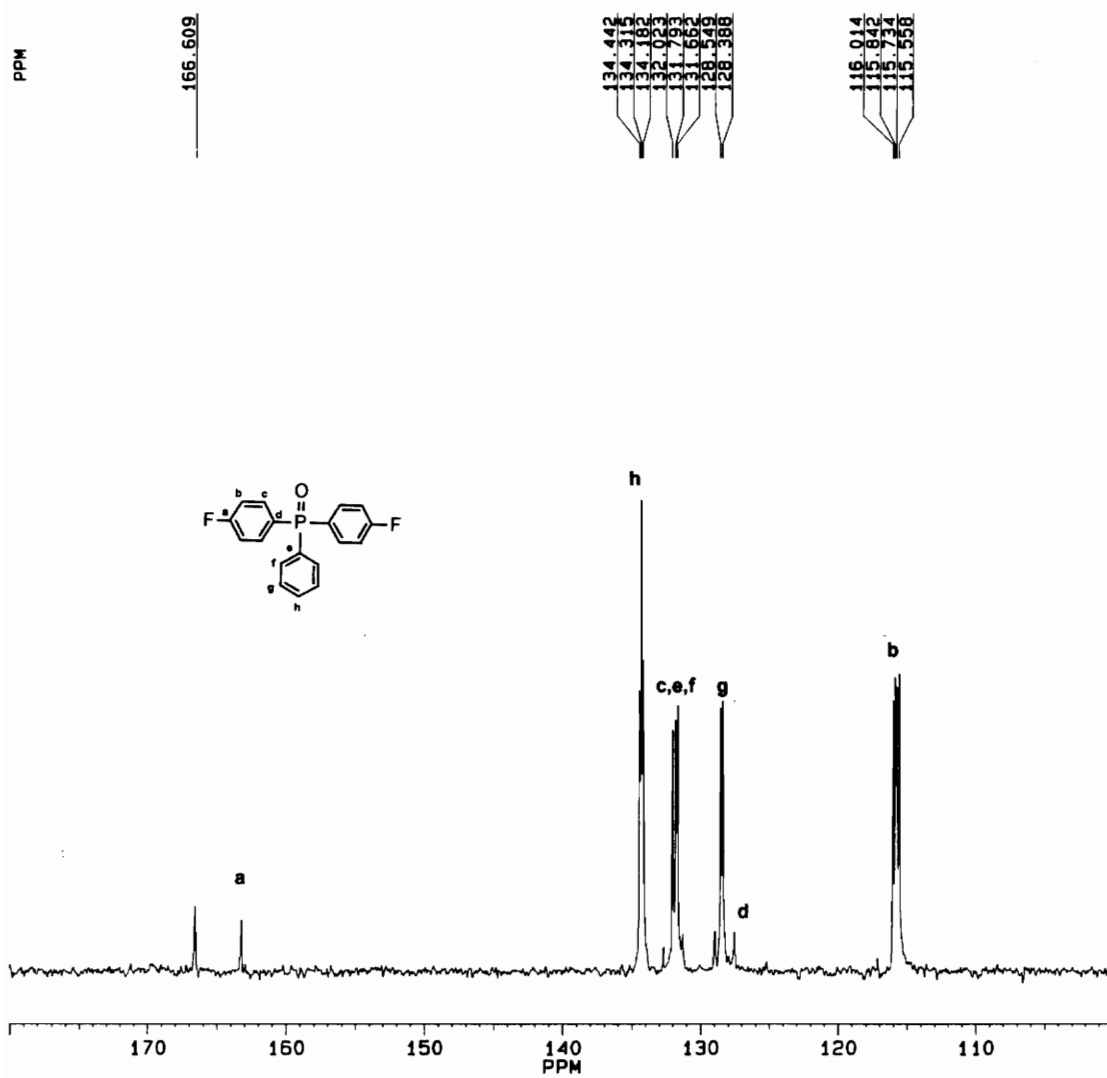


Figure 8.2.9 ^{13}C NMR spectrum of BFPPPO. (300 MHz, CDCl_3)

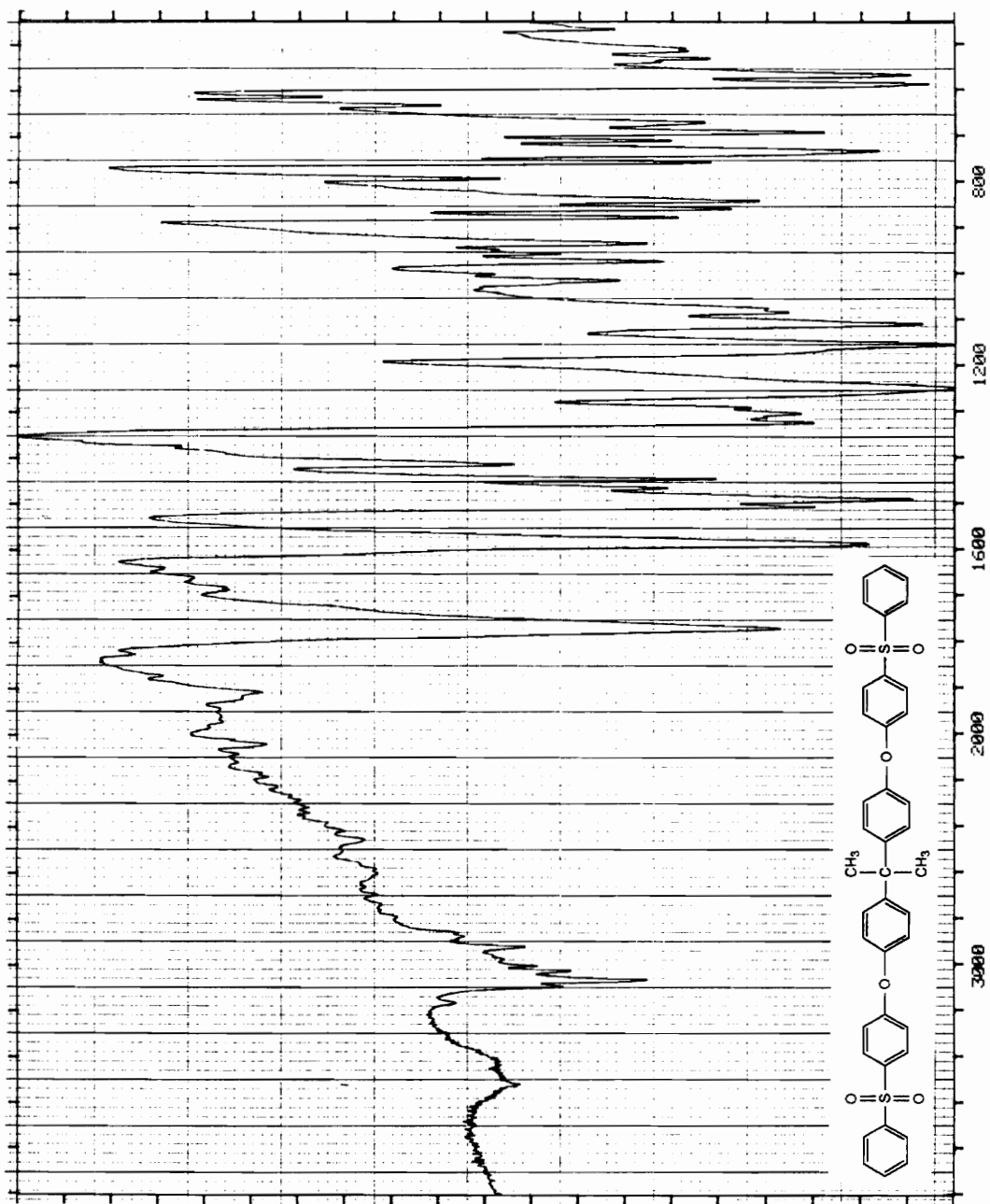


Figure 8.2.10 FTIR spectrum of BIS A-BDPS.

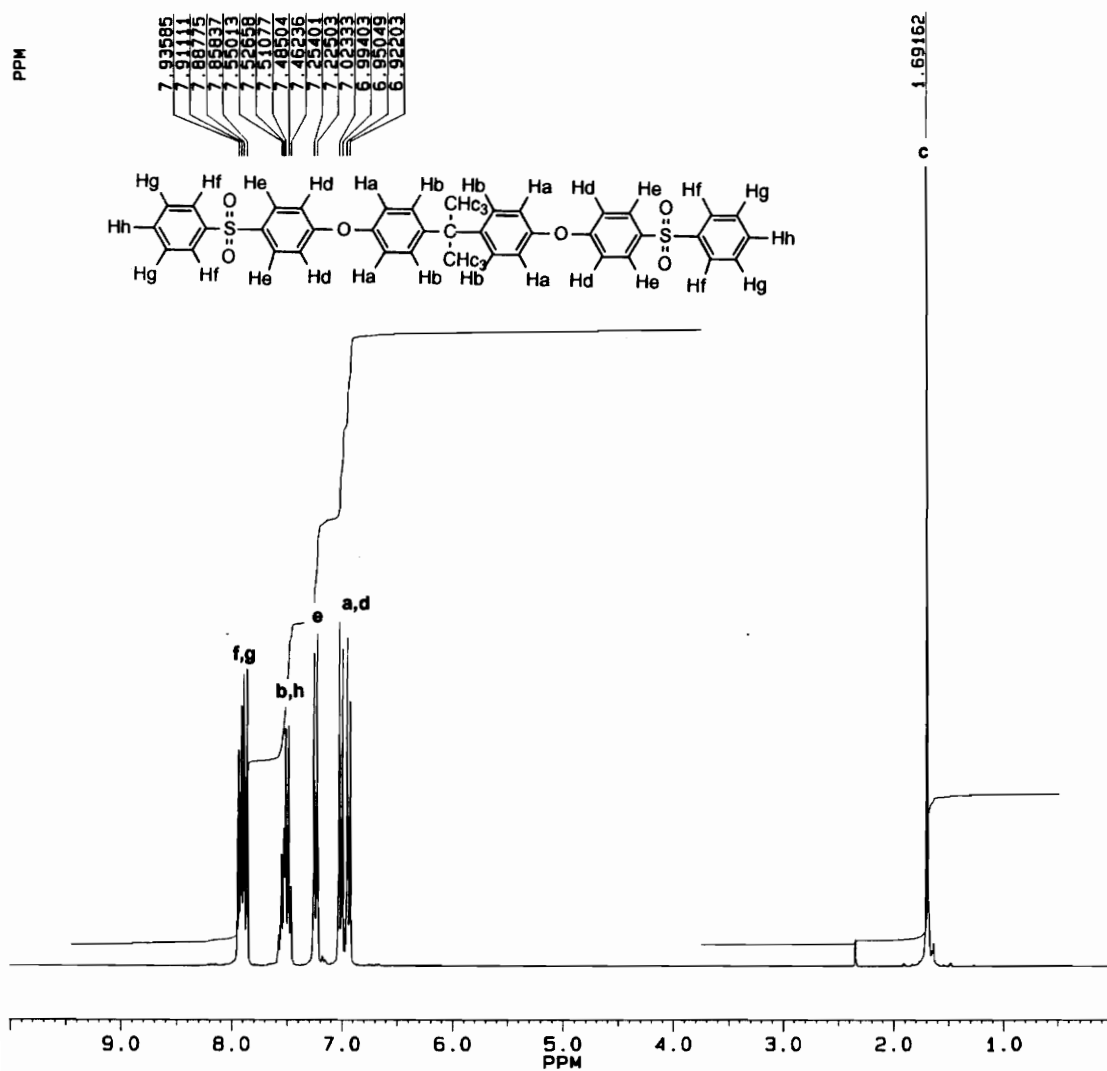


Figure 8.2.11 ^1H NMR spectrum of BIS A-BDPS. (300 MHz, CDCl_3)

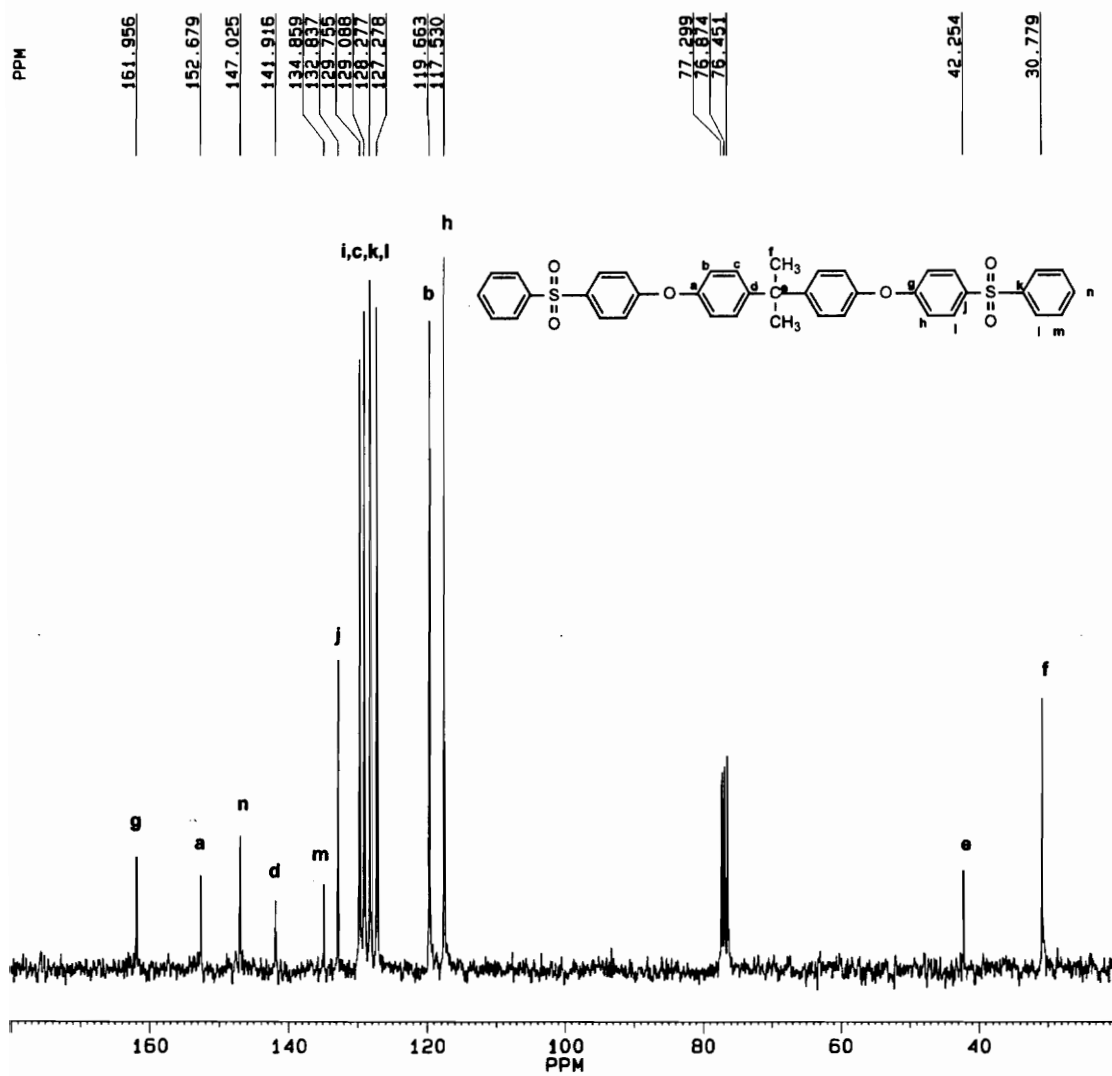


Figure 8.2.12 ^{13}C NMR spectrum of BIS A-BDPS. (300 MHz, CDCl_3)

