

SYNTHESIS AND CHARACTERIZATION OF PHOSPHORUS CONTAINING  
POLY(ARYLENE ETHER) SYSTEMS

by

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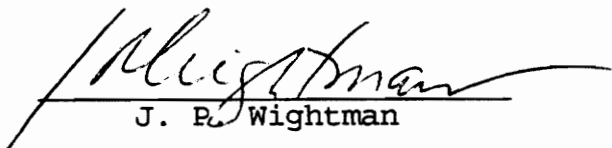
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SYNTHESIS AND CHARACTERIZATION OF PHOSPHORUS CONTAINING POLY(ARYLENE  
ETHER) SYSTEMS

by

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Chemistry

(ABSTRACT)

The synthesis and characterization of poly(arylene ether)s containing the phosphine oxide unit along the backbone were investigated and unique properties derived from the presence of this moiety were identified. The preparation of crucial phosphine oxide containing monomers which would be susceptible to the desired nucleophilic aromatic substitution polycondensation was achieved via Grignard routes. Thus, bis(4-fluorophenyl)phenyl phosphine oxide and bis(4-fluorophenyl)methyl phosphine oxide were found to undergo successfully polymerization by a nucleophilic displacement reaction with aromatic bisphenols in the presence of potassium carbonate and dipolar aprotic solvents. The resulting poly(arylene ether phosphine oxide)s had glass transition temperatures ranging from 195 to 285°C depending on the rigidity of the bisphenol and the pendant group on the phosphorus containing monomers. Many properties were typical of their poly(arylene ether sulfone) and

poly(arylene ether ketone) counterparts, including excellent hydrolytic, thermal and oxidative stability. Good dimensional stability and mechanical properties were also obtained. Physical blends and statistical copolymers, as well as polymers of controlled molecular weight and functionality, were also prepared via conventional techniques, yielding novel phosphorus containing compositions.

Unique features of these poly(arylene ether phosphine oxide)s (PEPO) were discovered initially by thermogravimetric analysis in air. All PEPO gave significant amounts of phosphorus containing char at temperatures where other engineering polymers were completely volatilized. This behavior was related to the very improved self-extinguishing behavior of all the phosphorus containing systems. Unlike most phosphorus containing polyphosphonates described in the literature, the phosphorus-aryl carbon bond was hydrolytically stable. Additionally, these PEPO materials were much more resistant to aggressive oxygen plasma environments due solely to unique oxidized phosphorus surface layers formed upon exposure to these harsh conditions. Finally, metal complexation through the phosphine oxide unit was discovered to be a novel way to modify polymer properties.



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## ABBREVIATIONS

In order of appearance in text

$S_NAr$  - Nucleophilic aromatic substitution mechanism  
DMSO - Dimethylsulfoxide  
DMAC - N,N'-Dimethylacetamide  
NMP - N-Methylpyrrolidone  
HMPT - Hexamethylphosphorus triamide  
EAS - Electrophilic aromatic substitution  
NAS - Nucleophilic aromatic substitution  
PES - Poly(arylene ether sulfone)  
DCDPS - 4,4'-Dichlorodiphenylsulfone  
ETP - Engineering thermoplastic  
PEK - Poly(arylene ether ketone)  
PEEK - Poly(arylene ether ether ketone)  
DFB - 4,4'-Difluorobenzophenone  
PBI - Polybenzimidazole  
PEI - Poly(arylene ether imide)  
PEPO - Poly(arylene ether phosphine oxide)  
BCPPO - Bis(4-chlorophenyl)phenyl phosphine oxide  
BFPPPO - Bis(4-fluorophenyl)phenyl phosphine  
DPS - Diphenylsulfone  
THF - Tetrahydrofuran  
HQ - Hydroquinone  
BP - 4,4'- Biphenol  
FL - 9,9-Bis(4-hydroxyphenyl)fluorene  
BFMPO - Bis(4-fluorophenyl)methyl phosphine oxide  
BHPPPO - Bis(4-hydroxyphenyl)phenyl phosphine oxide  
DSC - Differential Scanning Calorimetry  
TGA - Thermogravimetric Analysis  
TMA - Thermomechanical Analysis  
DMTA - Dynamic Mechanical Thermal Analysis  
DETA - Dielectric Thermal Analysis  
XPS - X-ray Photoelectron Spectroscopy  
DFDPS - 4,4'-Difluorodiphenylsulfone  
BAPPO - Bis(4-aminophenyl)phenyl phosphine oxide

## 1.0 INTRODUCTION

Poly(arylene ether)s now comprise a large section of the field of polymers termed engineering thermoplastics, which encompasses those materials employable where traditional engineering materials (metal, wood, etc.) would be utilized. This specific area of macromolecules has been known for some twenty five years, with the poly(arylene ether sulfone)s and poly(arylene ether ketone)s being by far the most well known. Applications include areas such as automotive, electrical, chemical processing, and high performance polymeric resins for carbon fiber composites. Because of their good dimensional stability below 0°C and above 100°C, good thermal and oxidative stability, and largely owing to their outstanding hydrolytic stability, research involving modification or preparation of new poly(arylene ether)s has been proceeding at a swift rate.

The present work has focused on the preparation and characterization of poly(arylene ether phosphine oxide)s, and related copolymers and blends. Incorporation of phosphorus into the backbone was expected to increase the flame retardancy relative to other poly(arylene ether)s, while retaining the desirable properties discussed above. Additionally, the presence of phosphorus in the backbone of such polymers was expected to lend thermal stability and the ability to perform further chemical modification on the materials via inorganic chemistry known in the literature.

The following chapter will outline the history of poly(arylene

ether) synthesis and characterization, followed by an introductory section on phosphorus containing macromolecules and their properties. With these two major sections, the platform will be laid for the purpose of utilizing nucleophilic aromatic substitution polycondensation to incorporate phosphorus containing activated dihalides into poly(arylene ether)s by conventional displacement techniques. Similar to the amorphous poly(arylene ether sulfone)s, these high molecular weight poly(arylene ether phosphine oxide) (PEPO) materials were found to be amorphous soluble and thermoplastic melt formable materials above their glass transition temperatures ( $T_g$ ). Depending on the rigidity of the bisphenol incorporated, the  $T_g$  could be tailored in the range of about 190-285°C. Additionally, polymers of controlled composition, functionality and molecular weight were synthesized and physical blends were prepared. Other physical properties of the high molecular weight homopolymers included good dimensional stability,  $\beta$  transitions typical of other poly(arylene ether)s which are indicators of impact resistance, thermal stability to nearly 500°C and good electrical properties.

Novel characteristics were discovered from thermogravimetric analysis studies, whereby all phosphorus containing systems were found to give high degrees of char yield in air at temperatures in excess of 600°C. Related to this char formation was the enhanced flame retardancy of such materials relative to other polymeric materials in general and poly(arylene ether)s in particular. The presence of phosphorus in the char was the key feature playing a role in the self-extinguishability of such polymers. Literature describes this behavior for other phosphorus

containing polymers, however, normally in the form of phosphorus containing additives or easily hydrolyzable oligomeric phosphorus compounds with not nearly the integrity of these poly(arylene ether) high molecular weight compounds.

Further investigations into the nature of these fascinating polymers uncovered the surprisingly high resistance to etching by oxygen plasma. Utilization of polymeric materials in space environments as coatings or structural units requires material resistance to atomic oxygen, a prime component of oxygen plasmas. Therefore, as a very good qualitative tool describing the conduct of polymers in space, ellipsometry along with surface analytical techniques were used to show the formation of a novel surface coating with oxygen plasma treatment, which then protected then underlying PEPO materials from etching.

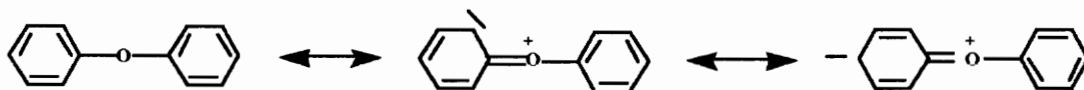
Finally, the presence of phosphine oxide units along the backbone allowed the utilization of inorganic complexation chemistry to modify the poly(arylene ether phosphine oxide) thermoplastics. By complexing these homopolymers with a variety of metal halide salts, chemically reversible crosslinking occurred. In solvents such as N,N-dimethylacetamide, which also complex with metal salts, homogeneous solutions of the PEPO were prepared, from which clear films were cast. These films were altered in terms of their physical characteristics relative to other poly(arylene ether)s modified in identical ways which gave very poor quality films with no desirable properties relative to their unmodified precursors.

## 2.0 BACKGROUND

### 2.1 POLY(ARYLENE ETHER)S

#### 2.1.1 Organic Chemistry of Nucleophilic Aromatic Substitution

The preparation of the aromatic ether bond is one of the classic reactions of organic synthesis [1]. Aromatic ether bonds are chemically and thermally stable and therefore favorable in the preparation of highly aromatic polymers which would be ideal for applications in which chemical and thermal stability would be desired. The bond strength of a carbon-oxygen ether bond (84.0 kcal/mol) is on the order of that of a carbon-carbon bond (83.1 kcal/mol), while additional stabilization is provided through resonance [2]. Scheme 1 illustrates the type of resonance structures through which these types of compounds can be stabilized.



Scheme 1. Resonance structures for aryl ethers.

In fact, diphenyl ether is well known to be a thermally stable material and has been utilized as a high temperature solvent in some cases. Therefore, chemical, thermal and oxidative stability could be expected of the aromatic polyethers.