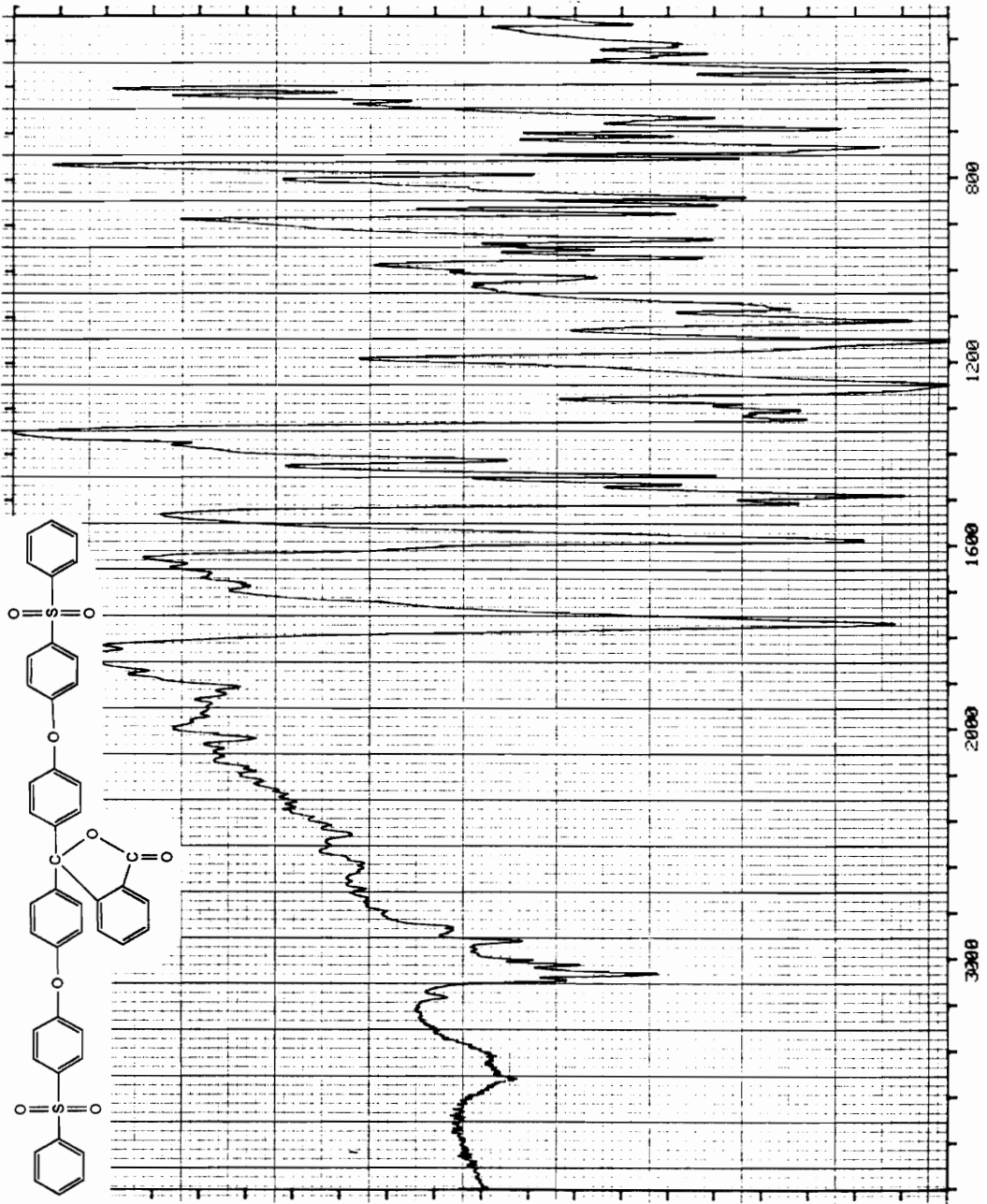


Figure 8.2.13 FTIR spectrum of PP-BDPS.

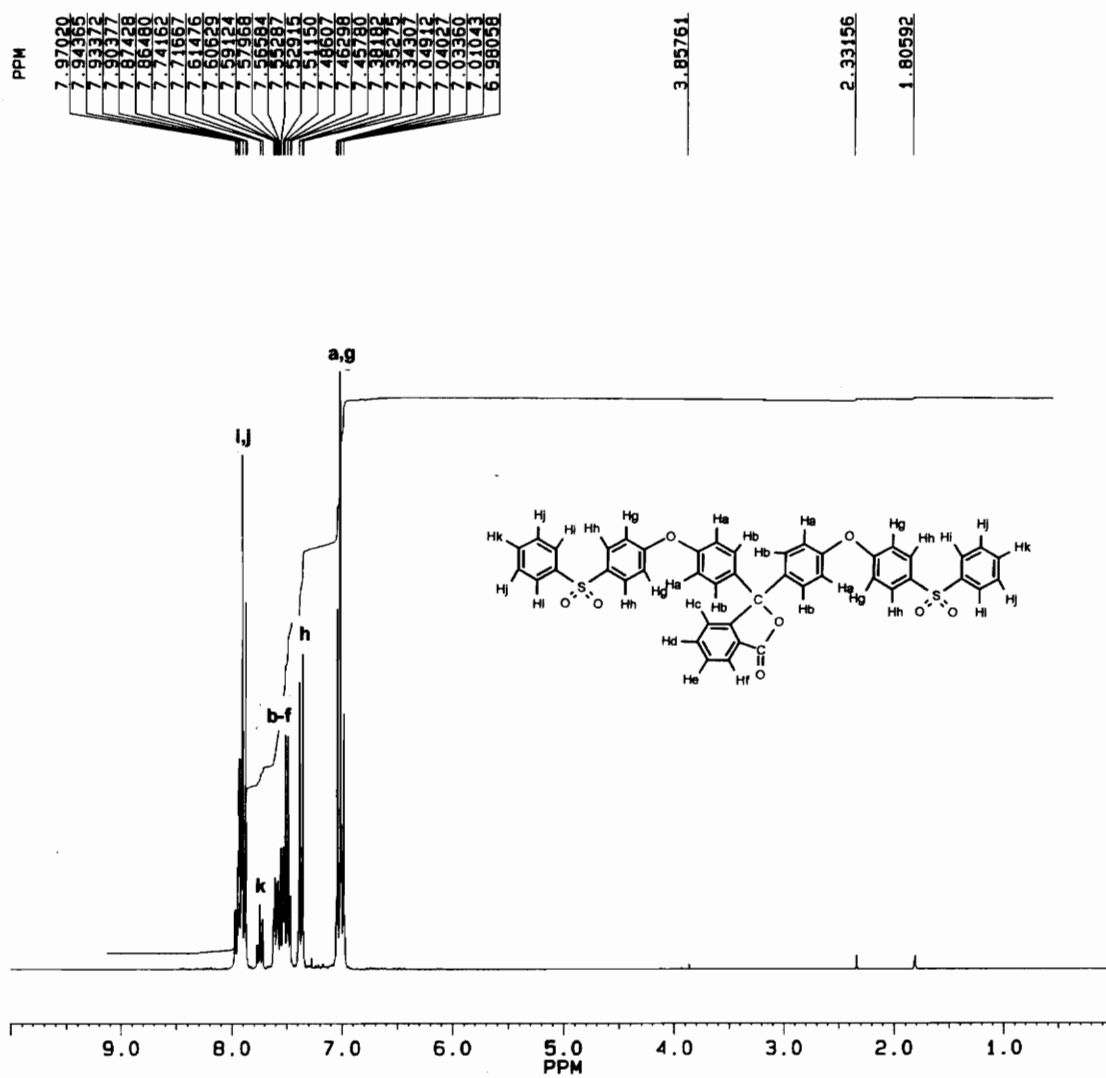


Figure 8.2.14 ¹H NMR spectrum of PP-BDPS. (300 MHz, CDCl₃)

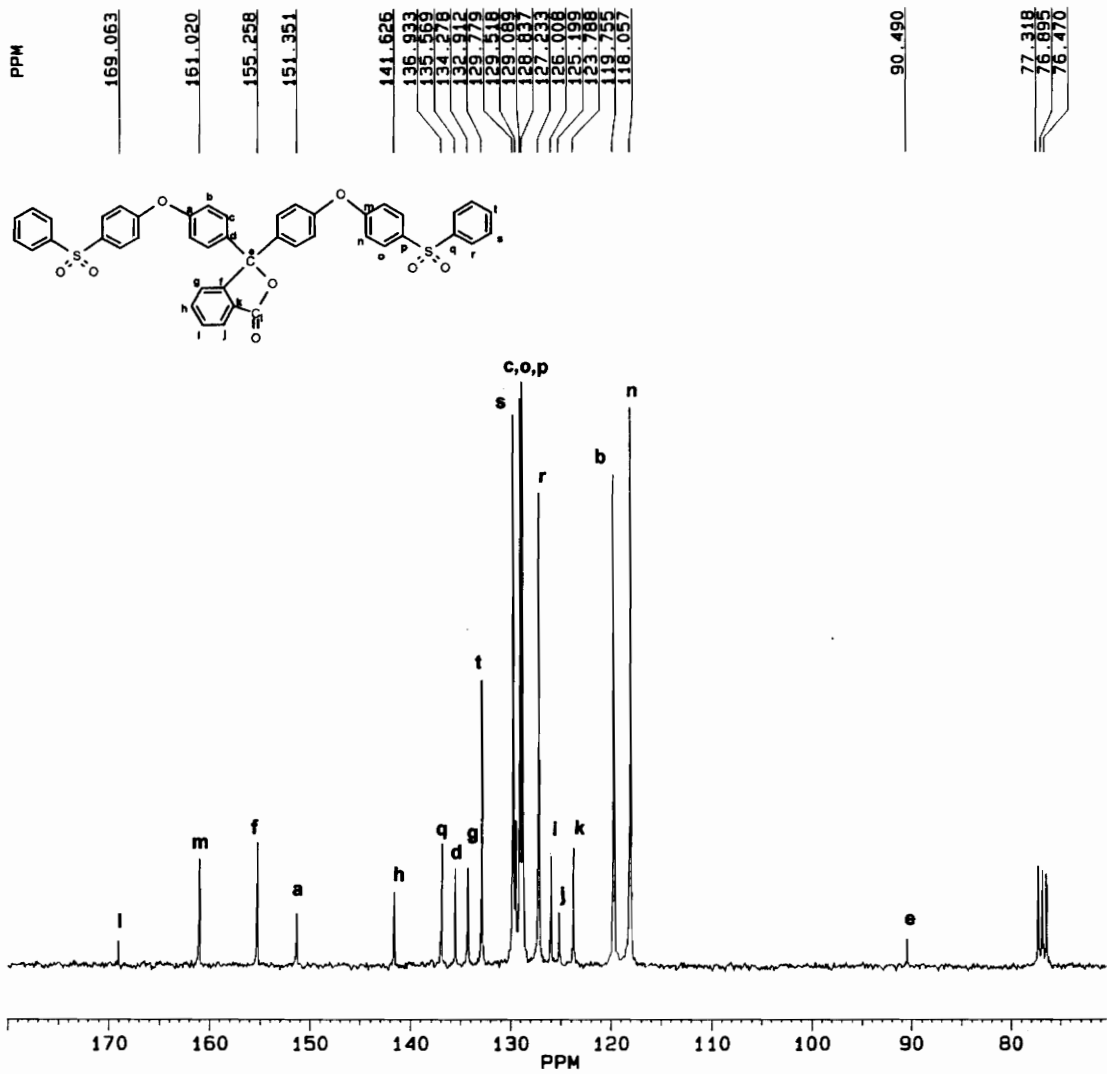


Figure 8.2.15 ¹³C NMR spectrum of PP-BDPS. (300 MHz, CDCl₃)

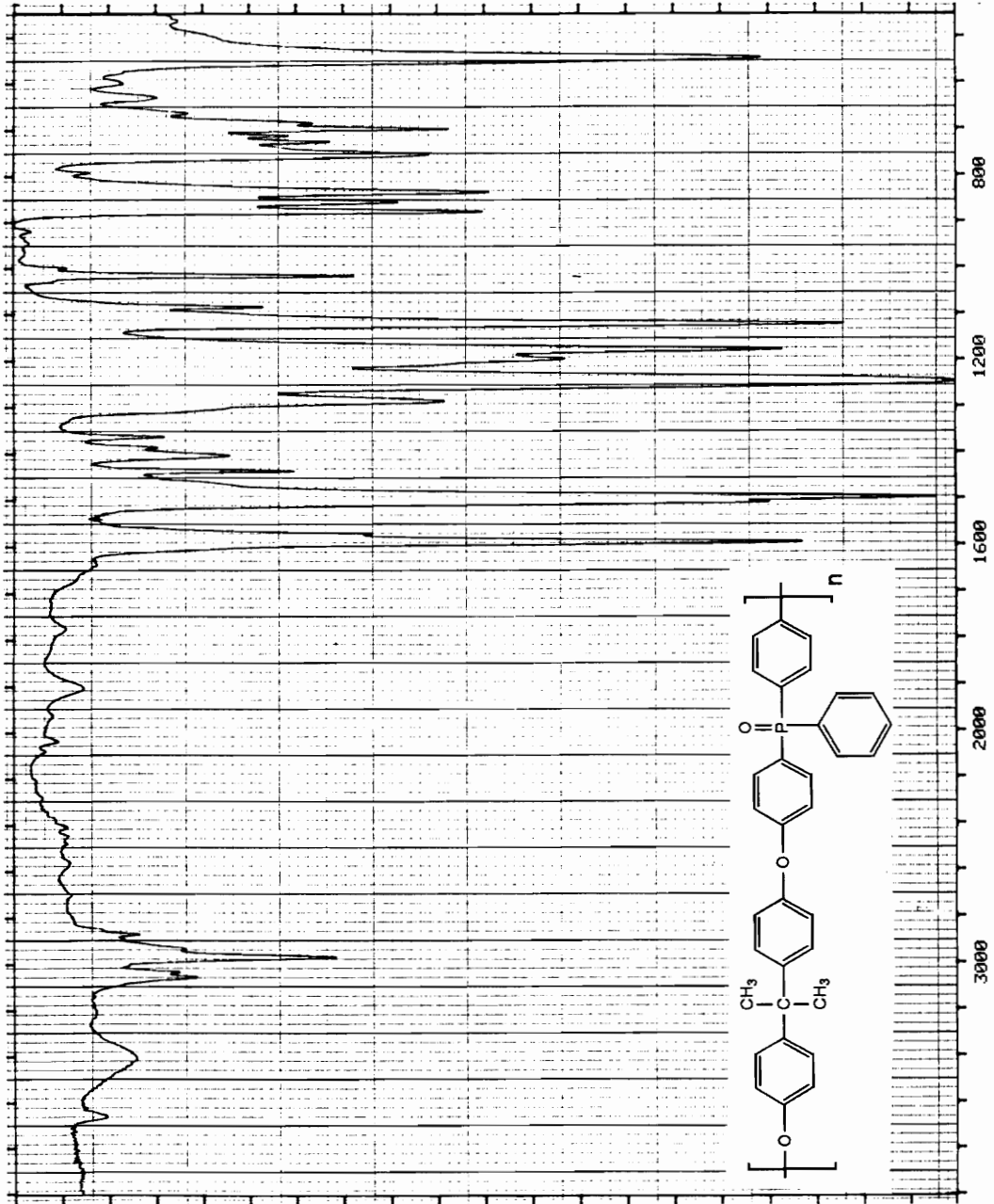


Figure 8.2.16 FTIR spectrum of BIS A-PEPO.

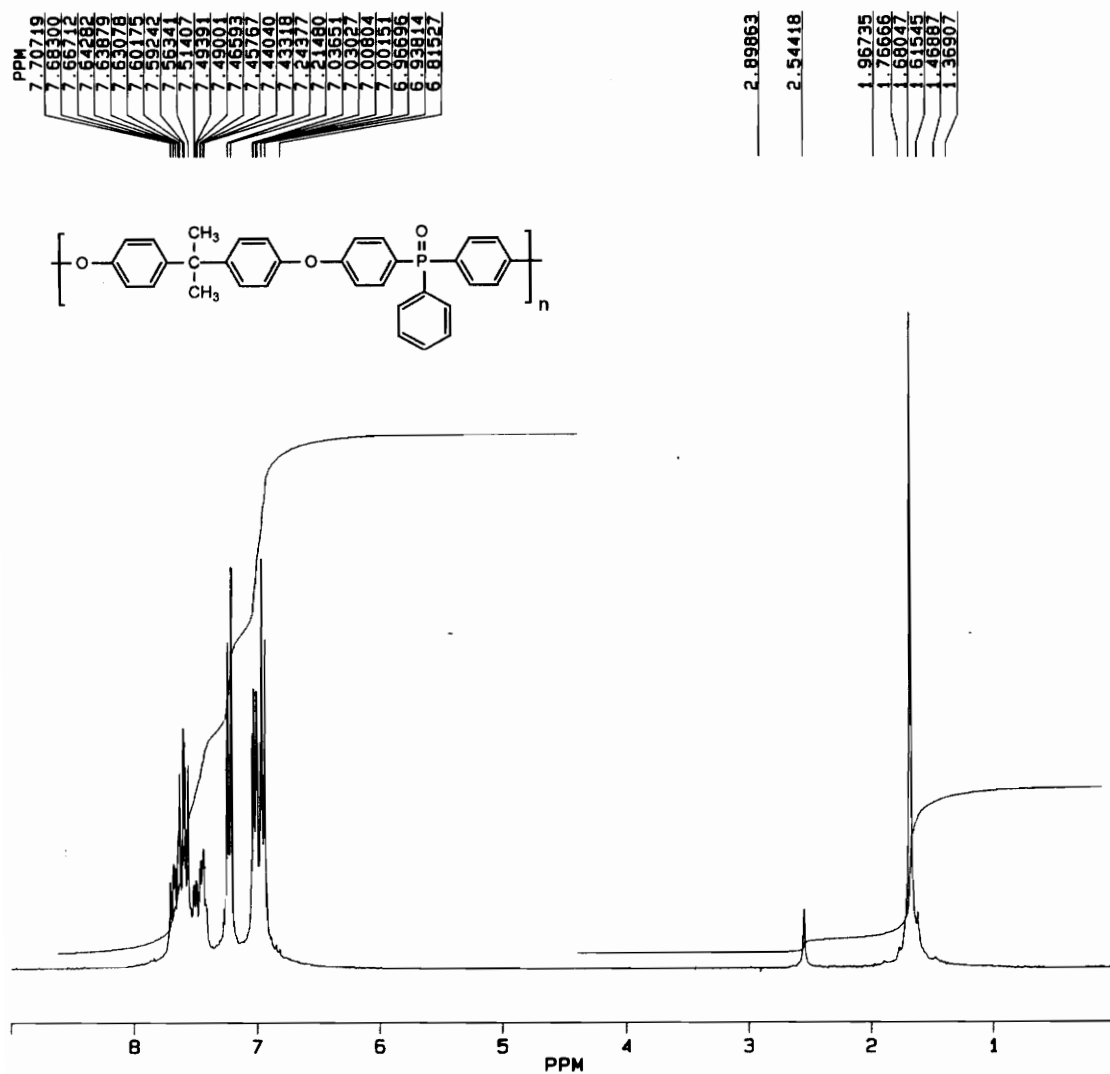


Figure 8.2.17 ¹H NMR spectrum of BIS A-PEPO. (300 MHz, CDCl₃)

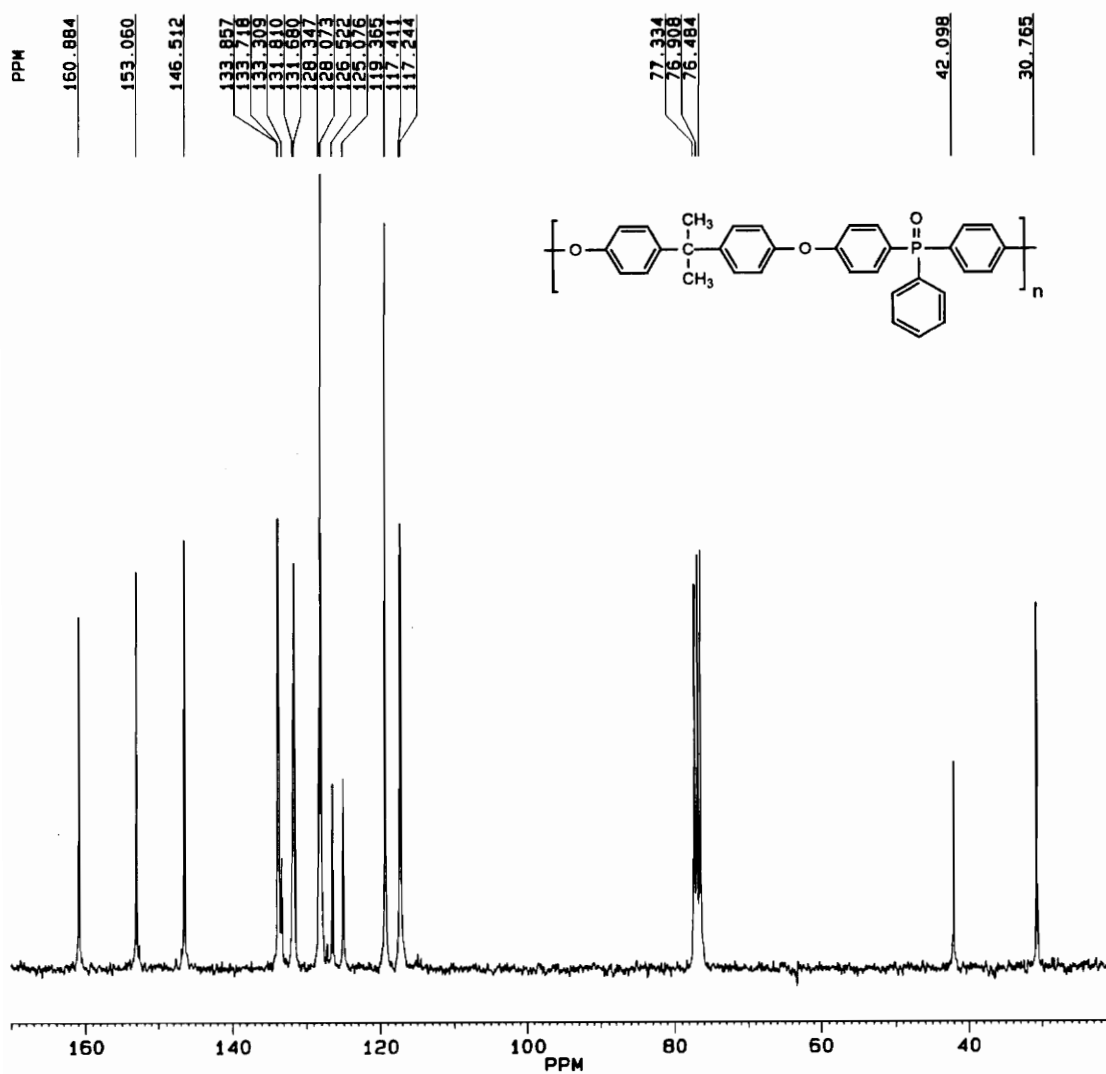


Figure 8.2.18 ^{13}C NMR spectrum of BIS A-PEPO. (300 MHz, CDCl_3)

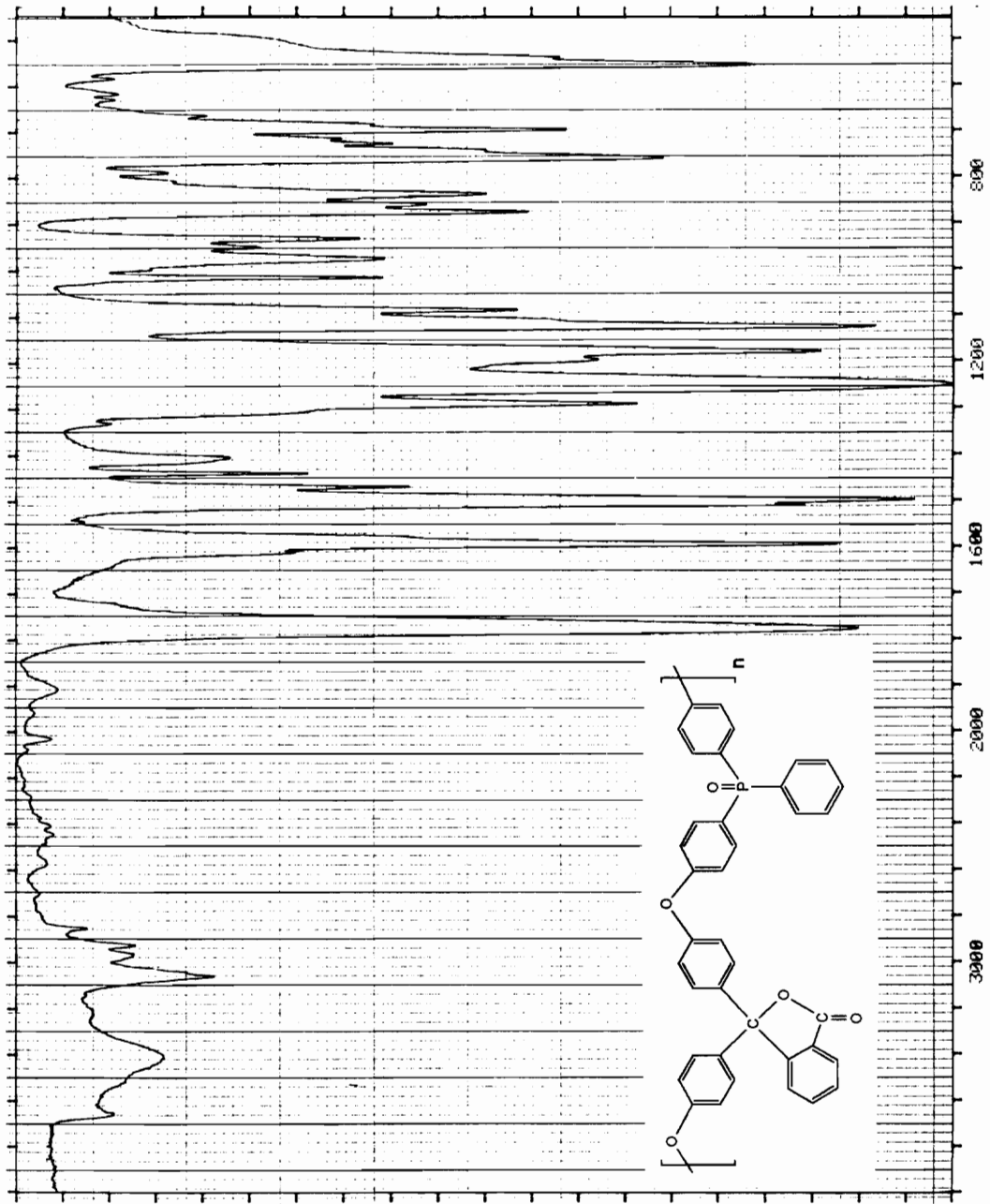


Figure 8.2.19 FTIR spectrum of PP-PEPO.

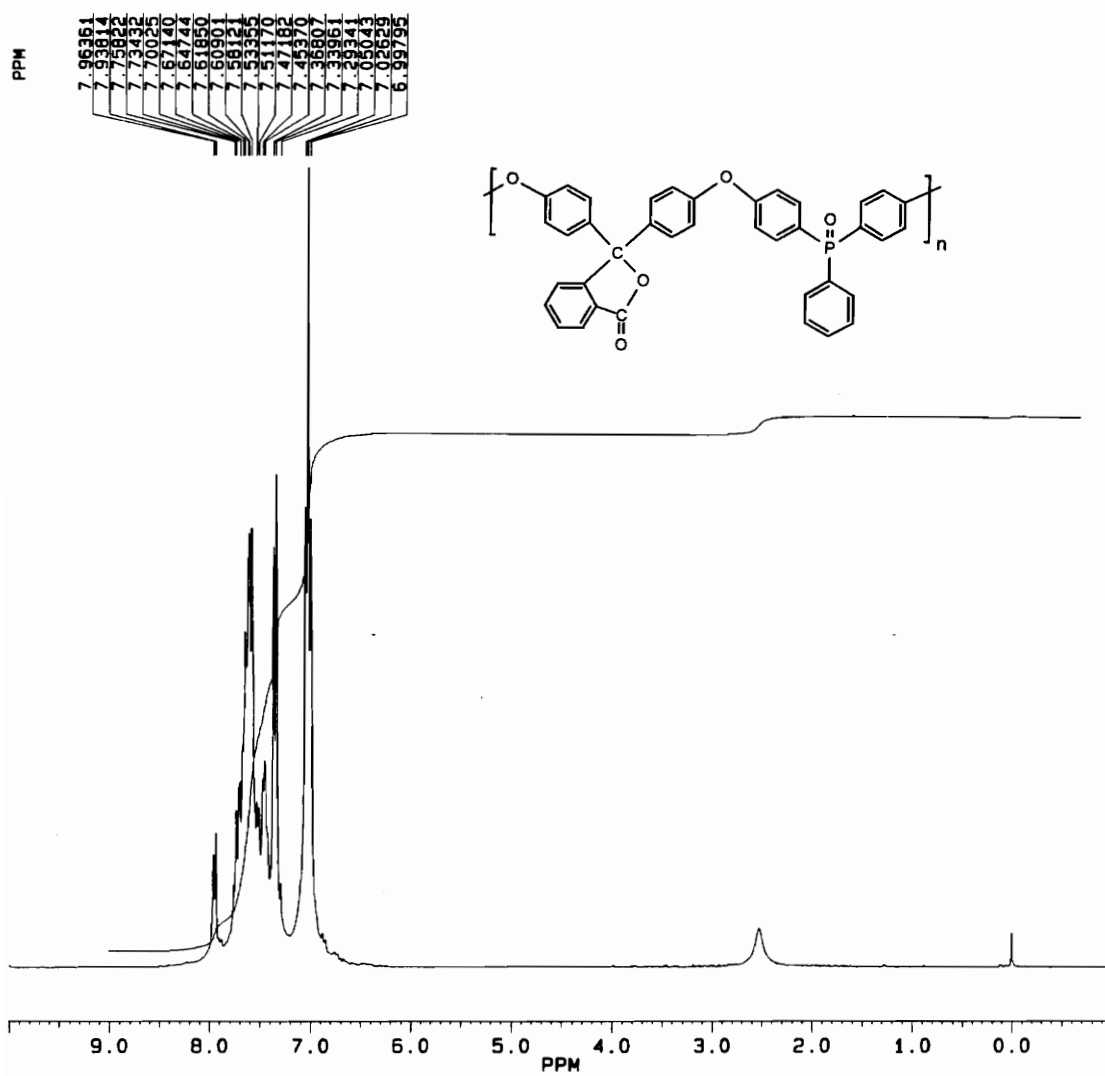


Figure 8.2.20 ^1H NMR spectrum of PP-PEPO. (300 MHz, CDCl_3)

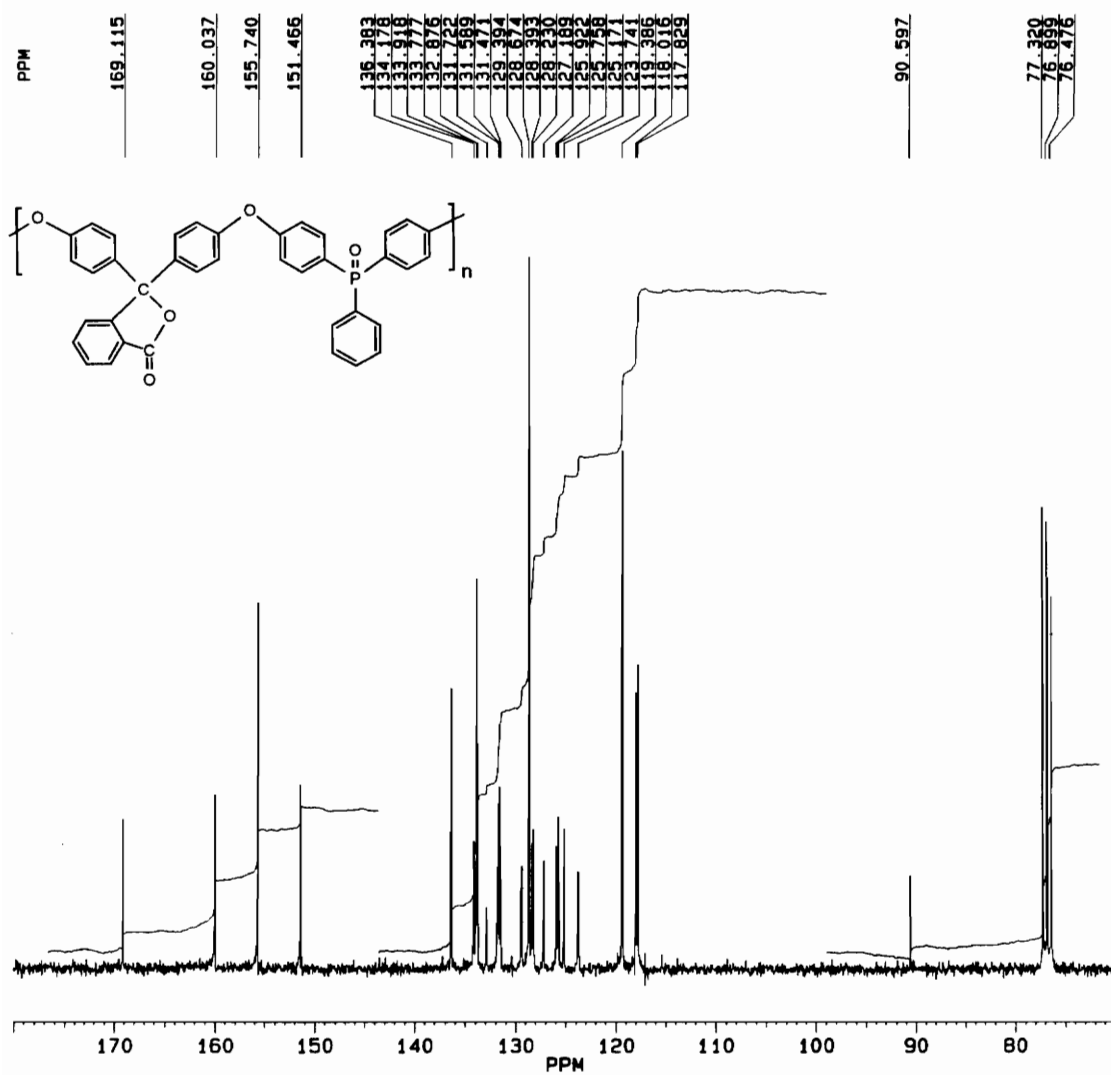


Figure 8.2.21 ^{13}C NMR spectrum of PP-PEPO. (300 MHz, CDCl_3)