Additionally, the barrier energies for rotation in aromatic and aliphatic ethers around the carbon-oxygen bond is about 2.4 kcal/mol and

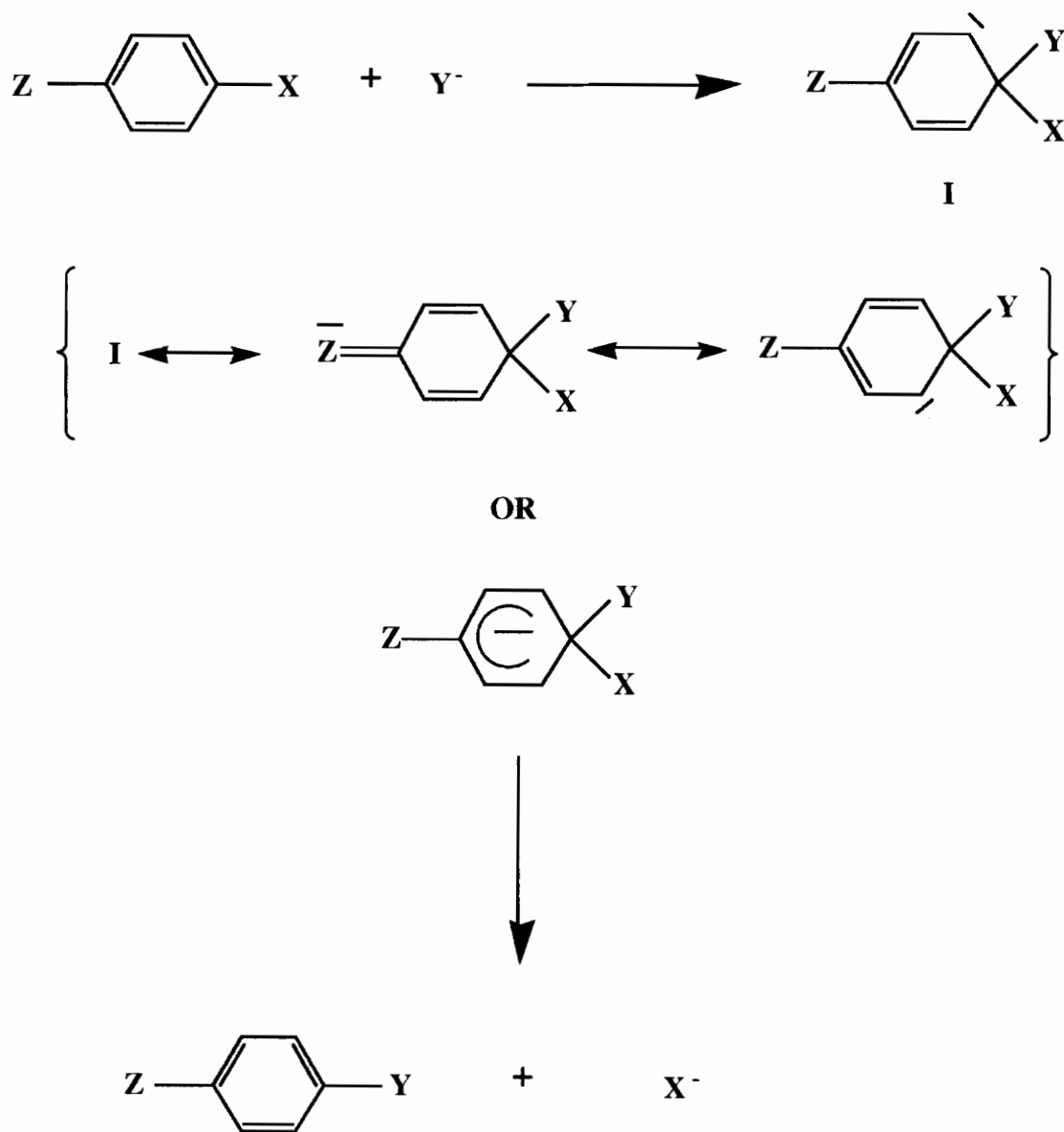


1.2 kcal/mol, respectively, compared to 3 kcal/mol for aliphatic carbon-carbon single bonds [2, 3]. As will be discussed later in this introduction, this low barrier to rotation about the aromatic ether bond is a primary reason for the toughness or impact resistance displayed by many aromatic polyethers, as it provides a mechanism for energy dispersion.

Aromatic ether synthesis has been extensively researched in the literature. The purpose of this background is not to cover this literature exhaustively, but to review the major points of nucleophilic aromatic substitution preparative methods, as those were the procedures used in this research. For an extensive discussion of ether forming synthetic methods, one can refer to any of several monographs or collections on the subject [4]. As discussed in the section on the history of poly(arylene ether) synthesis, another commercial route for the preparation of poly(arylene ether)s has been via an electrophilic aromatic substitution mechanism. The background will not emphasize the organic chemistry literature behind this mechanism since it was not utilized in this research and has been extensively discussed elsewhere [1].

Nucleophilic aromatic displacement reactions have been known since the mid 1850's, but it was not until about 100 years later when the classic compilation by Bunnett and Zahler [5] elucidated the mechanism behind this substitution type synthesis. Scheme 2 illustrates the basic principles behind this mechanism and the chemical requirements for it. In Scheme 2, X is the leaving group, Y is the nucleophile and Z is an

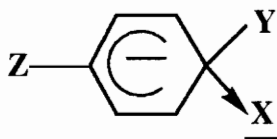
activating group for nucleophilic aromatic substitution. Since the nucleophile seeks a site with which to share its electrons, the activating group in nucleophilic aromatic substitution



Scheme 2. Generalized nucleophilic aromatic substitution mechanism.

is an electron withdrawing moiety, preferably in the *para* position to the site of nucleophile attack. This mechanism is referred to the  $S_NAr$  mechanism. Although some substitution will occur if the electron withdrawing is *ortho* to the leaving group, steric interactions prohibit formation of a stable intermediate and therefore high molecular weight polymers in most cases.

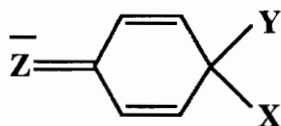
The first step in this mechanism is the attack of the nucleophile, yielding a resonance stabilized intermediate, which then loses the leaving group to form the substituted aromatic compound. Nearly always, the first step, attack of the nucleophile, is rate determining [6, 7]. Evidence for this fact lies with the work of Bunnett, who found the rate of reaction dependent on leaving group for the halogen series to be in the order  $F \gg Cl \geq Br \geq I$ . Since it is well known that the carbon fluoride bond is the strongest in that series, no bond breakage can occur in the rate determining step. The answer to the question as to why fluorine is the best leaving group for  $S_NAr$  reactions was a controversial issue, with most chemists now believing the highly electronegative atom stabilizes the intermediate **I** shown in the mechanism above through inductive electron withdrawing effects.



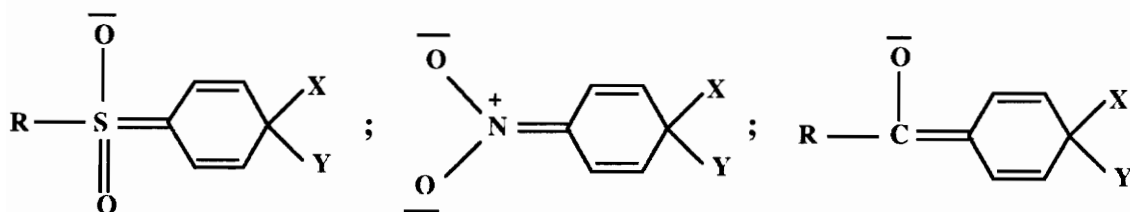
Additionally, it is likely that the steric hindrance effect plays a role in the leaving group effect, with fluorine being the smallest leaving

group. Finally, the carbon to which the highly electronegative fluorine is attached is made more electrophilic in character and thus more susceptible to nucleophilic attack.

More evidence supporting this type of mechanism lies in the study of the intermediate species formed in Scheme 2.



This type of intermediate has been termed the Meisenheimer complex after the scientist who discovered it in 1902 [8]. By accepting the negative charge from the ring during the displacement reaction, the group Z accelerates the rate of reaction if it is electron withdrawing, such as  $\text{NO}_2$ ,  $\text{SO}_2\text{R}$ ,  $\text{COR}$ , etc., as shown in Scheme 3.



Scheme 3. Meisenheimer type complexes for sulfone, nitro and ketone activating groups.

Meisenheimer complexes have been experimentally observed for several systems via NMR [9] or X-ray crystallography [10] studies. Again, for *ortho* substituted substrates, this complex is sterically unfavored.

Thus, four important variables control the reaction kinetics for the  $S_NAr$  mechanism : identity of the activating group, reactivity of the nucleophile, effect of the leaving group and the reaction conditions (solvent, temperature, etc.). While it is important to recognize the maximum and minimum performance of each variable, it must also be understood that only the successful combination of all of these parameters will produce the desired displacement in high yields and therefore acceptable polymer conditions.

The activating group has been studied in detail throughout the literature with much attention paid to the comparison of relative reaction rates of molecules differing only by electron withdrawing group with identical nucleophiles, leaving groups and conditions. The remainder of this discussion will focus only on *para* linked substrates and nucleophiles. The approximate order of electron withdrawing power found by a collection of workers [6, 11-13] is summarized in the following approximate order :  $NO > NO_2 > SO_2Me > CF_3 > CN > CHO > COR > COOH > Br > Cl > I > H > F > CMe_3 > Me > OMe > NMe_2 > OH > NH_2$ . Obviously, the trend favors those groups with electron withdrawing ability as giving the most facile displacement reactions, with moieties such as the nitro, sulfone and ketone groups affording substitution at much milder conditions and higher yields than other electron withdrawing groups. These groups were followed of course by those substituents which are electron donating, such as methoxy or amine.

Reactivity of the nucleophile also plays an important role in the ease of the  $S_NAr$  reaction. As expected for nucleophilic substitution

reactions, those reactants with higher nucleophilicity given the particular conditions and identical substrates will proceed to react in a much more facile manner than weaker nucleophiles [5, 14-16]. Nucleophilicity can generally be correlated with basicity, but several exceptions exist. Nevertheless, an approximate order of nucleophile strength is :  $\text{ArS}^- > \text{RO}^- > \text{R}_2\text{NH}^- > \text{ArO}^- > \text{OH}^- > \text{ArNH}_2 > \text{NH}_3 > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{H}_2\text{O} > \text{ROH}$  [5]. As is readily observable, the highly polarizable thiophenoxide anion is the best nucleophile, with phenoxide and hydroxide ions reactivities approximately midway between the halogens and the thio nucleophiles. As must be the case from the discussions above, electron accepting groups (e.g.  $\text{NO}_2$ ,  $\text{SO}_2\text{R}$ ) bound to the aromatic nucleophiles in any position lower reactivity, while electron donating groups (e.g.  $\text{CH}_3$ ,  $\text{OCH}_3$ ,  $\text{C}(\text{CH}_3)_3$ ) accelerate reactions.

The leaving group in  $\text{S}_{\text{N}}\text{Ar}$  reactions has been thoroughly studied throughout the chemical literature. A compilation of some of the data available [5, 6, 15, 16] shows the following trends:  $\text{F} > \text{NO}_2 > \text{SOPh} > \text{Cl} > \text{Br} \approx \text{I} > \text{OAr}, \text{OR}, \text{SR}, \text{etc.}$  Compared to conventional  $\text{S}_{\text{N}}1$  or  $\text{S}_{\text{N}}2$  reactions, this order is reversed in many cases, due to the entirely different mechanisms operating. Since the rate determining step in  $\text{S}_{\text{N}}\text{Ar}$  mechanisms is the attack of the nucleophile and not the separation of the leaving group, the explanation of this order may lie in the electron withdrawing nature of these groups or the polarizability of the carbon-leaving group bonds. Since the best leaving groups are able to stabilize the anionic charge built upon the intermediate, the energy of the first step, the rate determining one, is reduced and therefore the reaction is

avored.

Reaction conditions vary widely between investigations, but several general statements can be made concerning the conditions employed. One of the most important decisions for a  $S_NAr$  reaction is the choice of solvent [17]. Some of the requirements for the solvents are seemingly obvious: they must not react with the nucleophile or substrate and they must be solvents for both reactants and preferably the reaction products (this is especially important for polymer formation, as will be discussed later). However, the critical issue regarding solvent choice lies in the dissociating power of the solvent on the nucleophile, thus allowing much more facile substitutions to take place on the activated site. Preferred solvents are in the dipolar aprotic family of solvents. Included in this category are dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), N-methylpyrrolidone (NMP), hexamethylphosphorus triamide (HMPT) etc. These solvents readily solvate cations, thus dissociating to a large extent the salts of phenols and giving much faster nucleophilic reactions [17]. High boiling solvents are not the only acceptable solvents which can be used, as evidenced by application of another class of solvents in this family, including tetrahydrofuran (THF), acetone, methylene chloride, etc. [18]. Dissolution of the nucleophile is often the deciding factor in solvent choice, particularly when the nucleophile is the alkali metal salt of a phenol or thiophenol. The most widely utilized solvent has been DMSO; however, it, along with almost all of the solvents listed, has drawbacks, including degradation at high temperatures and difficulty

of solvent removal from product.

Solvent purification must also be carefully verified to prohibit side reactions from taking place (also especially important for polymer synthesis). Presence of water in these highly polar solvents is probably the most destructive impurity, as it can act as a nucleophile in the presence of base to hydrolyze the activated substrate. Also, any impurities which can react with either of the reactants must be avoided. Finally, any side products of the actual nucleophilic displacement must not further react with either of the reactants. This is rarely a problem, as side products are often inorganic salts.

Temperature and time of reaction are the last two reaction condition variables to be discussed in this part of the background. These parameters are generally determined by the three other factors described above. For highly reactive nucleophiles and/or activated substrates, lower temperatures and times can be used for acceptable yields, whereas higher temperatures and times must be employed for poorer nucleophiles and leaving groups.

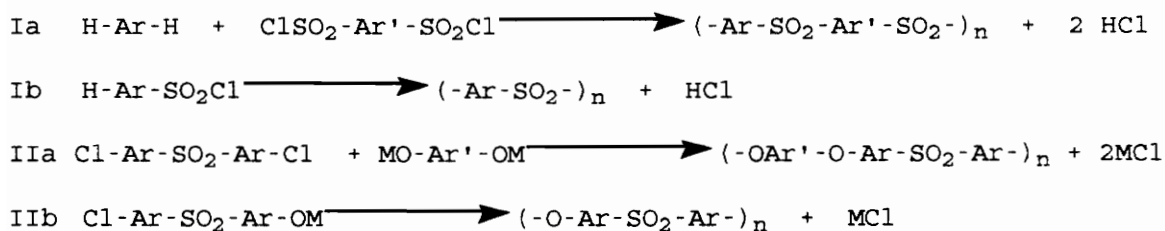
## 2.1.2 History of poly(arylene ether) sulfone and ketone synthesis

### 2.1.2.1 Poly(arylene ether sulfone)s

In the early 1960's, three industrial firms, ICI in England and Union Carbide and 3M in America [19-22], almost simultaneously developed synthetic strategies for the production of poly(arylene ether sulfone)s (PES). Although two routes existed for the formation of PES, each company was able to secure patents for their particular process. From



the discussion on the ether bond, and from the knowledge that diphenyl sulfone was stable up to 379°C, it became apparent that a polymer combining all of these predicted attractions based entirely on model compounds would be highly desirable. The two routes devised for the preparation of PES are outlined in Scheme 4. Synthetic schemes Ia and Ib were electrophilic aromatic substitution (EAS) or polysulfonylation routes and routes IIa and IIb were nucleophilic aromatic substitution (NAS) or polyetherification routes. These two methodologies differed in the manner in which bonds were formed during the polycondensation process, with the EAS route forming sulfone-aromatic carbon links and the NAS route forming ether-aromatic carbon links throughout the polymerization process, hence the names in parentheses above.



Scheme 4. Generalized routes to poly(arylene ether sulfones) [23].

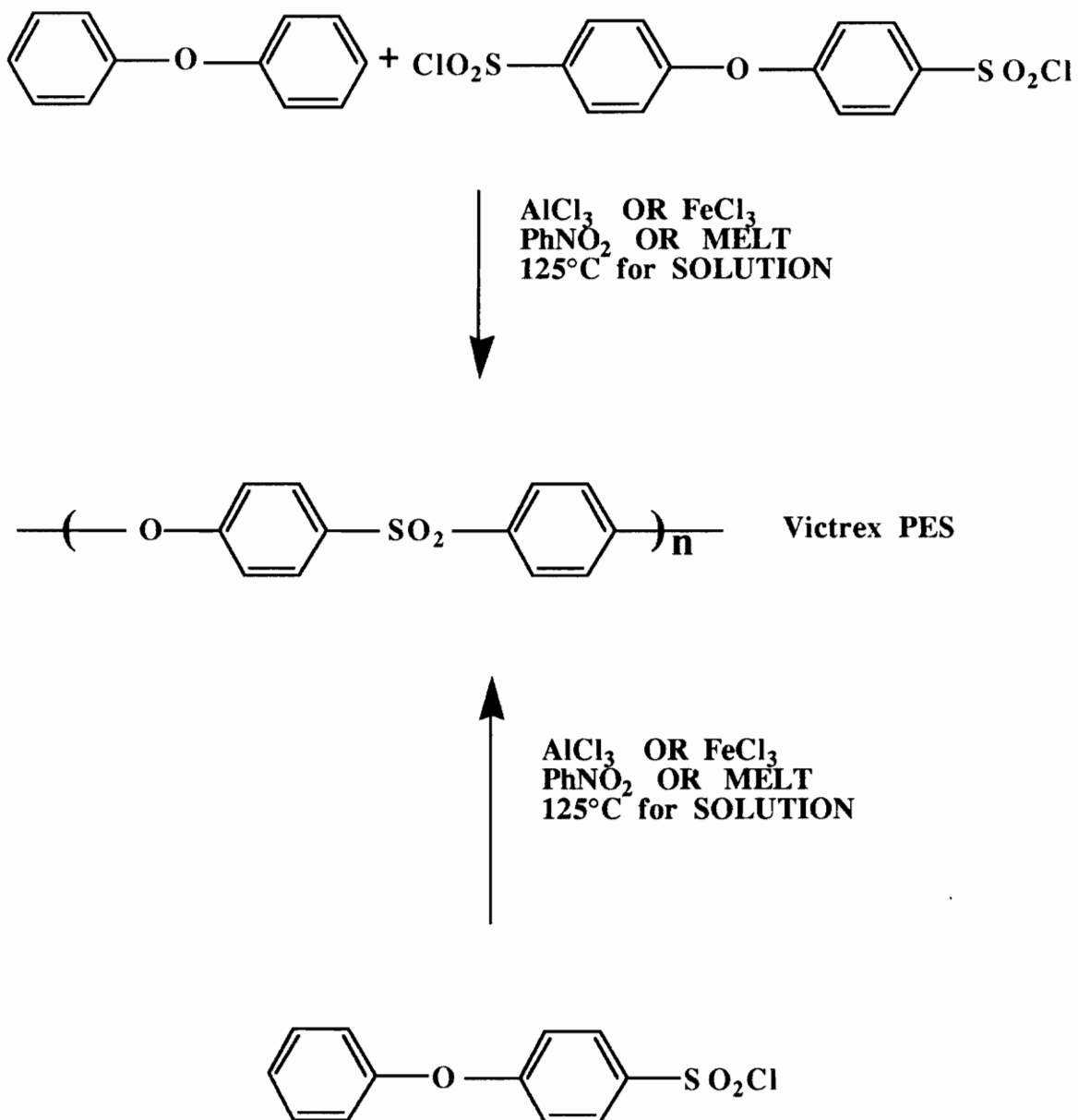
The reactions designated with (a) in Scheme 4 are AA + BB type syntheses, whereas those designated as (b) are AB polymerizations.

ICI and 3M initially developed the electrophilic process, while Union Carbide's process was based on the nucleophilic route. Eventually, 3M stopped producing their poly(arylene ether)s, and ICI developed new

nucleophilic routes to their PES due to several problems which existed with the EAS route to PES. This introduction will briefly discuss the EAS route and the problems associated with it before going on to elaborate on the NAS path to PES, as this seems to also be the order in which polysulfones were developed.

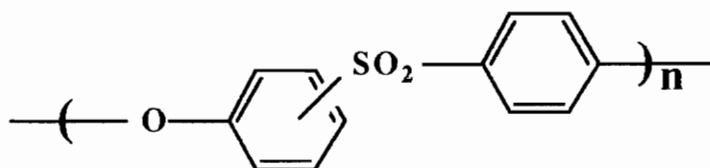
A representative synthetic route for the preparation of PES via an EAS mechanism is illustrated in Scheme 5 [24-32]. The AA-BB polymerization of diphenyl ether with bis(4-chlorosulfonylphenyl) ether in either the molten state or with conventional Friedel-Crafts catalysts in nitrobenzene at 125°C gave PES of acceptable molecular weight and therefore theoretically acceptable mechanical properties. Additionally, the AB polymerization of 4-phenoxybenzenesulfonyl chloride under the same conditions also gave acceptable viscosities. This AB polymerization was utilized for some time by ICI, and a similar reaction was applied by 3M (the difference being a slight difference in polymer composition-the 3M material, Astrel 360, had some biphenylene units along the backbone). Mechanical and electrical properties were retained up to around the 200°C range.