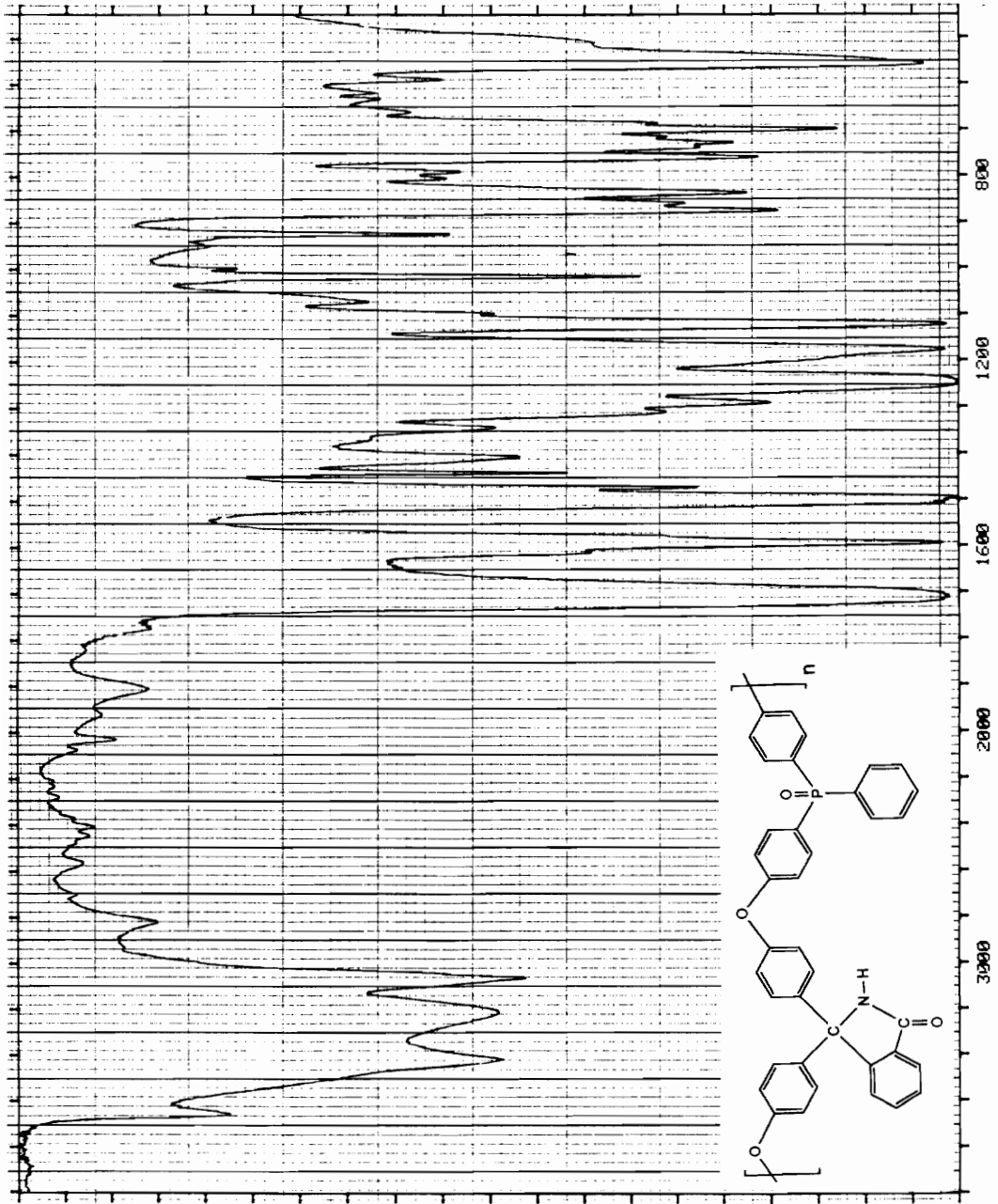


Figure 8.2.22 FTIR spectrum of PI-PEPO.

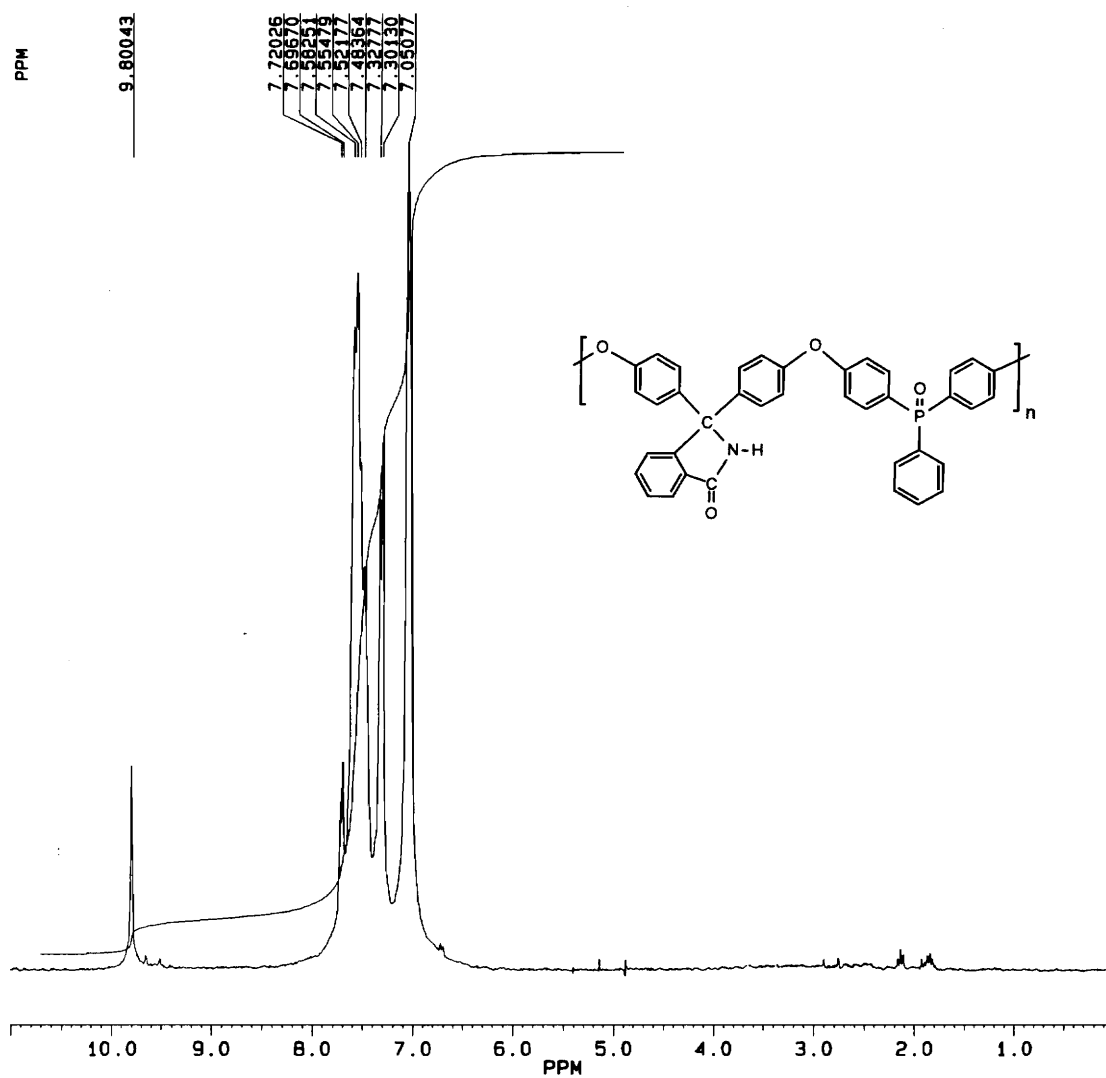


Figure 8.2.23 ^1H NMR spectrum of PI-PEPO. (300 MHz, d_6 -DMSO)

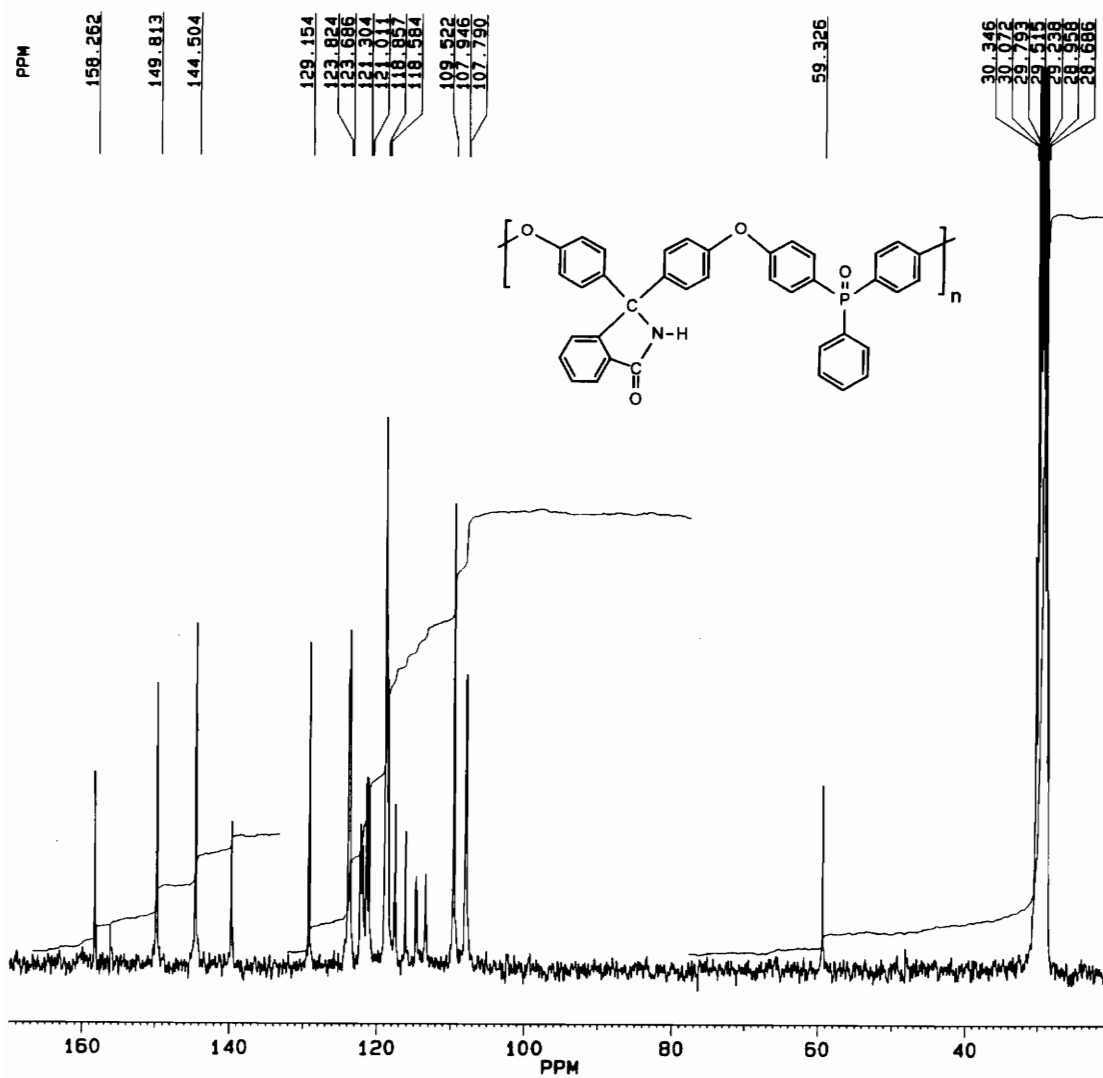


Figure 8.2.24 ^{13}C NMR spectrum of PI-PEPO. (300 MHz, d_6 -DMSO)

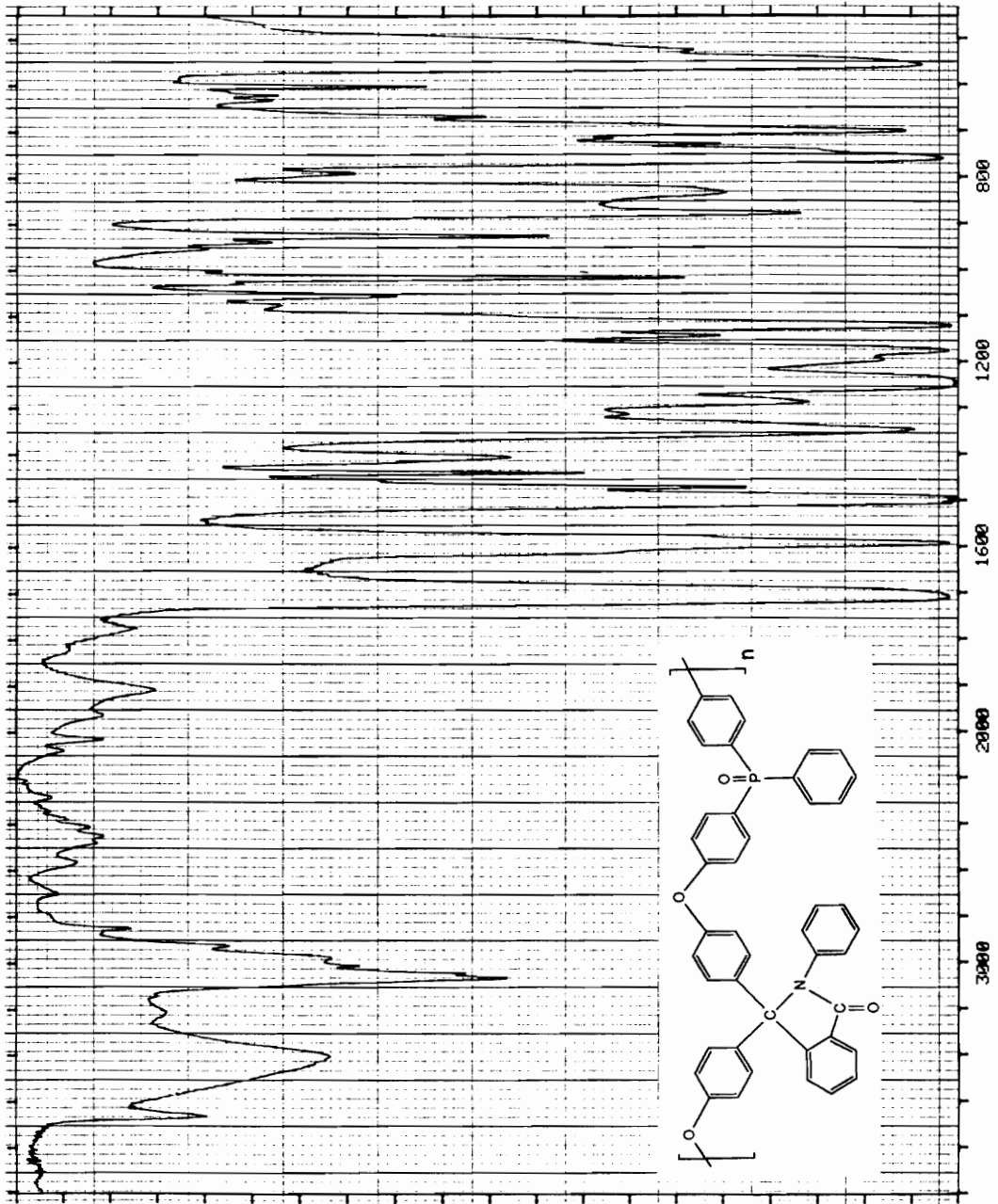


Figure 8.2.25 FTIR spectrum of PA-PEPO.

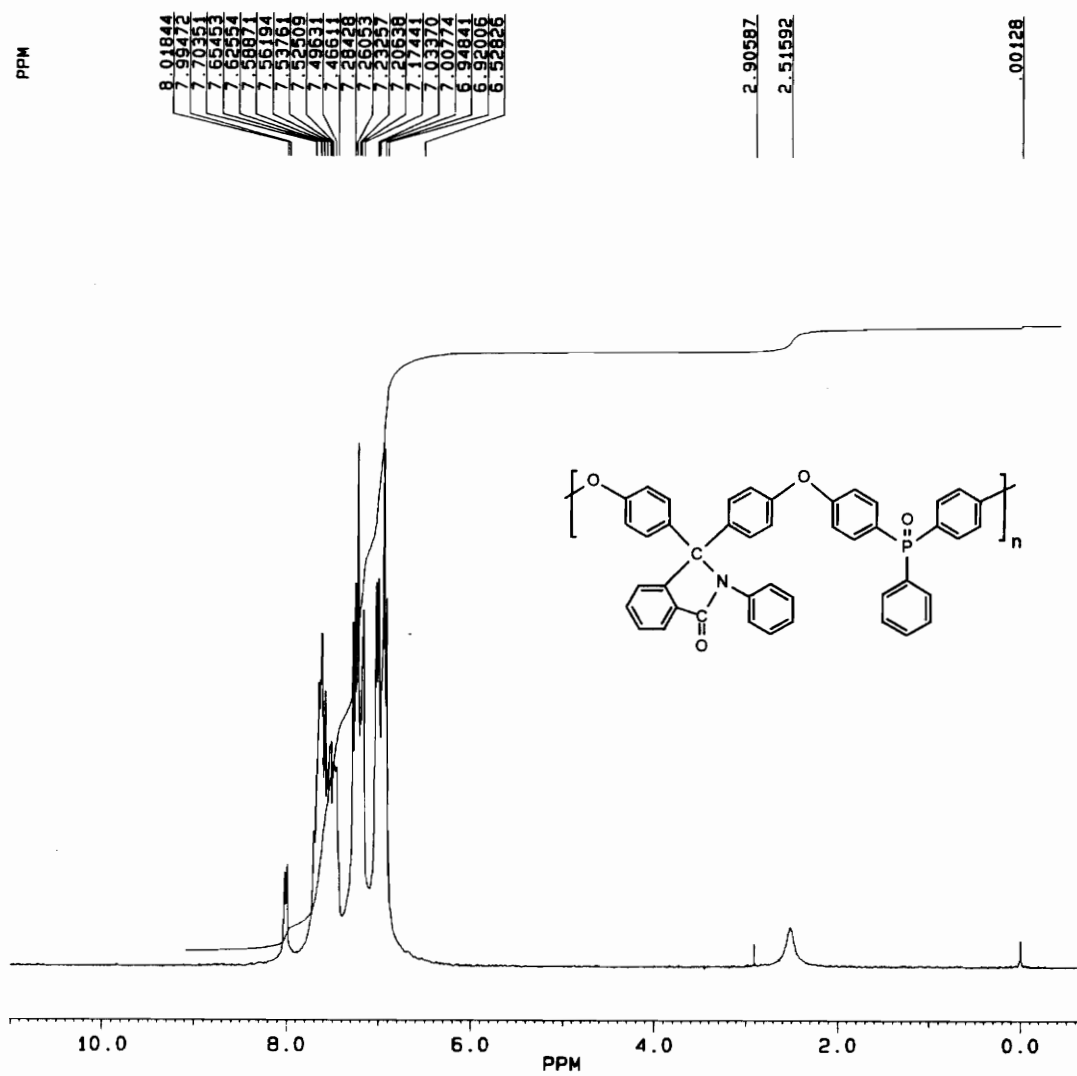


Figure 8.2.26 ^1H NMR spectrum of PA-PEPO. (300 MHz, CDCl_3)

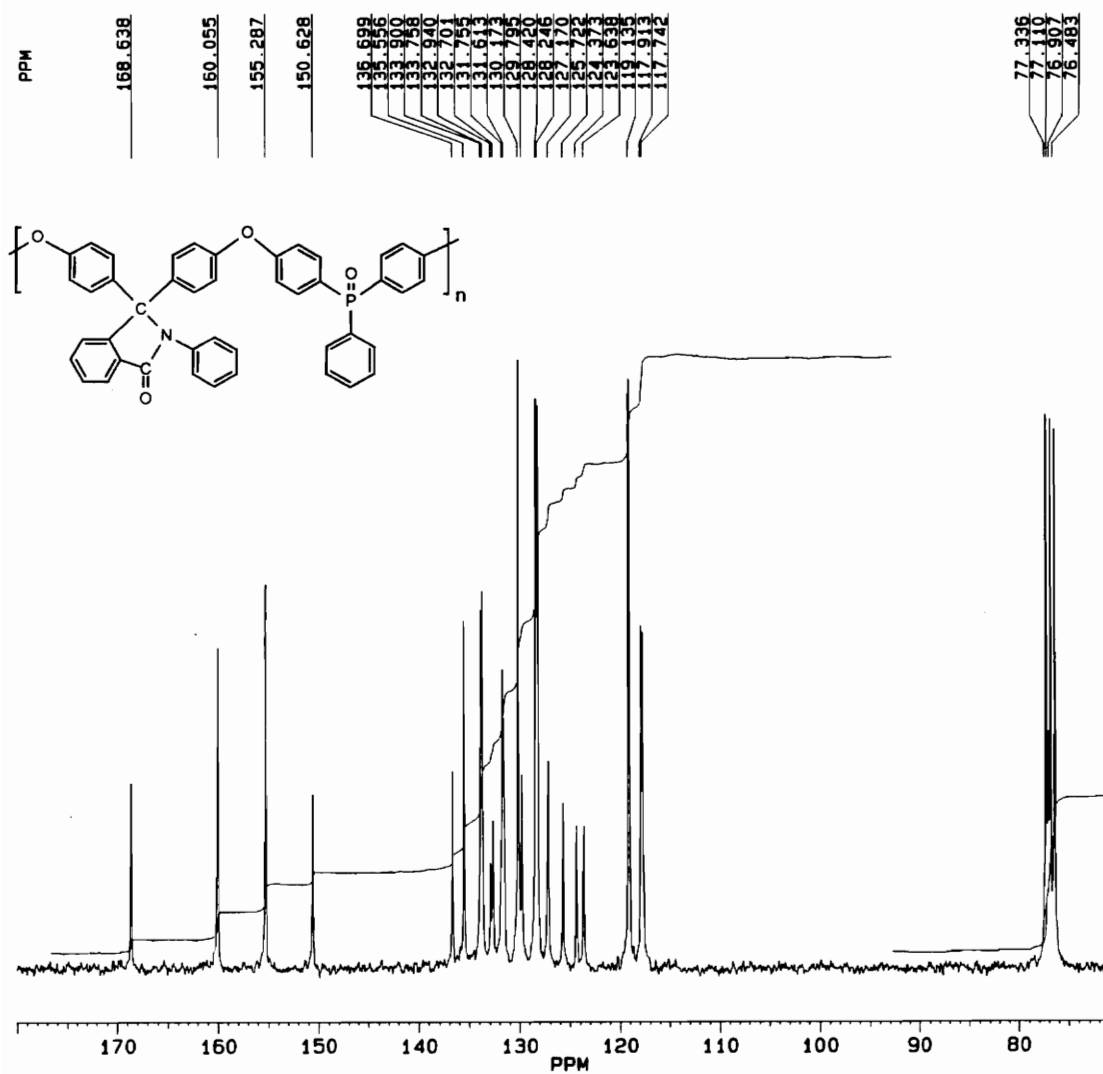


Figure 8.2.27 ^{13}C NMR spectrum of PA-PEPO. (300 MHz, CDCl_3)

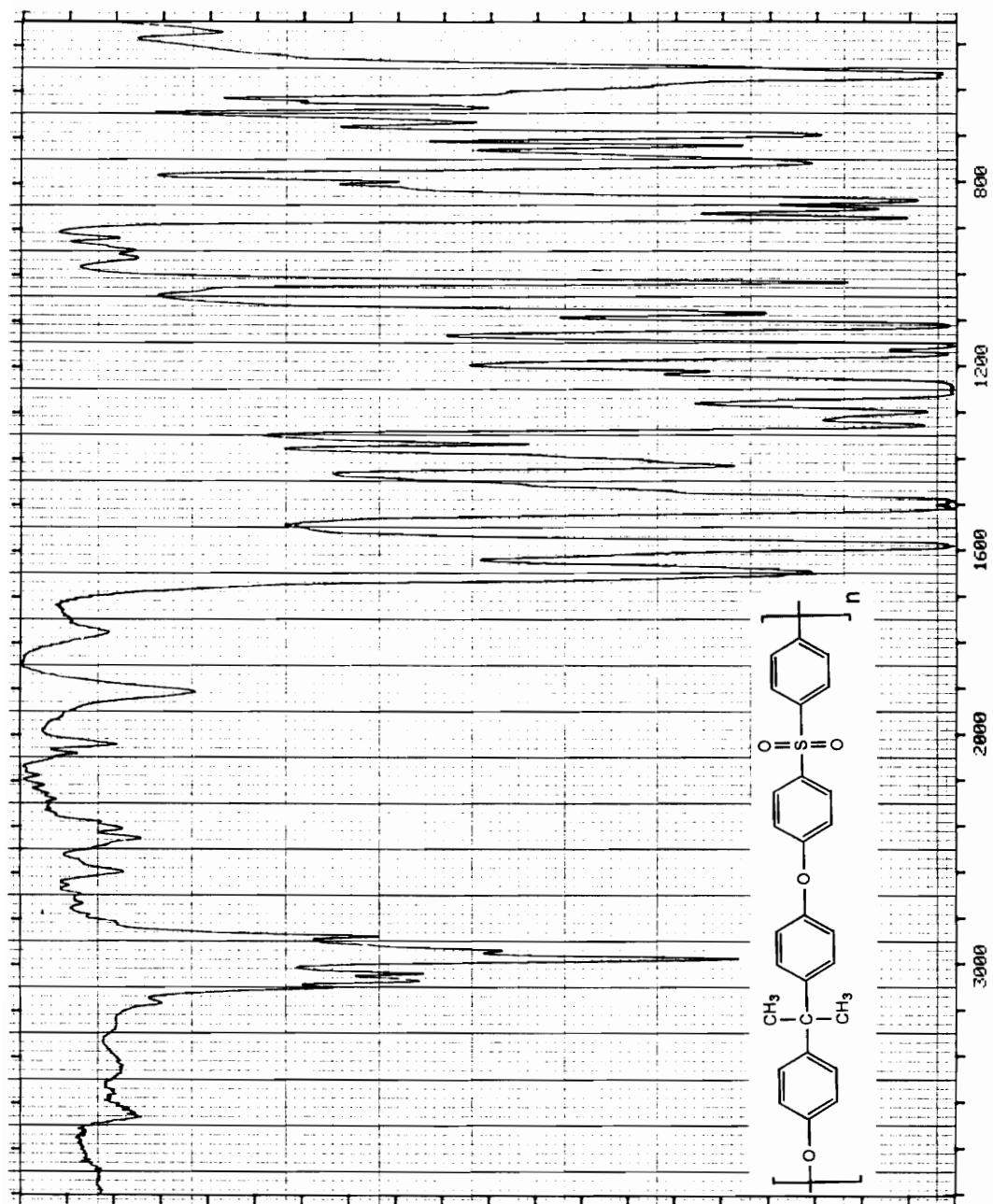


Figure 8.2.28 FTIR spectrum of BIS A-PES.

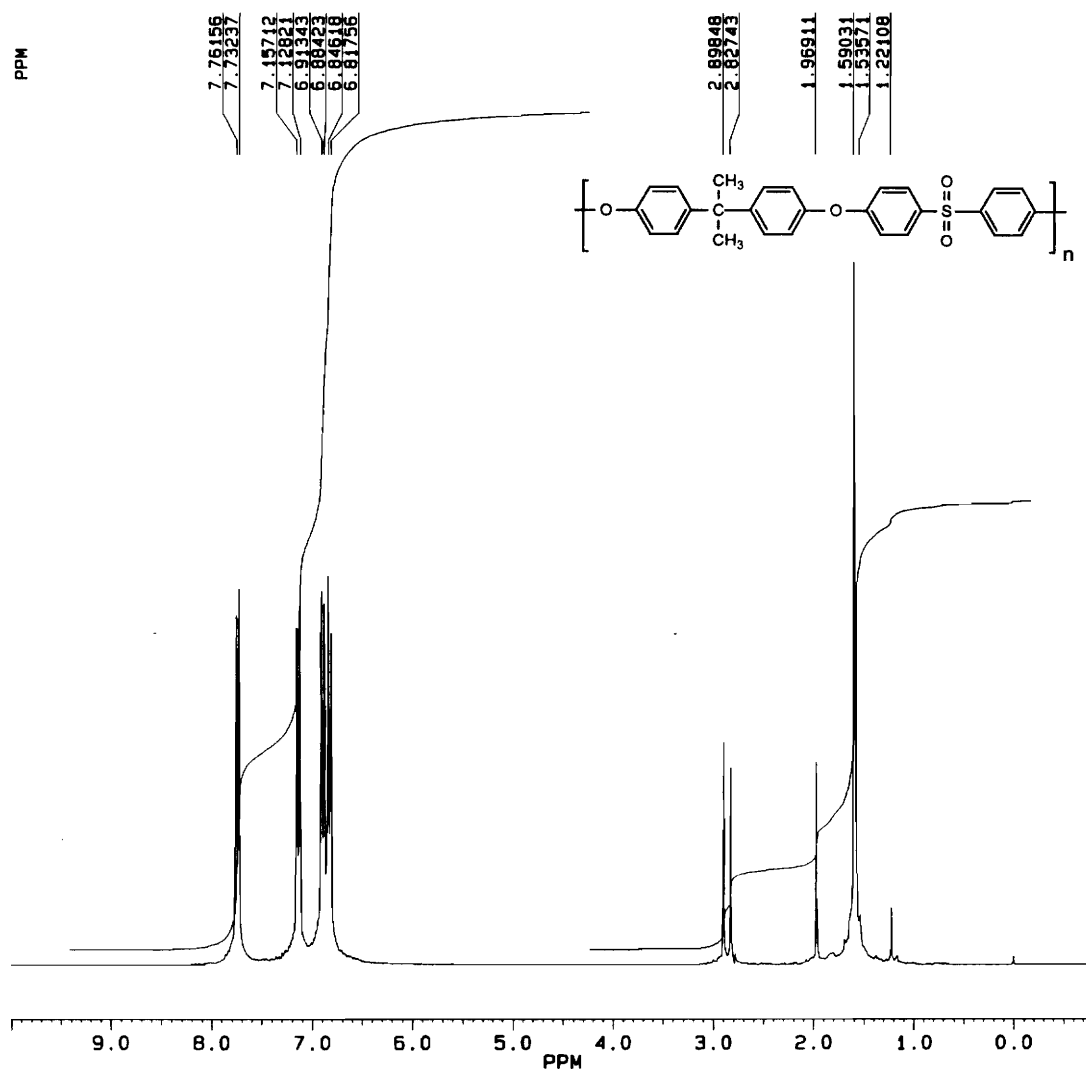


Figure 8.2.29 ^1H NMR spectrum of BIS A-PES. (300 MHz, CDCl_3)