Although the electrophilic route looked initially promising as an alternative to the Union Carbide process, ICI soon began to discover problems with the final products. In Scheme 5, the top process was the favored route commercially because of the readily available monomers. The second process was more expensive, but was found later to give superior product. Regioisomers and slight amounts of branching were found to result in severely reduced toughness. Formation of isomers was



Scheme 5. Poly(arylene ether sulfone) via electrophilic aromatic substitution polymerization.

inherent in the EAS polymerization, as the final polymer from the top half of Scheme 5 was better represented as



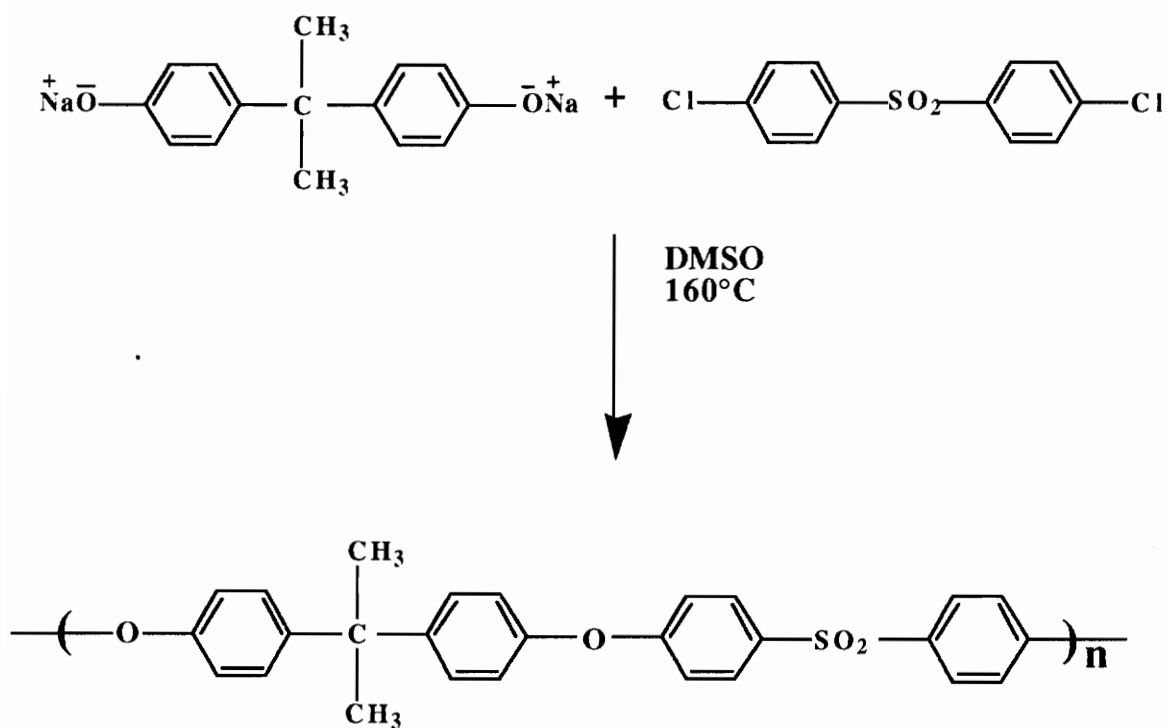
due to of the partial negative charge which could be built up *ortho* to the diphenyl ether monomer. It was later found [31] that about 20% of this type of *ortho/para* repeat unit was formed in the rest of the all *para* EAS, while the NAS mechanism, as discussed later, gave an all *para* system. The AB polymerization in Scheme 5 did give the wholly *para* polymer because the site *para* to the ether group was much more electronegative in character due to the electron withdrawing power of either the sulfone or sulfonyl chloride moiety. Therefore, results for this route to PES were comparable to the NAS. To get an idea of the economics involved with this competitive field, the last notation of the EAS route to PES in a research article was in 1974 [31].

From the discussion on EAS mechanisms leading to poly(arylene ether sulfone)s, it should be obvious that the nucleophilic aromatic substitution route would be the superior synthetic method. Indeed, it was the pioneering work by Johnson, et al. [21, 33-35], that set the standards by which all NAS polycondensations have been investigated. In 1967, Johnson et al. published their discoveries regarding poly(arylene ether)s via nucleophilic aromatic substitution polymerizations. Several

amorphous PES were prepared via this mechanism from the alkali metal salts of various aromatic bisphenols with activated dihalides (e.g., see Scheme 6).

For step-growth polycondensations to be successful in producing high molecular weight linear macromolecules, several key requirements must be met, the so-called polymer parameters. Briefly, these are high purity monomers (>99.5%), high extent of conversion (>99+%), 1:1 stoichiometry, reactive group accessibility and no side reactions. Johnson found that under the proper NAS conditions discussed in Section 2.1.1 (correct activating group, nucleophile reactivity, leaving group and reaction conditions), all of these requirements were met, and high molecular weight poly(arylene ether)s could be prepared. Sulfone groups were previously known to be acceptable activating groups, and Johnson found that indeed either chloride or fluoride leaving groups gave high polymer yields and molecular weights, due to the high electron withdrawing power of the sulfone. Aromatic phenates had also been believed to be good nucleophiles, and reaction conditions were optimized for this particular polymerization. Therefore, all conditions were proper for polymer production.

Polysulfones were successfully prepared in anhydrous DMSO at 160°C utilizing 4,4'-dichlorodiphenylsulfone (DCDPS) and alkali metal bisphenates as illustrated in Scheme 6. A crucial condition in this procedure was the preparation of the metal bisphenates. An exact 2:1 ratio of sodium hydroxide to bisphenol was required to give the bisphenate in high yields from the DMSO/chlorobenzene azeotroping



Scheme 6. Bisphenol-A based poly(arylene ether sulfone) synthetic route of Johnson, et al. [34].

system. Chlorobenzene was then removed from the reaction, and the insoluble salt of the bisphenol became soluble at 160°C in DMSO. At this point, DCDPS was added in anhydrous chlorobenzene, and polycondensation occurred rapidly with additional distillation of chlorobenzene. Utilizing this procedure, several problems became apparent, most notably the presence of excess water or base (NaOH). Upon addition of DCDPS to the reaction mixture, if any excess water or base were present, hydrolysis could take place, resulting in substitution of some of the active chloro groups by hydroxide ion giving a chain terminating hydroxyl group.

Reaction conditions were modified for some of the more rigid

polymers or deactivated bisphenols, with higher temperatures and sulfolane (tetramethylene sulfone) being used as the solvent to keep the growing chains in solution. A summary of many of the PES synthesized from DCDPS with various aromatic bisphenols by Johnson is given in Table 1.

As Table 1 illustrates, many PES were prepared from either the DMSO or sulfolane routes. All of the PES were amorphous, with the exception of the hydroquinone based PES, which was semicrystalline, showing a melting temperature around 310°C. Also, the PES based on 4,4'-sulfonyldiphenol (SDP) was synthesized in sulfolane due to the low reactivity of the deactivated bisphenate. Glass transition temperatures increased from 175°C to 245°C from the sulfide to the sulfone connecting groups. These poly(arylene ether)s were tough, rigid and in most cases soluble, with good mechanical, thermal and electrical properties. Problems inherent in this polymerization route included the necessity of the exclusion of water and the absolute 2:1 hydroxide:dihalide stoichiometric ratio needed to avoid hydrolysis of the dihalide as described above. This side reaction was found to limit molecular weight, as it was essentially a chain terminating mechanism. The kinetics of this polymerization were also investigated by Schulze and Baron [36], who found that the polycondensation followed a second order rate law.

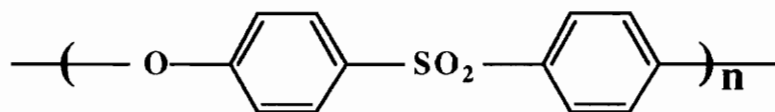
Soon after these discoveries by Johnson, et al., workers at ICI began to explore alternative routes to their problematic electrophilic aromatic substitution polycondensations [23]. Their EAS work had shown, as discussed previously, undesired side reactions which led to low

Table 1. Summary of aromatic bisphenols polymerized with DCDPS by Johnson, et al.

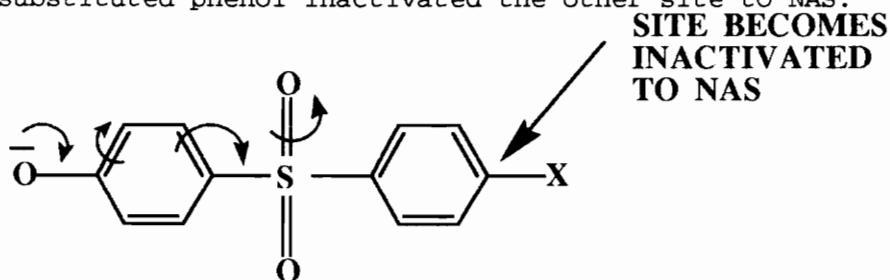
<b>BISPHENOLS</b>	<b>SOLVENT (TEMP, °C)</b>	<b>T<sub>g</sub></b>
	DMSO (160)	195
	DMSO (130)	180
	SULFOLANE (235)	210
	DMSO (165)	(T <sub>m</sub> =310) 230
	SULFOLANE (235)	245
	NOT GIVEN	200
	NOT GIVEN	230
	NOT GIVEN	205
	NOT GIVEN	205
	DMSO (160)	175
	NOT GIVEN	205
	NOT GIVEN	235
	NOT GIVEN	180

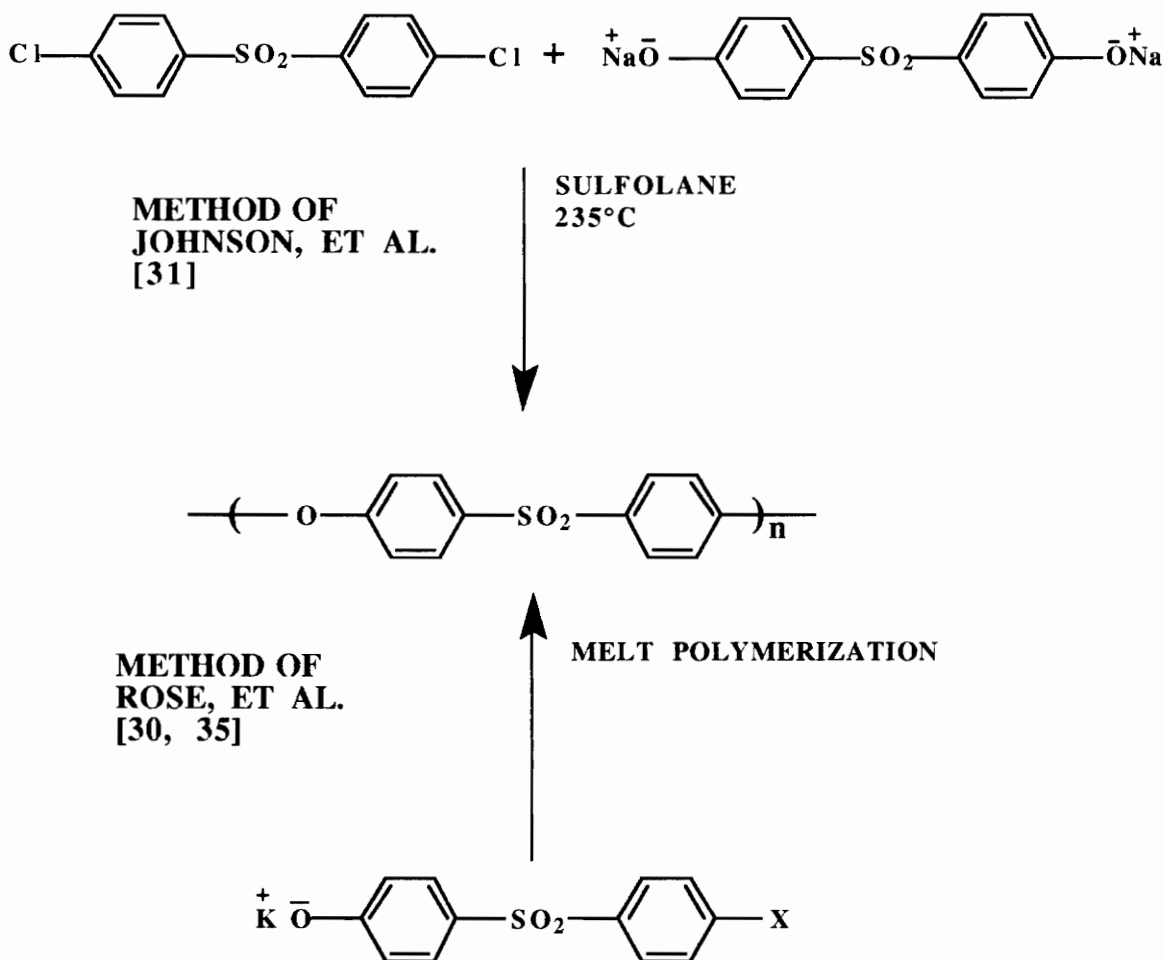


mechanical property values; therefore, investigations to apply the NAS to their advantage were undertaken. The identical polymer structure