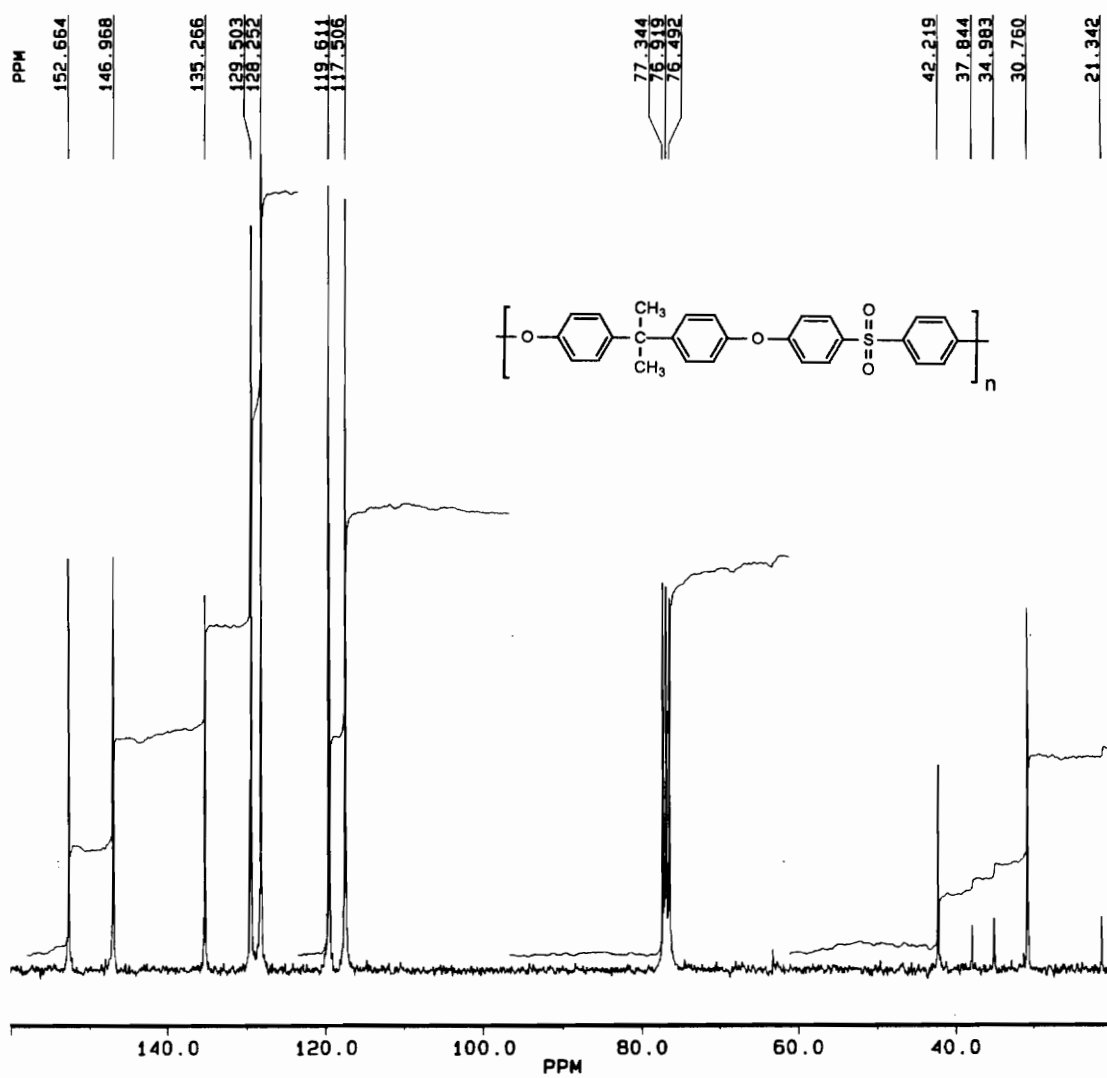


Figure 8.2.30 ^{13}C NMR spectrum of BIS A-PES. (300 MHz, CDCl_3)

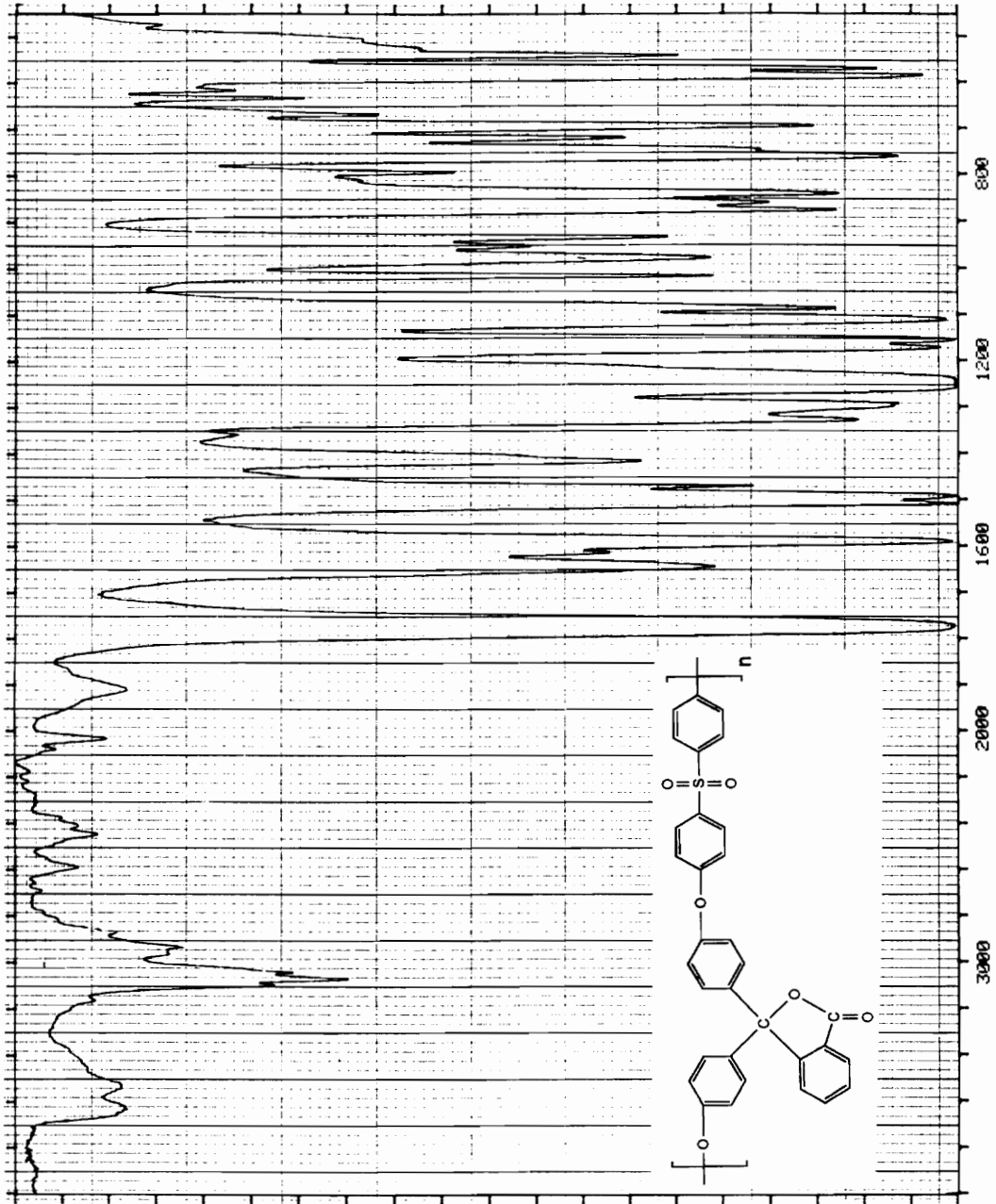


Figure 8.2.31 FTIR spectrum of PP-PES.

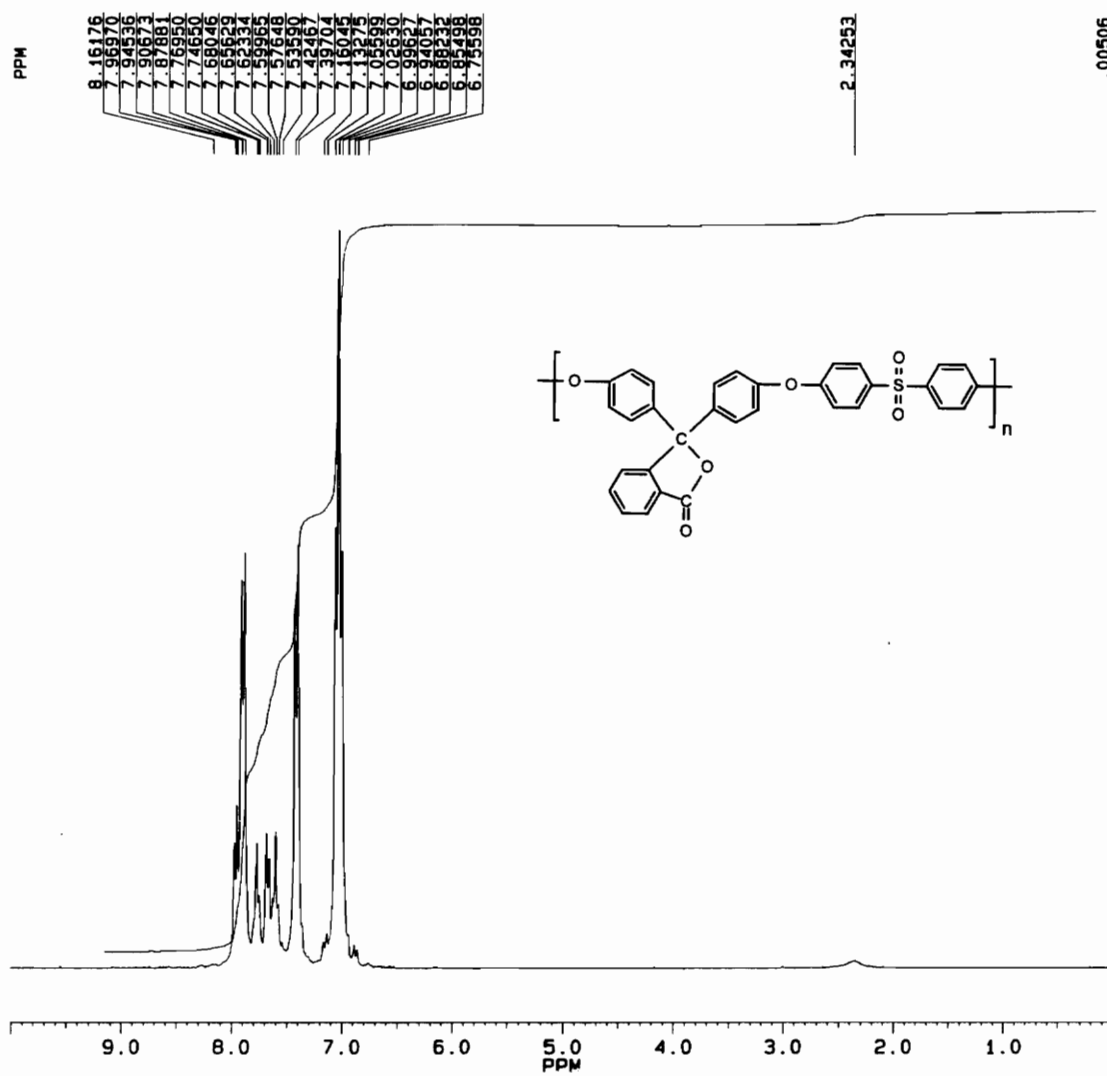


Figure 8.2.32 ^1H NMR spectrum of PP-PES. (300 MHz, CDCl_3)

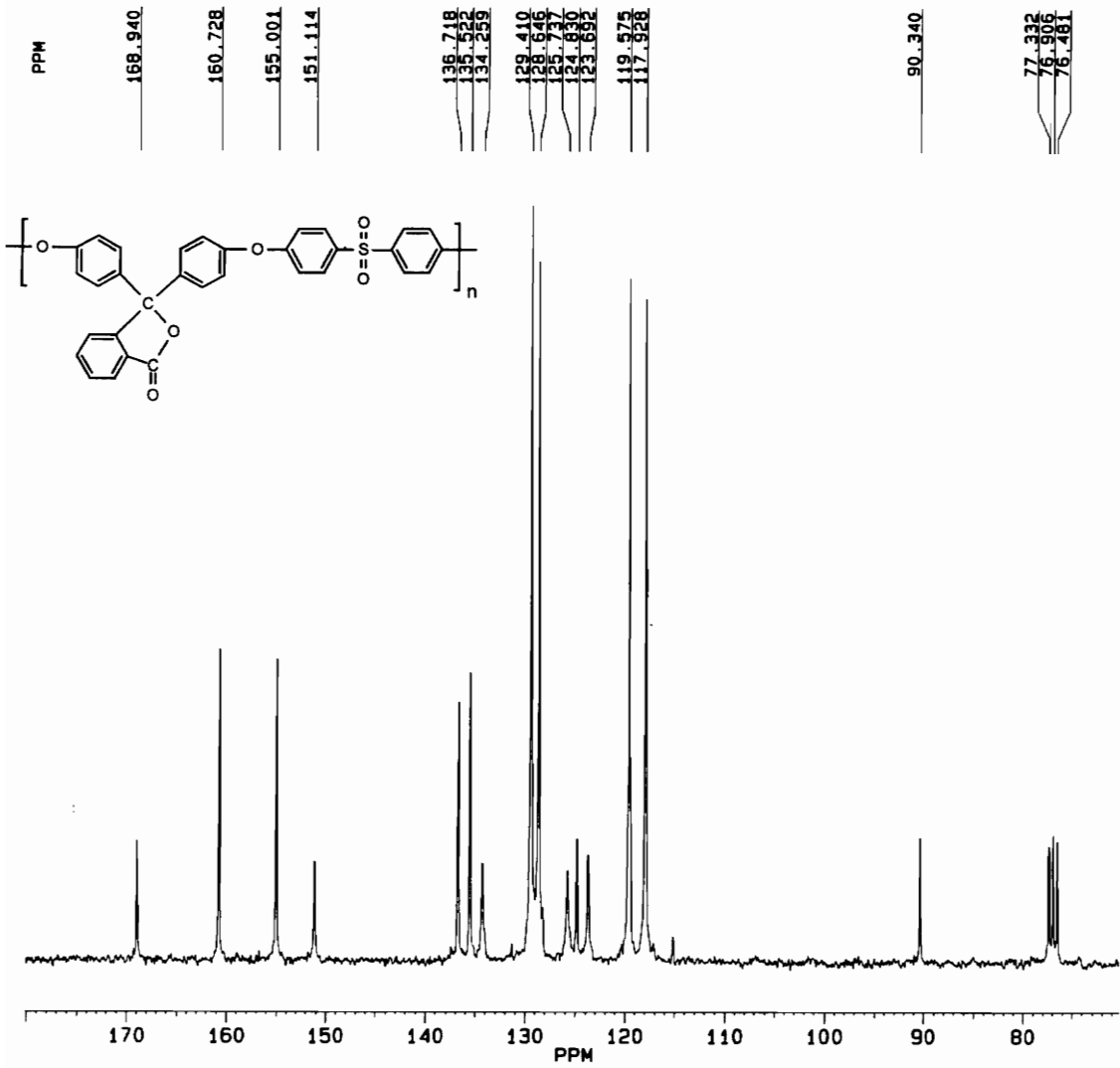


Figure 8.2.33 ^{13}C NMR spectrum of PP-PES. (300 MHz, CDCl_3)

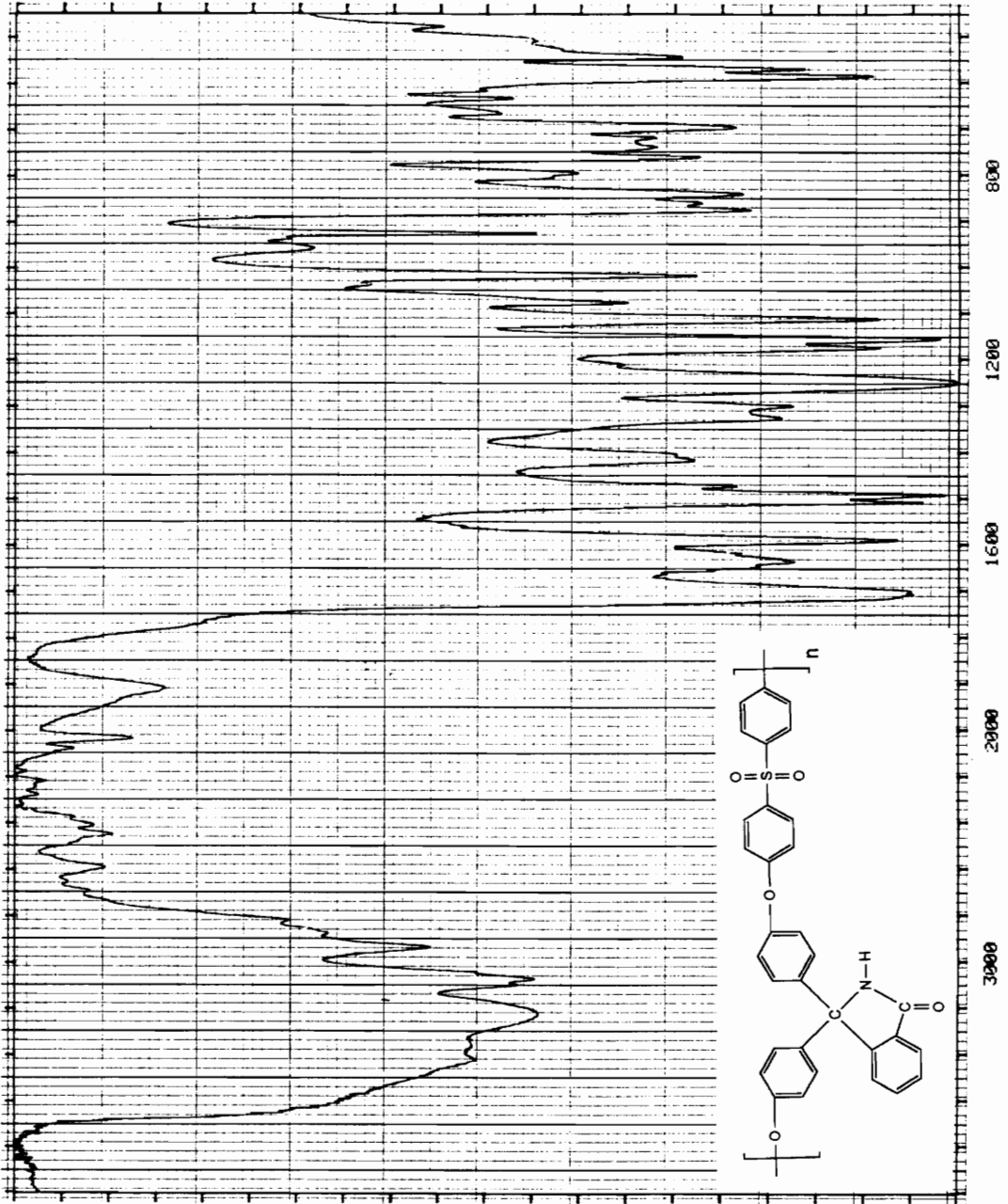


Figure 8.2.34 FTIR spectrum of PI-PES.

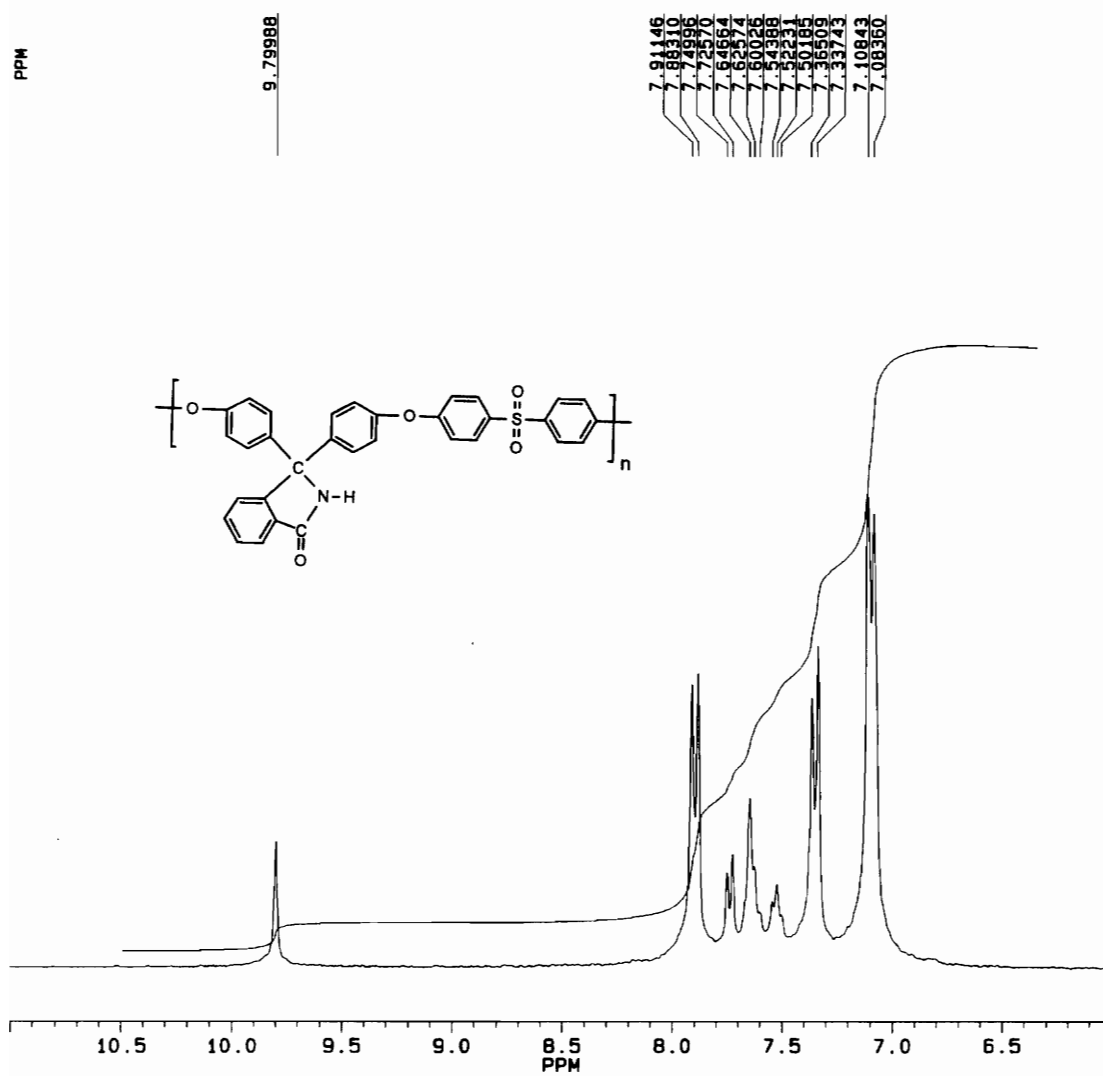


Figure 8.2.35 ¹H NMR spectrum of PI-PES. (300 MHz, d₆-DMSO)

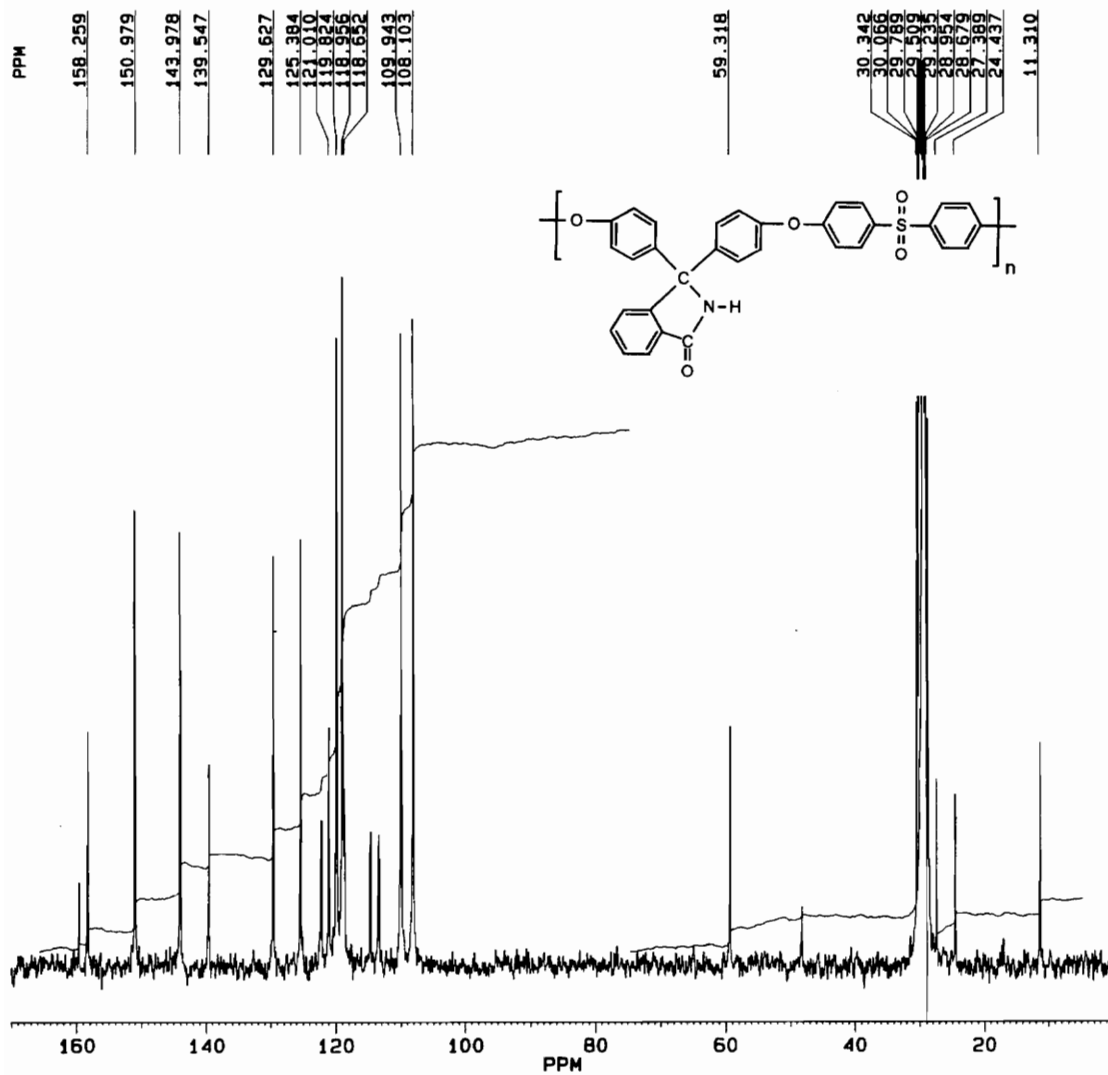


Figure 8.2.36 ^{13}C NMR spectrum of PI-PES. (300 MHz, d_6 -DMSO)

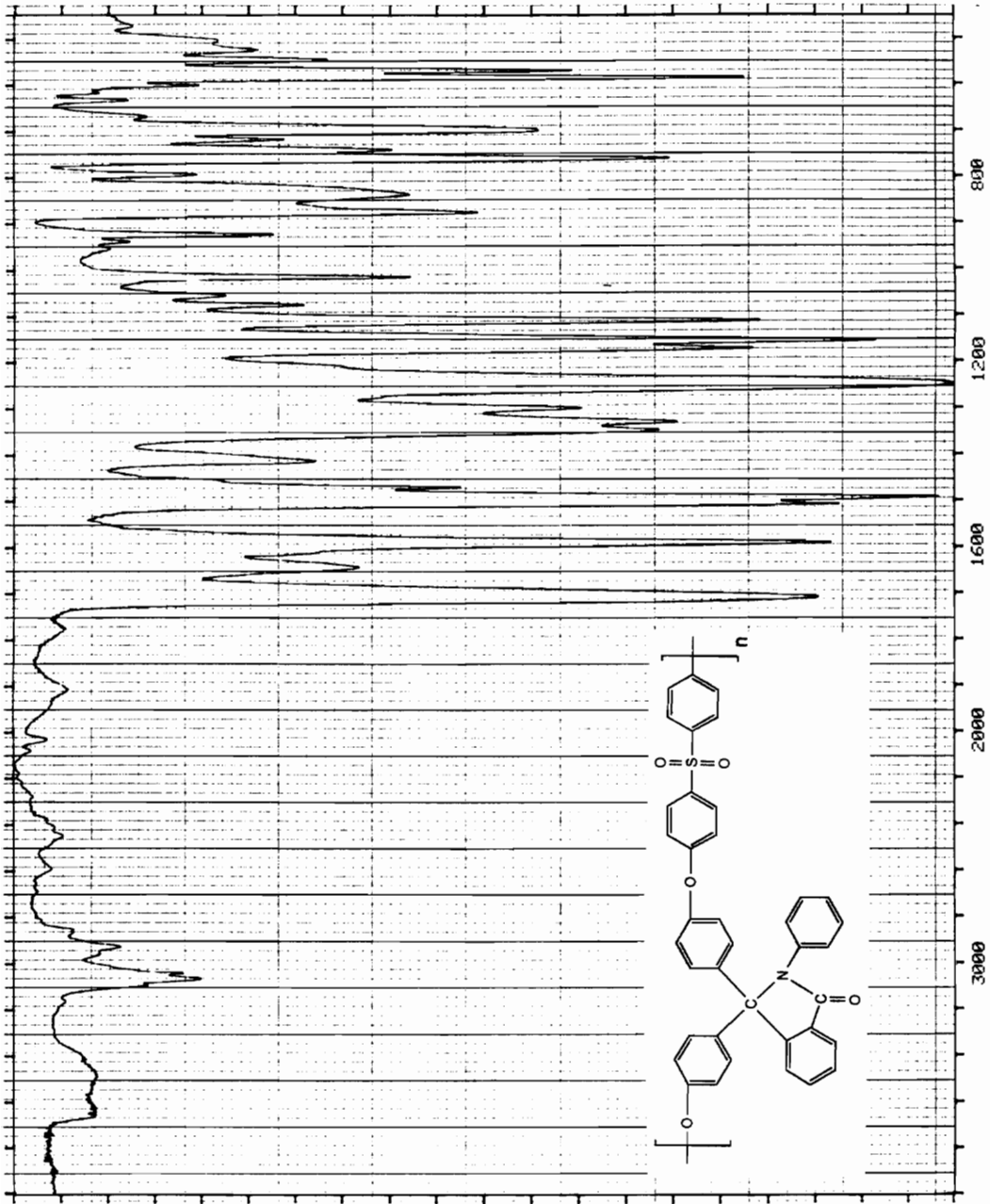


Figure 8.2.37 FTIR spectrum of PA-PES.

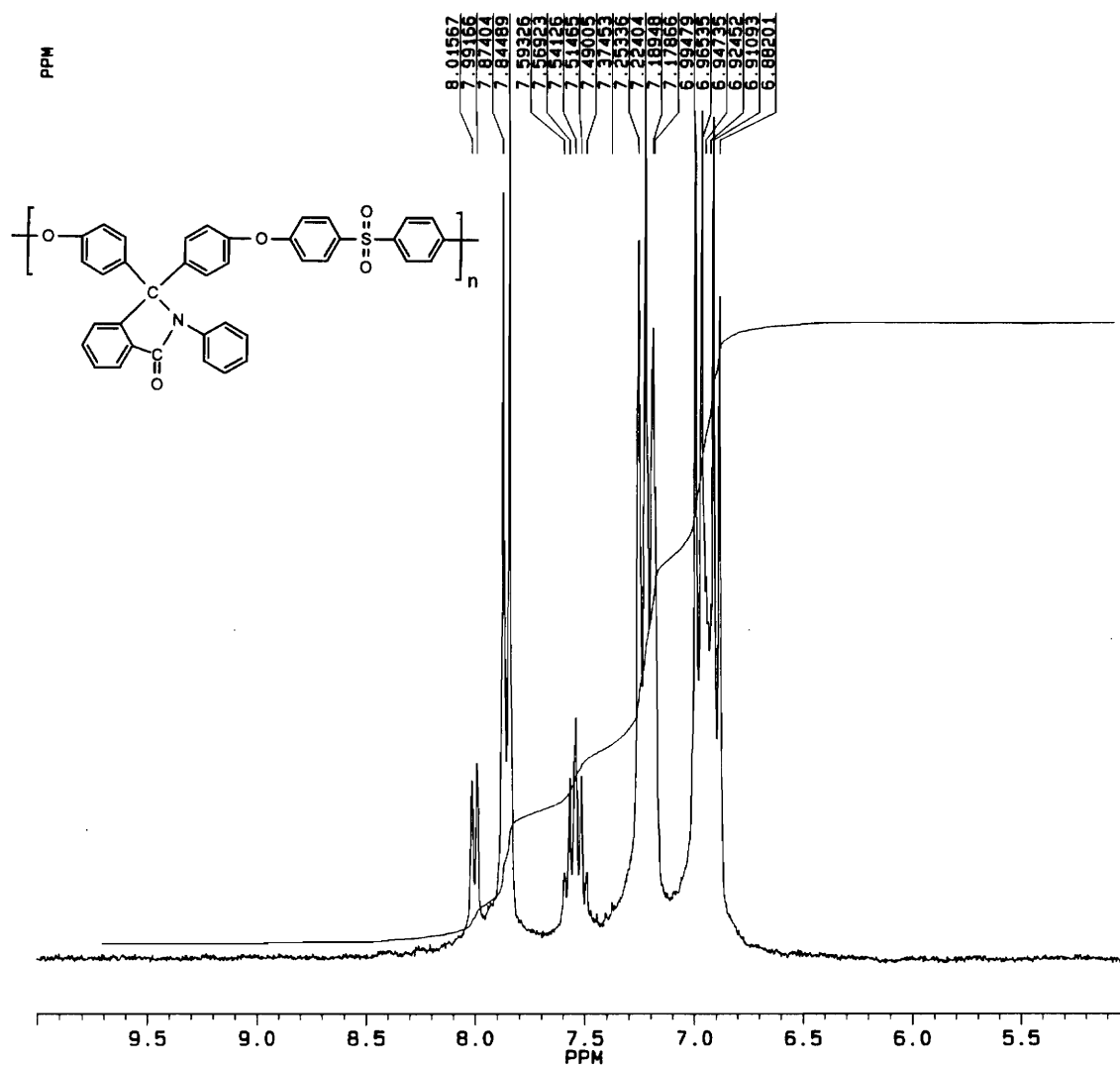


Figure 8.2.38 ^1H NMR spectrum of PA-PES. (300 MHz, CDCl_3)