was desired, but had already been prepared by Johnson, *et al.* by the NAS polymerization of 4,4'-sulfonyldiphenol with DCDPS, as discussed earlier (see Scheme 7). Initially, dihalides which were incorrectly activated or contained inadequate leaving groups were chosen by ICI, and therefore only low molecular weight oligomers were synthesized [25, 26]. However, once the 4-halophenyl-4'-hydroxyphenylsulfone AB type monomer was shown to be conveniently prepared by substitution of DCDPS with hydroxide ion [29, 31, 37], ICI then began a much larger investigation of PES via NAS (Scheme 7). The synthesis of this AB monomer was accomplished in DMSO utilizing excess potassium hydroxide. It was found that under the correct conditions, high yields of this monomer could be formed. The bisphenol of DCDPS was not formed at low temperature due to what was termed a "bridging effect" [29], in which once one hydroxide ion displaced a single halogen on the dihalide, the electron donating power of this substituted phenol inactivated the other site to NAS.





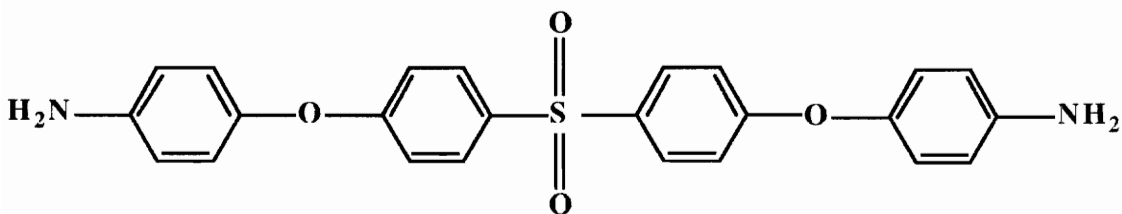
Scheme 7. Preparation of PES via routes of Johnson and Rose.

Therefore, a convenient, low cost and high yield synthesis to this important monomer had been devised. Had this monomer not been discovered, ICI would have been without the means to prepare its flagship poly(arylene ether) sulfone, Victrex. Nevertheless, melt polycondensation of the AB monomer proceeded smoothly, yielding high molecular weight PES with attractive thermal and oxidative stability, mechanical properties and resistance to hydrolysis [31]. Later, both

monomer synthesis [38] and polymer preparation in sulfolane solution [39] were investigated in more detail.

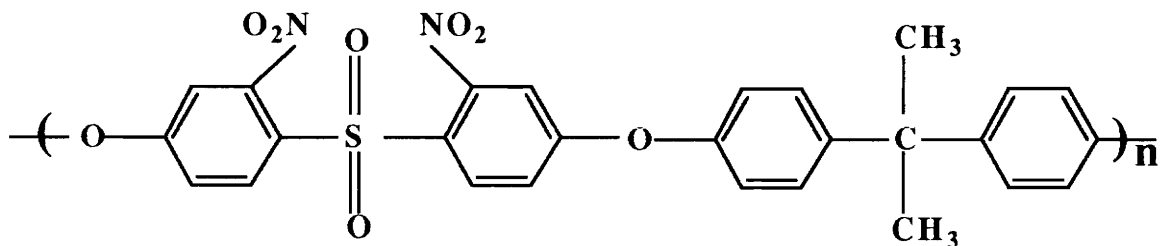
Soon after the disclosures of Johnson and Rose, new PES structures and polymerization techniques began appearing in the literature, all involving the nucleophilic aromatic substitution route. Attempts were made to synthesize higher glass transition temperature PES through the use of cardic or cyclic main chain containing bisphenols [40]. Although high molecular weights were not always obtained,  $T_g$ 's in the range of 230-300°C were observed for some of the phenolphthalein or fluorenone based PES.

Research was also underway to develop new ways to incorporate these tough polymers into other traditionally brittle systems. In 1974 [41] Brode, et al. began investigating amine terminated "polysulfones." Although claims were made for polymeric diamines for inclusion into polyimide and polyamide-imide systems, most of the data given were for the p-aminophenol adduct of DCDPS.



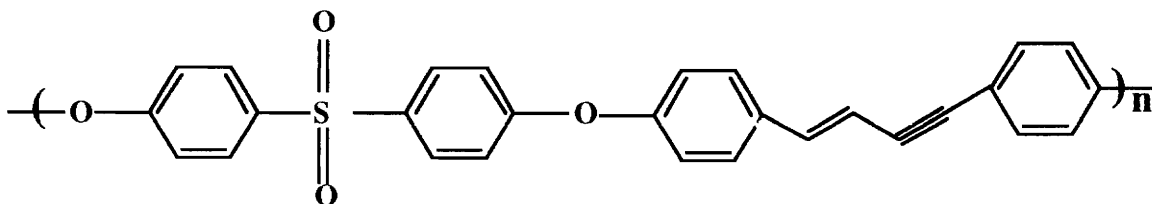
As will be discussed later, preparation of polymers of this type was more fully researched and understood for the purpose of toughening thermosetting networks. An interesting variation on this theme was nearly discovered by Imai in 1978 [42]. Poly(arylene ether sulfone)s with pendant nitro groups along the polymer chain were formed from the

reaction of nitro substituted DCDPS with Bisphenol A.



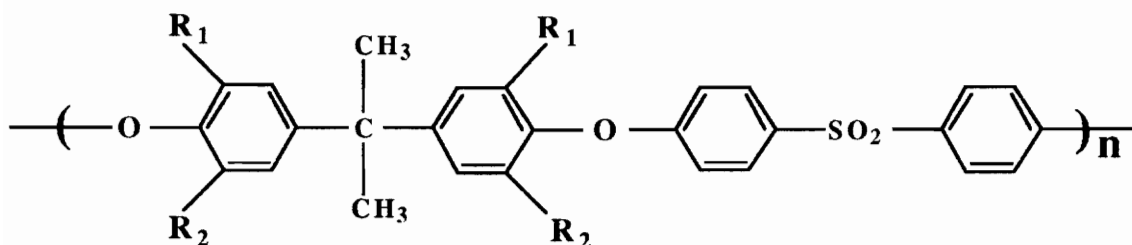
The authors never attempted to reduce these nitro side groups to give multifunctional amine pendant PES; however, at the same time these authors discovered a new polymerization process. Their technique involved the fluoride anion assisted polycondensation with potassium fluoride and dipolar aprotic solvents; unfortunately, only low molecular weights resulted.

Another novel PES which was researched in hopes of giving high thermal stability, tough thermosets was conjugated enyne main chain containing poly(arylene ether) homo- and copolymers [43]. An enyne containing diol monomer was prepared and reacted with DCDPS under the DMSO/KOH conditions to give high molecular weight polysulfones.



These materials were either thermally or photo curable, but gave very brittle networks.

New compositions were investigated in hopes of studying dynamic mechanical behavior [44]. The physical behavior aspects of poly(arylene ether)s will be covered later, but the synthesis of these novel materials will be discussed here. As illustrated in Scheme 8, several new alkyl substituted bisphenols were incorporated into PES, yielding enhanced  $T_g$ 's. Interestingly, substitution of two methyl groups onto the Udel type chain substantially increased  $T_g$ , but if only one methyl group was substituted, the  $T_g$  was decreased relative



<u>R<sub>1</sub></u>	<u>R<sub>2</sub></u>	<u>T<sub>g</sub></u>
CH <sub>3</sub>	CH <sub>3</sub>	235
CH <sub>3</sub>	H	178
Cl	H	205
CH(CH <sub>3</sub> ) <sub>2</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	175

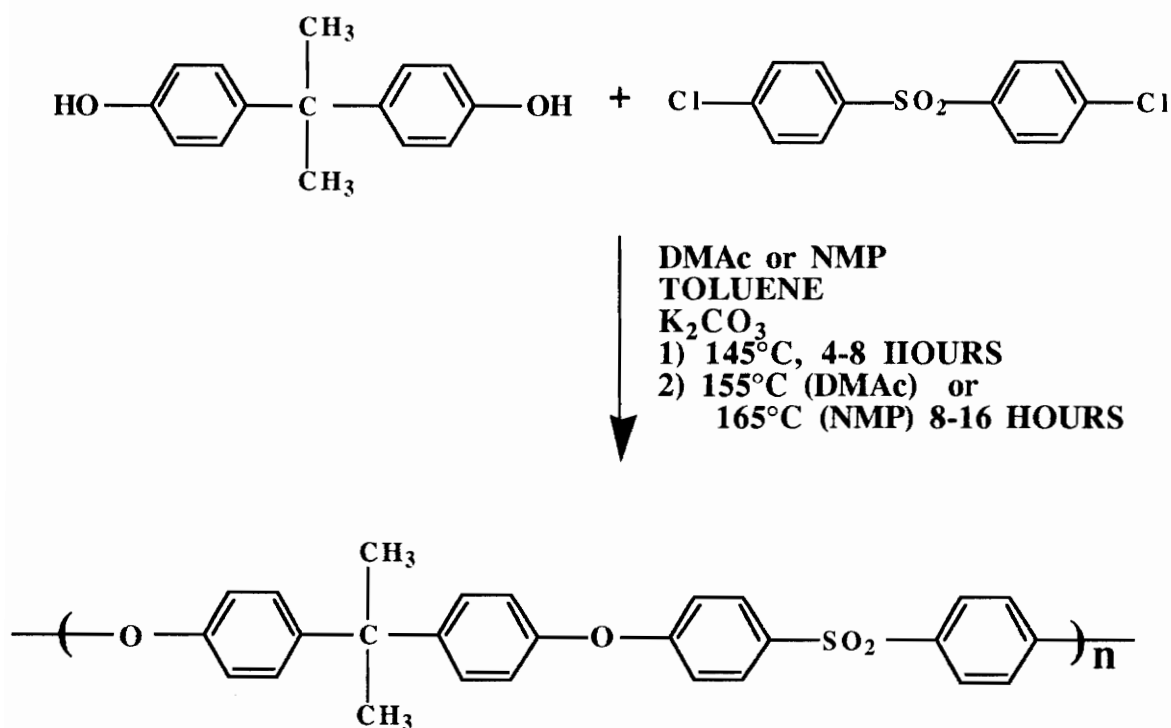
Scheme 8. Alkyl substituted Udel type PES synthesis [44].

to Udel, presumably due to loss of symmetry. Halogen substitution, even though lowering symmetry, caused an increase in  $T_g$ , while longer alkyl chains, although symmetrically substituted, gave lower  $T_g$ 's.