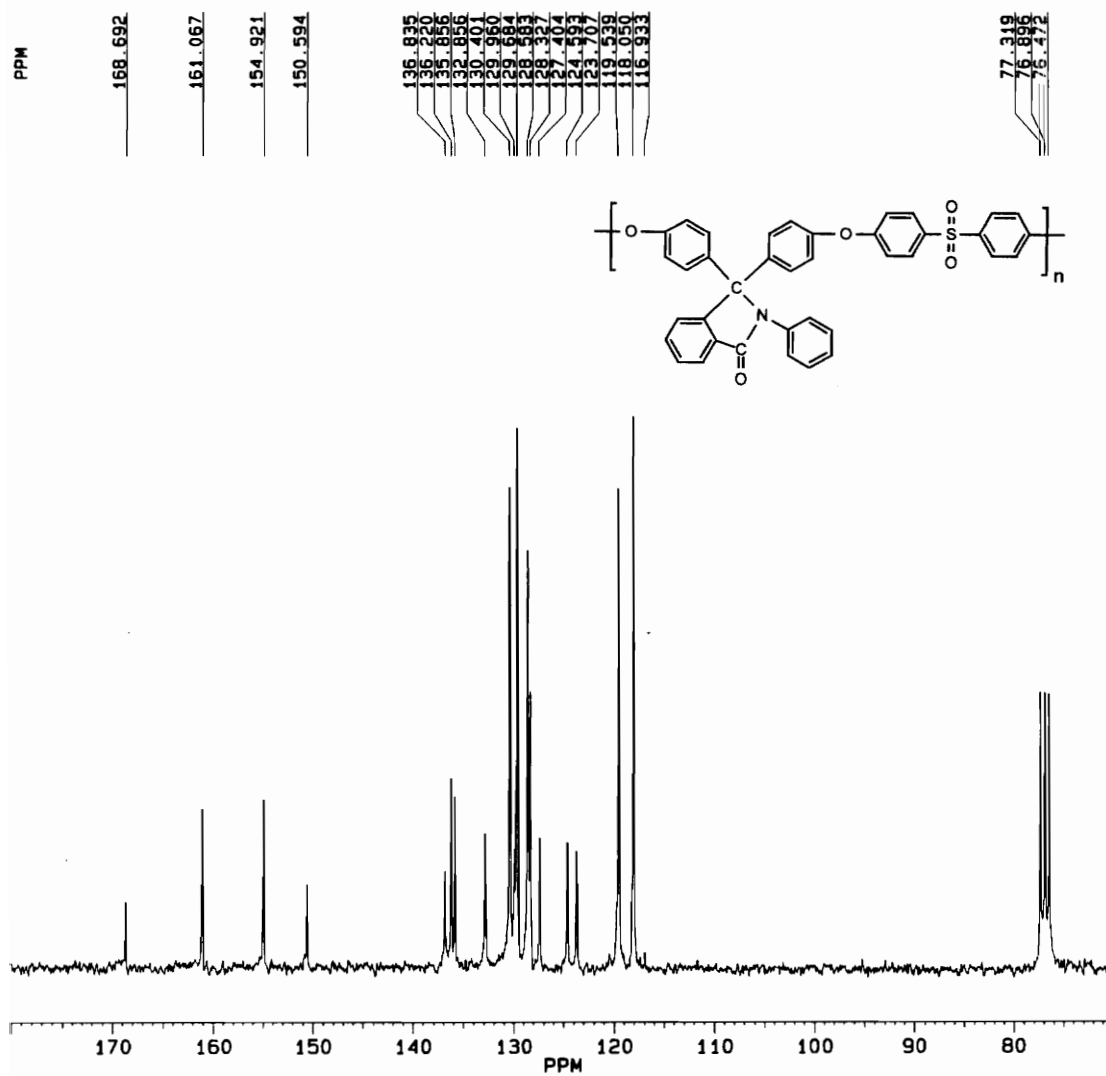


Figure 8.2.39 ^{13}C NMR spectrum of PA-PES. (300 MHz, CDCl_3)

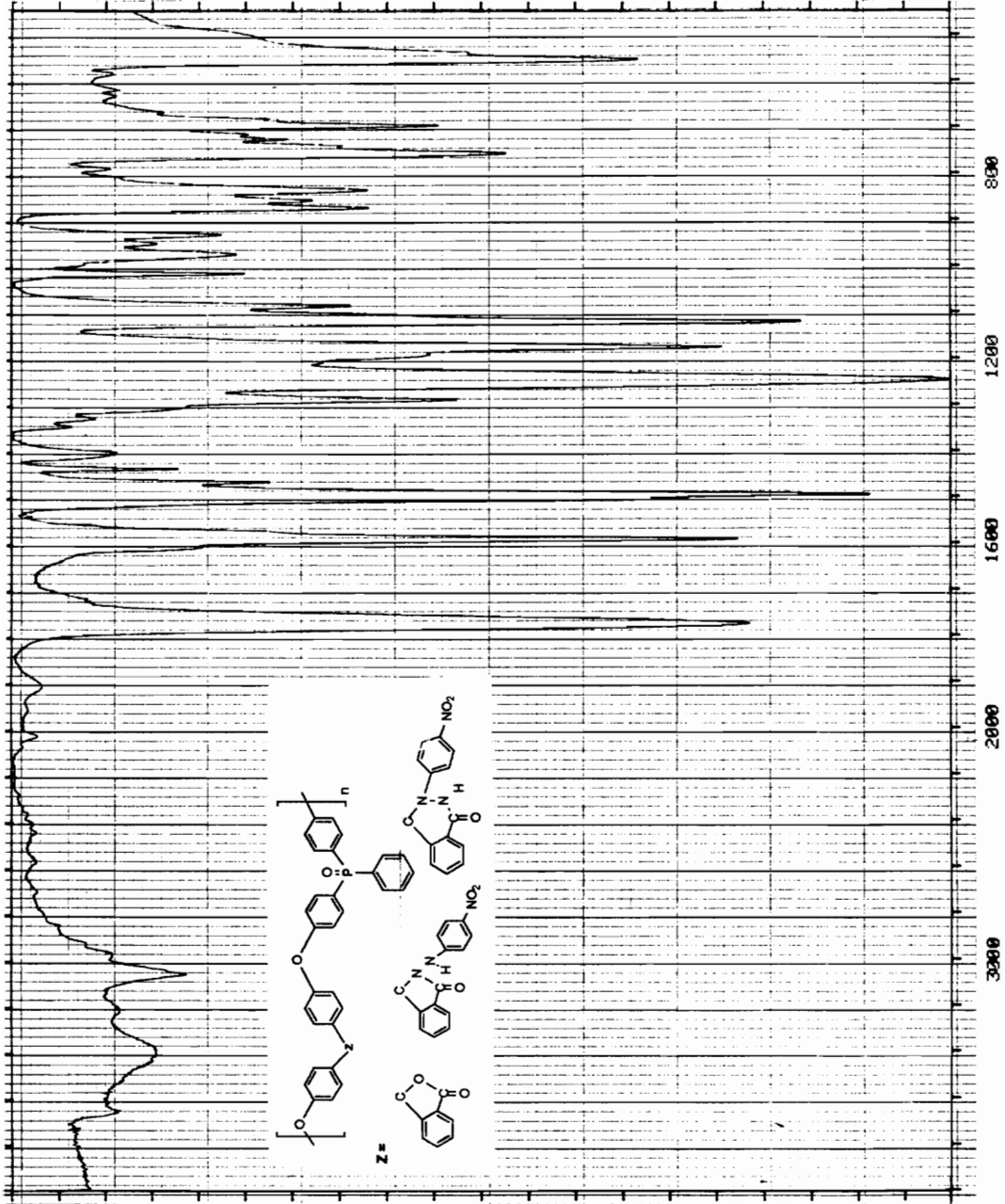


Figure 8.2.40 FTIR spectrum of 10 mole % derivatized PP-PEPO.

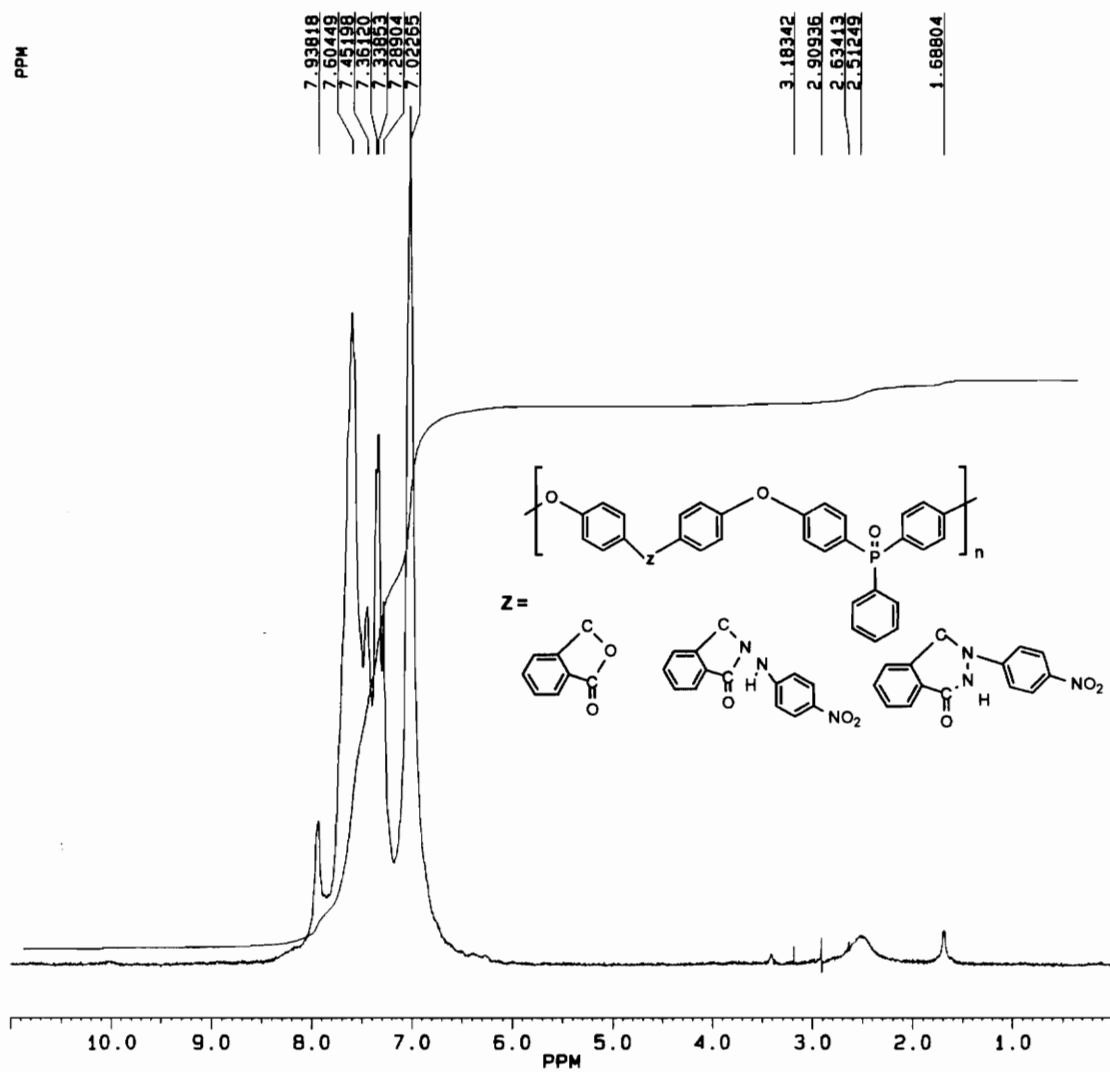


Figure 8.2.41 ¹H NMR spectrum of 10 mole % derivatized PP-PEPO. (300 MHz, CDCl₃)

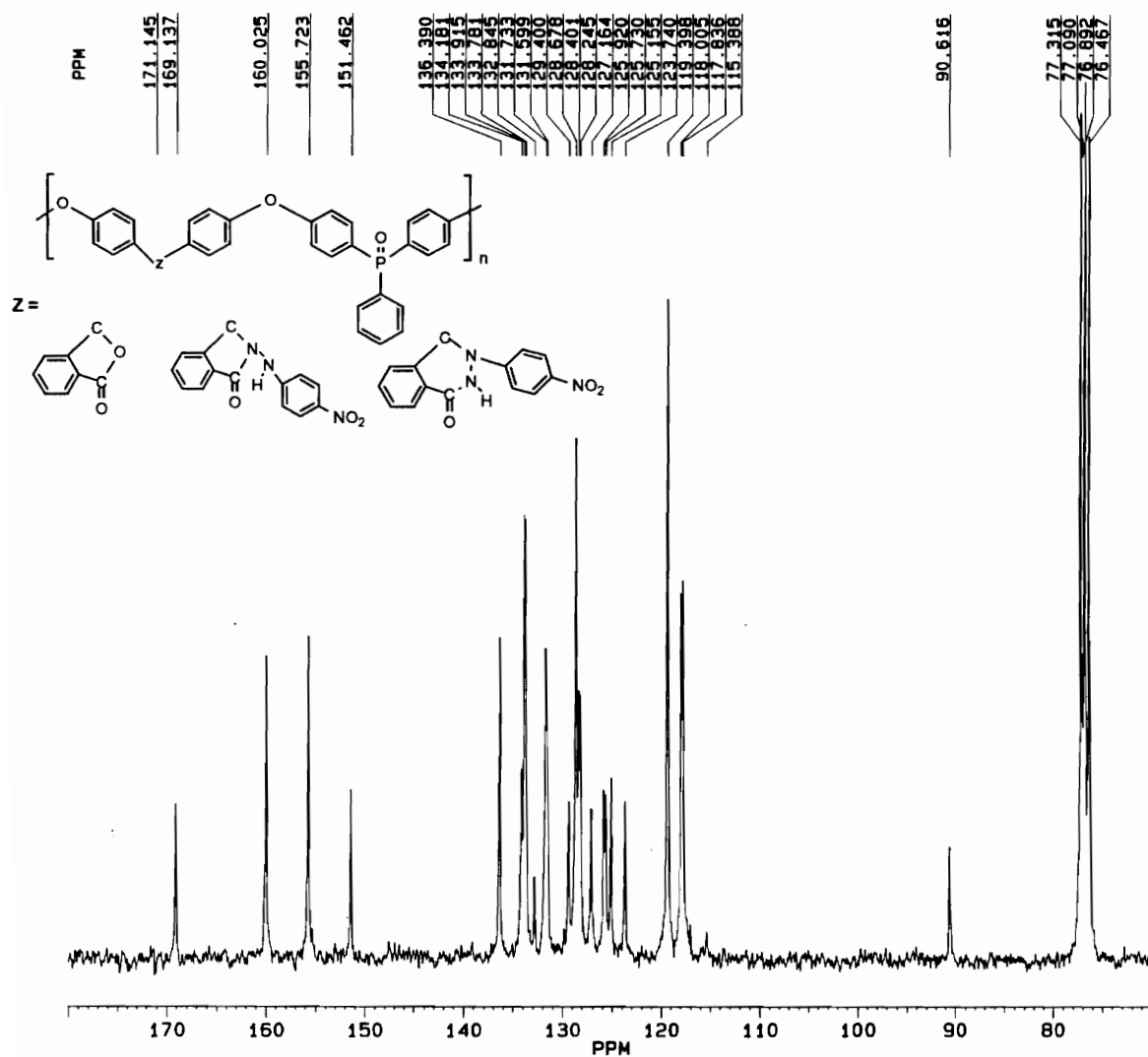
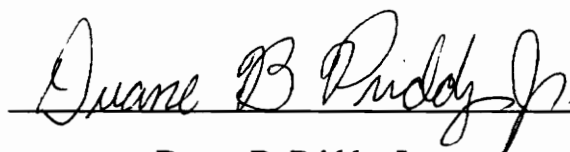


Figure 8.2.42 ^{13}C NMR spectrum of 10 mole % derivatized PP-PEPO. (300 MHz, CDCl_3)

9.0 VITA

Duane Bruce Priddy, Jr. was born in Midland, Michigan on May 1, 1968. He entered Cedarville College in Cedarville, Ohio in September 1986 and graduated with a B.A. in Chemistry in May, 1990. The author then entered the graduate program in Chemistry at Virginia Polytechnic Institute and State University in September, 1990. Under the direction of Dr. James E. McGrath, Duane began his dissertation research centered on the synthesis and characterization of phosphorus, sulfur, and pendant heterocycle containing high performance polymeric systems. He received his Ph.D. in Chemistry with an emphasis in polymer science in May, 1994. Immediate plans for Duane include marriage to Alisa Renee on June 18, 1994. Duane and Alisa will then move to Pittsburgh, Pennsylvania where he will begin a career in polymer research at Miles, Inc.

A handwritten signature in cursive script that reads "Duane B Priddy Jr." The signature is written in black ink and is positioned above a horizontal line.

Duane B. Priddy, Jr.