A new synthetic method which changed the course of NAS poly(arylene ether) synthesis was introduced in the late 1970's [45-47]. By utilizing

potassium carbonate as the weak base for phenate formation *in situ*, several disadvantages of the DMSO/KOH route were solved. These drawbacks included the necessity of absolute stoichiometry of 2 moles of KOH to 1 mole of dihalide to inhibit halide hydrolysis. Employment of potassium carbonate with dipolar aprotic solvents such as DMAC [46, 47] or NMP [45] resulted in a process which was much easier to control due to the possibility of using excess base in the polymerization. Also, all of the reagents could be charged initially in a "one-pot" synthesis (see Scheme 9). Additionally, toluene was used as an azeotroping agent, thus removing one of the byproducts from the system and driving the reaction to high conversion.

These techniques were similar to those which had been disclosed by workers at General Electric in the mid-1970's and early 1980's for the preparation of poly(arylene ether imide)s (PEI) [48-50]. Similar to the work discussed above, potassium carbonate/dipolar aprotic solvent routes proved to be successful methods for the synthesis of high molecular weight PEI's. Also, a method which has never been demonstrated in the literature for the preparation of poly(arylene ether)s was shown, that of using metal alkoxides as phenate formers, with the side products being alcohols, which were easily removed from the reaction media. Although water may have been more difficult to remove than alcohols during poly(arylene ether) synthesis, excess potassium carbonate could be utilized without hydrolysis or side reactions, whereas metal alkoxides would certainly result in nucleophilic substitution side products with the dihalides.



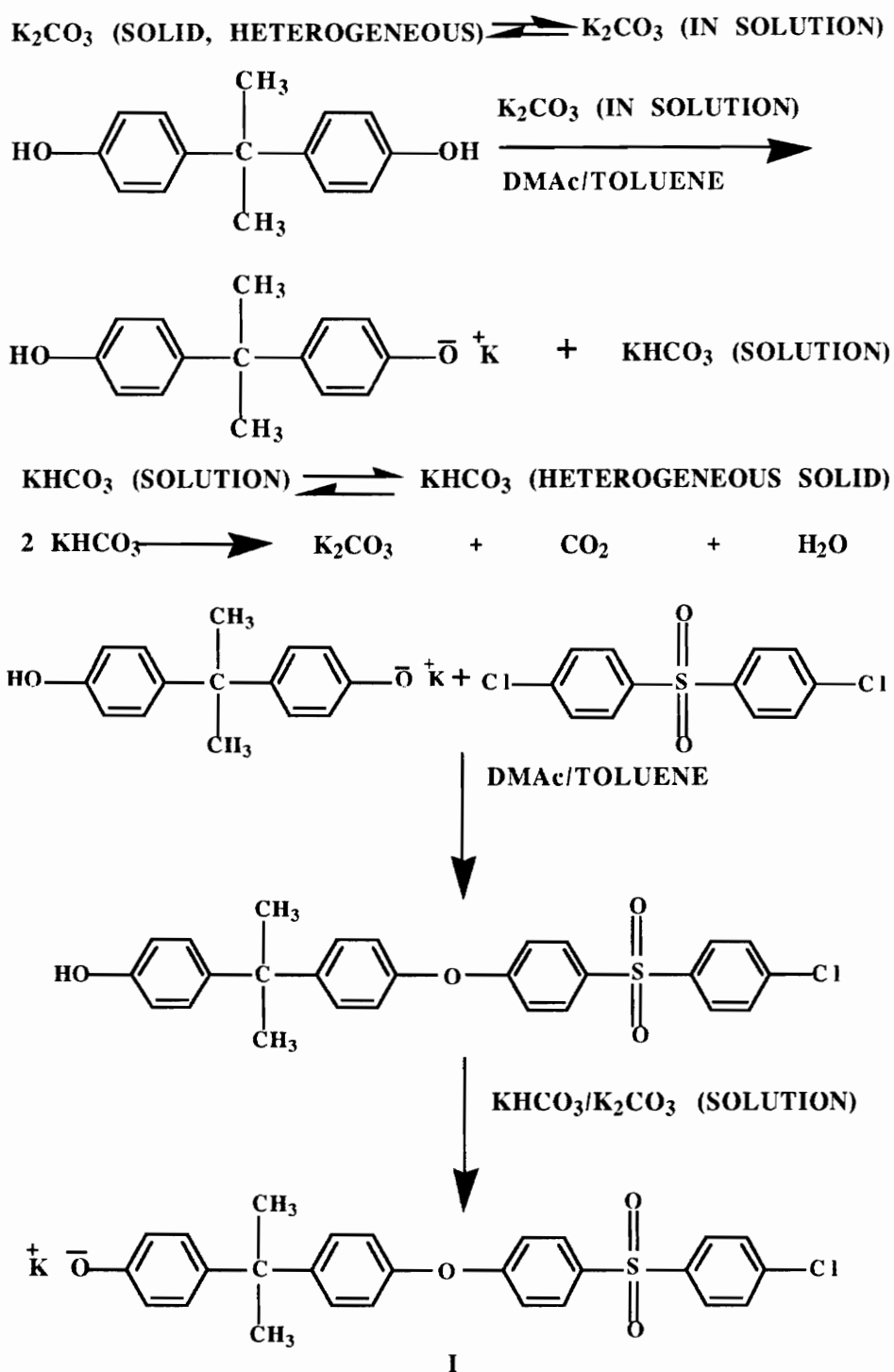
Scheme 9. Revised PES synthetic route utilizing potassium carbonate with dipolar aprotic solvents [45-47].

Copolymers were also prepared utilizing these processes [45, 46]. Semicrystalline PES were synthesized with hydroquinone/DCDPS polycondensations, however, by preparing a copolymer of biphenol/hydroquinone (50/50) with DCDPS (100), no crystallinity was observed. The DMSO route was reportedly not acceptable in this case due to insolubility of the bisphenate salts of hydroquinone or biphenol. Copolymers of this type were much more resistant to radiation (electron beam) due to the absence of aliphatic character [51-53].

Viswanathan and McGrath also studied the kinetics of Udel type PES formation using the DMAc/potassium carbonate route. The simple second

order kinetics found previously [36] were not observed by this new route. A two step reaction process, with the first step azeotroping off water around 145°C and the second driving the polycondensation to completion at 155°C was the primary reason for the different kinetic parameters. Previously, second order kinetics had been observed for polymerizations in which only DMSO and the bisphenate were present during polycondensation; however by the new synthetic method proposed by McGrath, toluene was present during phenate and polymer formation. Therefore, the ability of this DMAc/toluene cosolvent system to solubilize a bisphenate was highly unlikely, but this solvent system was able to keep both monophenates and growing phenate terminated polymer in solution. The authors then proposed a two step mechanism (Scheme 10) in which initially monophenates of the Bis A were formed, followed by attack of the dihalides by these mononucleophiles, giving the intermediate I. This intermediate then must be formed in high yields, as all of the by products from potassium hydrogen carbonate ( $\text{KHCO}_3$ ) were being removed. Thus, this AB type monomer, formed *in situ*, is the primary polymer forming reactant, which helped explain the somewhat more complicated kinetics involved with this new method. The polycondensation of I should be a slower reaction than the initial nucleophilic attack to form I, since the intermediate I will exhibit the "bridge effect" discussed earlier. Therefore the second polymer forming step of this mechanism is inhibited by this effect, explaining the complicated kinetics of this polymerization; this is the reason a second



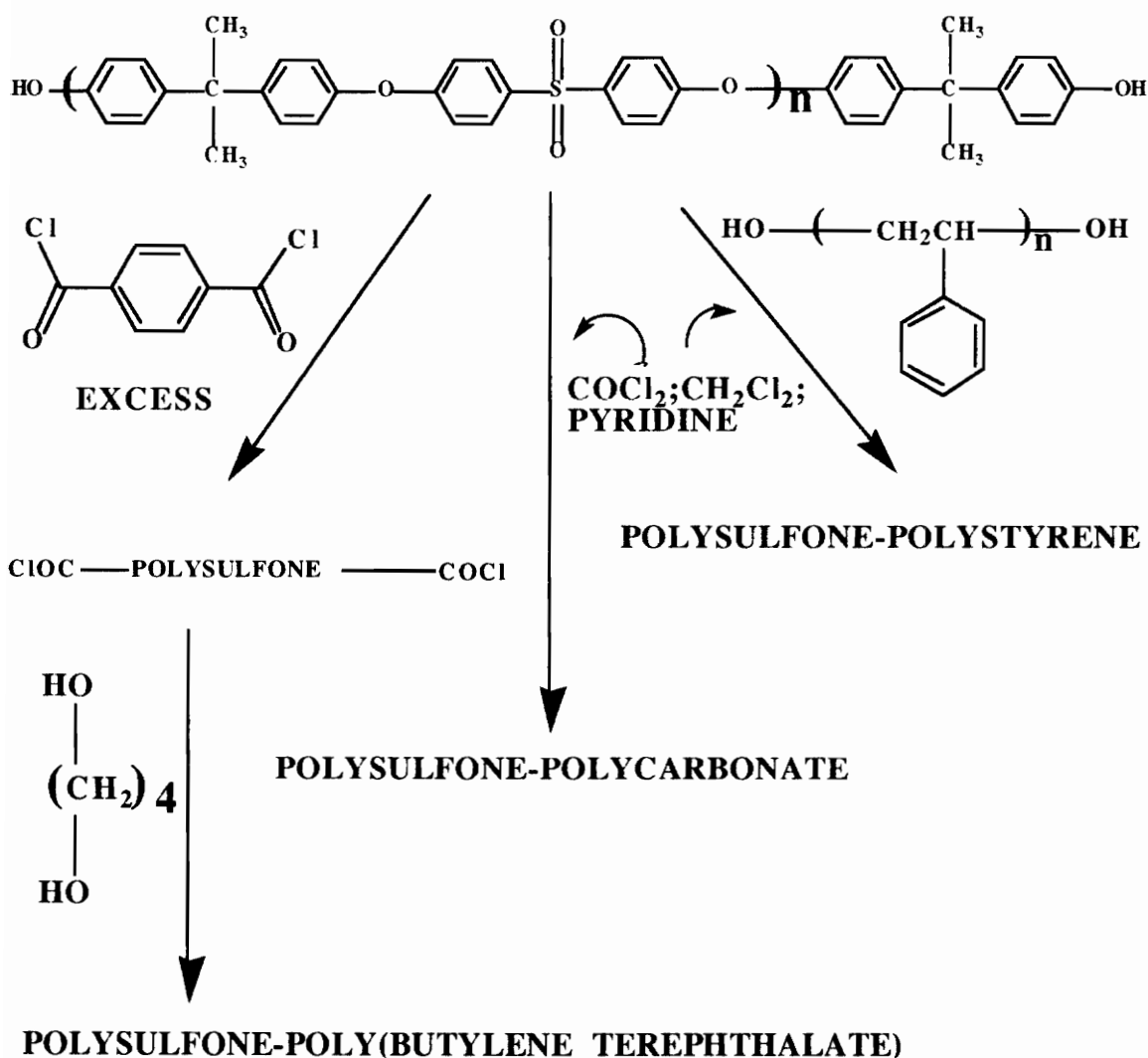


Scheme 10. Proposed mechanism of PES formation via AB type intermediate I synthesis [47].

higher temperature step is used in the polymerization. Later, others studied the kinetics of Victrex type polymer formation, but by the DMSO/NaOH route [54, 55].

Also in the late 1970's, another contribution was made to the literature which significantly affected many other future investigations, that of molecular weight and end-group control in poly(arylene ether sulfone)s [56-59]. Through the use of stoichiometric imbalances of the initial monomer ratio, a wide range of molecular weight PES oligomers could be synthesized. These oligomers could initially be either halogen or hydroxyl terminated, depending on the monomer in excess. Ratios were determined by modifications [60] of equations set forth by Carothers many years earlier [61]. Initially, these polymerizations continued to be carried out by the DMSO/NaOH route, but it was soon found that the DMAc/K<sub>2</sub>CO<sub>3</sub> process could be equally as effective [62]. In order to determine the validity of the process, both titration with alcoholic tetramethylammonium hydroxide [58] and spectroscopic [56] techniques were developed to measure the molecular weights of such materials. Therefore, a method had been established to synthesize and characterize reactive oligomers of controlled molecular weight (2000-20000 g/mol) with predetermined endgroups.

Eventually, these techniques became conventional ways to produce such desirable materials, with applications in block copolymer and toughened thermoset fields. For hydroxyl terminated PES, the option existed for producing any number of block copolymers, as summarized in



Scheme 11. Preparative methods for polysulfone block copolymers.

Scheme 11. Poly(aryl ester), polycarbonate and polystyrene block copolymers were prepared by a variety of techniques [57, 59].

Additionally, these hydroxyl functional polysulfones could be utilized in the formation of perfectly alternating polysulfone-polysiloxane copolymers [63].

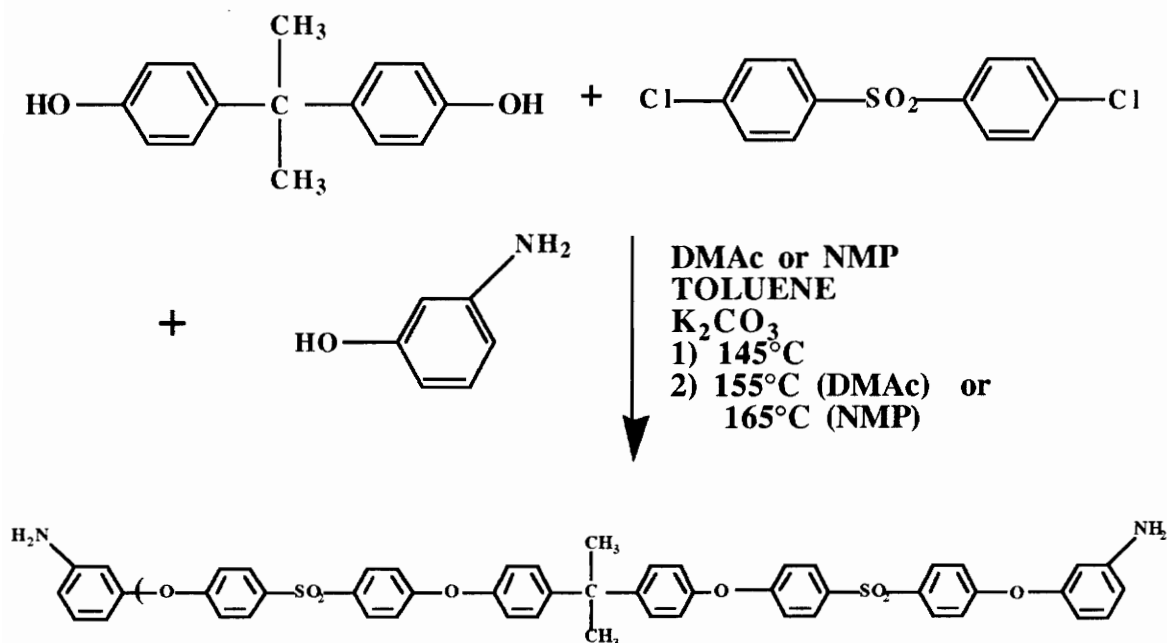
Hydroxyl terminated PES were also utilized for toughening of traditionally brittle thermosetting networks via several methods. Either

a chemically crosslinkable end-group was prepared by reaction with the hydroxyl moiety or the hydroxyl terminated PES was chemically reacted into a thermosetting network, such as an epoxy resin. For example, Hergenrother and others have published several papers dealing with the crosslinking of ethynyl terminated PES [64-69] prepared by post-reacting hydroxyl terminated PES with ethynyl containing aromatic compounds. Additionally, these hydroxyl ended oligomers were incorporated into epoxy resins [70]. Characteristics such as solvent resistance and modulus were observed to increase for these crosslinked systems.

Later, another process was discovered for the preparation of amine terminated PES of controlled molecular weight, again accomplished by modifications of the Carothers equation [71-73]. In this method, certain calculated amounts of a monofunctional end-capper, typically *m*- or *p*-aminophenol were added to the reaction mixture (see Scheme 12). Molecular weights, which were quite close to theory, could be determined via titration with hydrobromic acid in acetic acid. By this type of procedure, similar polymers to those discussed above were produced. These functional polymers could then be reacted in related methods to those for the hydroxyl terminated PES.

Examples of copolymers prepared from amine terminated PES of controlled molecular weight include polyimide-PES [74] block copolymers. These copolymers, while retaining the thermal stability characteristic of the PES blocks, also had improved solubility and therefore processability.

Thermosetting systems have perhaps taken the most advantage of the



Scheme 12. Amine terminated PES synthesis.

amine ended PES systems. These oligomers have been utilized in many studies to toughen epoxy networks, since epoxies traditionally cured with 4,4'-diaminodiphenylsulfone were inherently brittle [71]. Also, bismaleimide (BMI) thermosets are also very brittle crosslinked materials with almost no toughness; however, incorporation of these amine terminated PES (or the maleic anhydride adduct of these oligomeric diamines) into these BMI's greatly improved toughness while retaining high thermal stability [75].

Finally, as a last example to illustrate the utility of end-group and molecular weight control, the preparation of carboxylic acid terminated PES has been demonstrated [76-78]. These oligomers were utilized in liquid crystalline poly(aryl ester)-PES block copolymers.

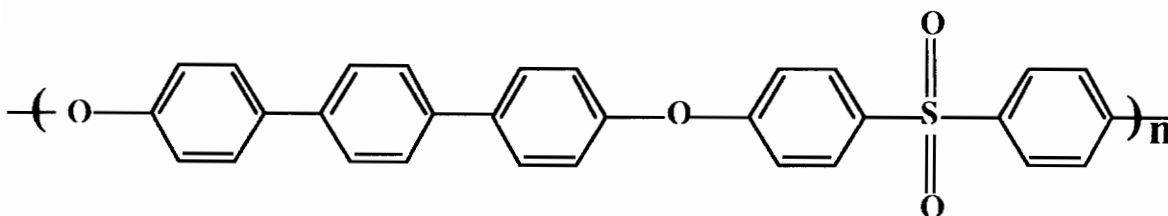
While retaining the high thermal stability and interesting morphologies of the liquid crystalline blocks, these copolymers were substantially more soluble and processable due to the presence of the polysulfone segments.

In the past several years, the focus of attention on PES has shifted to basically two areas, those of new methods for the synthesis of these poly(arylene ether)s and modifications of existing PES. Typical nucleophilic aromatic polycondensation conditions producing PES were thought unattractive by several groups of workers who sought to eliminate the dipolar aprotic solvents and/or the necessity of the removal of inorganic salts from the reaction mixture. For example, Kricheldorf [79] investigated the melt polymerization of trimethylsilyl substituted bisphenols with activated difluorides at 250-270°C. He found acceptable molecular weights were formed in the presence of potassium or cesium fluoride catalysts, with the only side product being volatile trimethylsilyl fluoride. This chemistry has recently been reviewed [80].

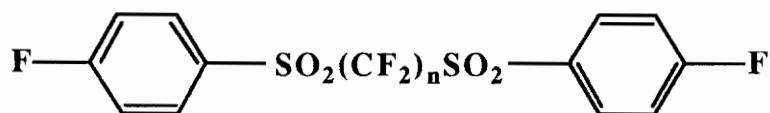
Phase transfer catalyzed NAS model reactions and polycondensations leading to substituted sulfones has been studied in recent years [81-84]. Perfluorinated benzene or biphenyl were found to give linear high molecular weight PES in the presence of  $K_2CO_3$ , a crown ether, a bisphenol and polar solvents (DMAC, acetonitrile, chlorobenzene, etc.). Another novel method for the preparation of high molecular weight PES has been through the Scholl reaction of di(1-naphthyl) aromatic ethers [85]. Finally, inorganic catalysis of the reaction between aromatic dichlorides has been utilized to produce a versatile range of PES in

DMAc at 70°C [86]. The catalysis system consisted of NiCl<sub>2</sub>/Zn/triphenyl phosphine/NaI which was easily prepared as were the linear high molecular weight poly(aryl ether)s of varying composition.

As a concluding remark on the preparation of new PES via NAS mechanisms, and a thought as to possible future pathways for research on these materials, Staniland has recently introduced a new PES based on terphenol which was semicrystalline with T<sub>g</sub>'s in the high 200°C range and T<sub>m</sub>'s above 400°C [87, 88].



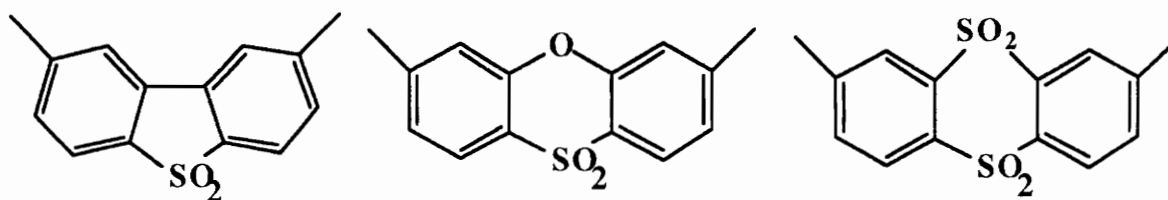
However, preparative methods for the synthesis of terphenol were very limited. Also, Feiring introduced fluorinated alkyl sulfones as electron withdrawing groups into PES, yielding high thermal stability, lower T<sub>g</sub> materials [89].



Several reviews are helpful in understanding this mass of literature pertaining to PES synthesis [28, 90, 91].

Cyclic groups containing sulfone and/or ether groups have been studied sparsely in the literature, mainly for introduction into

polyamides or other types of heterocyclic containing polymers [92-94]. Groups such as those shown in Scheme 13 have not been incorporated into poly(arylene ether) systems, although they are simply closed ring analogs of linear sulfone containing monomers. By designing proper monomers, new poly(arylene ether)s could certainly be prepared which would be thermally stable, with perhaps increased  $T_g$ 's.



Scheme 13. Proposed structures for incorporation into poly(arylene ether)s.

Although not new methods for the synthesis of PES, modifications of existing polysulfones can be an invaluable method for the preparation of novel materials. Bis-A based polysulfones have been sulfonated [95], lithiated [96] and brominated [97], while hydroquinone based PES has recently been aminated [98]. The positions of each substitution reaction and the efficiency of these modifications have been documented by the respective workers. Interesting functional groups, as well as new polymer structures could be generated by the methods listed above.

#### 2.1.2.2 Poly(arylene ether ketone)s

The field of poly(arylene ether ketone) (PEK) synthesis has



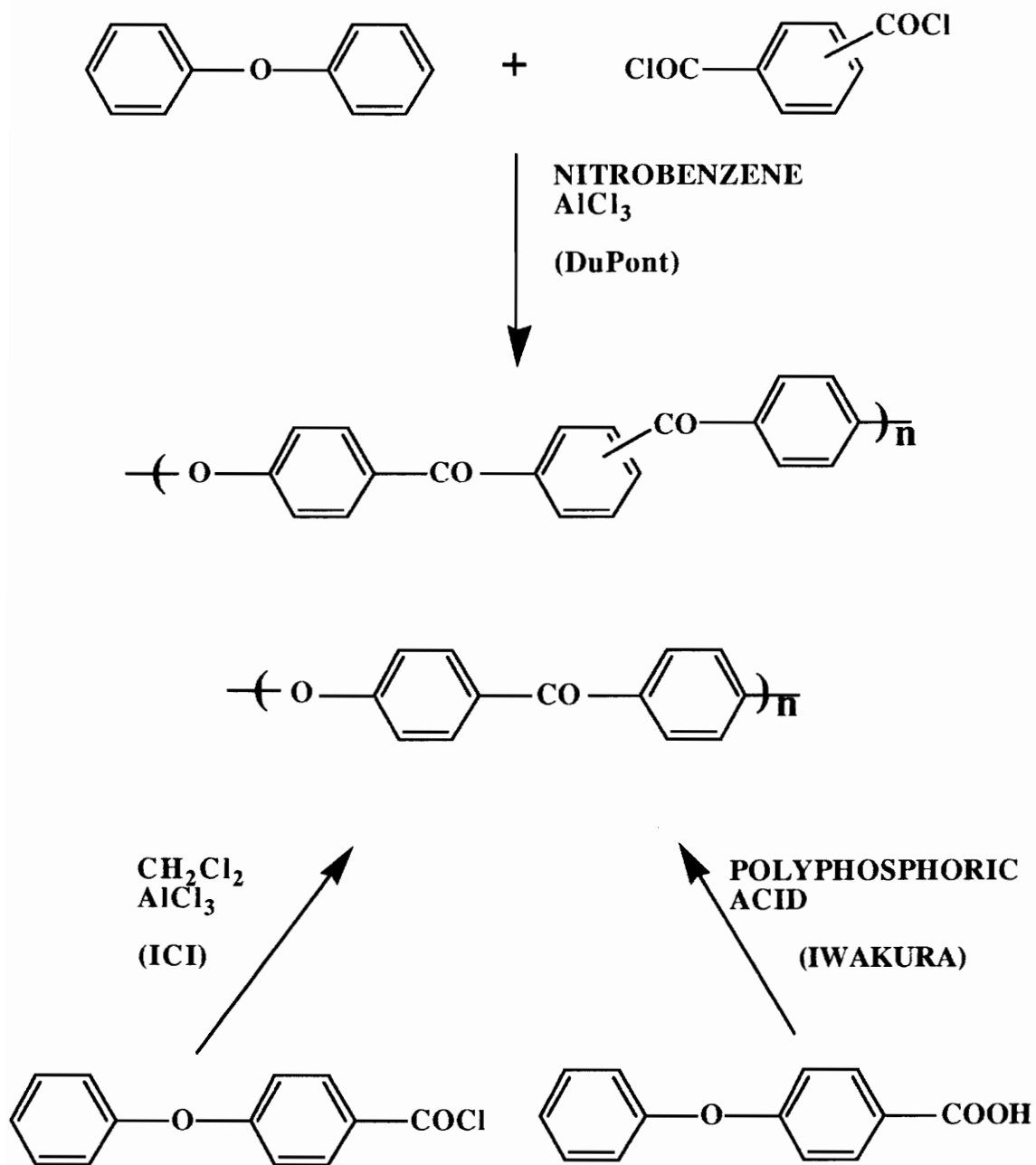
somewhat lagged behind that of PES preparative methods due primarily to the fact that most PEK's are semicrystalline and therefore difficult to prepare in solution because of premature precipitation. However, many of the above mentioned topics discussed for PES were eventually essentially identical to their respective PEK counterparts and will only be mentioned in passing.

Synthesis of PEK's can follow the identical types of processes outlined in Scheme 4, with the exception that the sulfone groups were replaced by ketones. Either EAS or NAS mechanisms can theoretically be utilized for the preparation of these engineering thermoplastics. Thus, the Friedel-Crafts type reaction becomes polyacylation or polyaroylation, while the nucleophilic displacement route remains the same except for activation by the ketone electron withdrawing group. This group of poly(arylene ether)s was first reported by Bonner at DuPont [99] by the polycondensation of simple aromatic diacid chlorides (terephthaloyl or isophthaloyl) with diphenyl ether in nitrobenzene catalyzed by aluminum chloride. Utilizing the same catalyst, but methylene chloride as solvent, ICI followed this announcement with the homopolyacylation of 4-phenoxybenzoylchloride [100]. The other early work involving the preparation of all aromatic PEK's was performed by Iwakura [101], who prepared the same polymer as ICI, but by the homopolymerization of 4-phenoxybenzoic acid utilizing polyphosphoric acid as both solvent and catalyst. All three of these procedures (Scheme 14) had one major disadvantage which greatly limited the usefulness of the final products, that of polymer precipitation. This was also

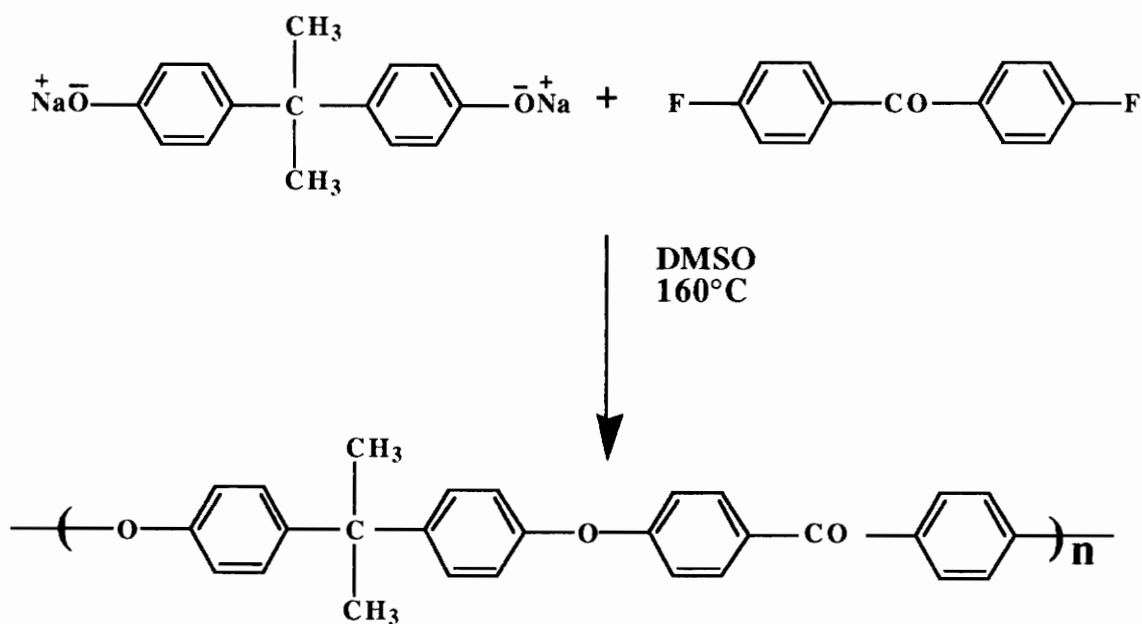
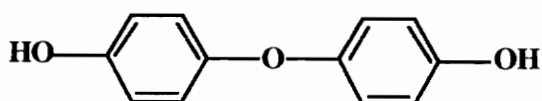
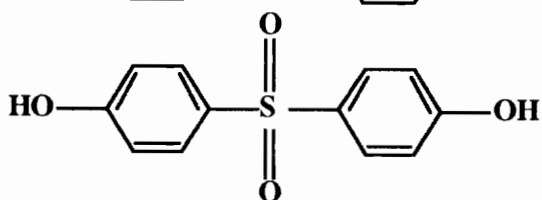
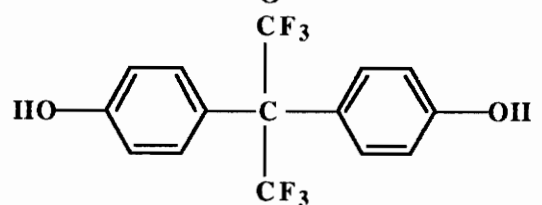
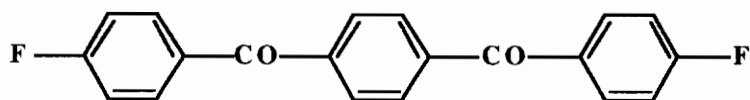
actually the downfall of the early attempts at all aromatic PEK's by NAS by Farnham and Johnson [34, 102].

Although successful in NAS polycondensations yielding amorphous PES, or even slightly semicrystalline PES with sulfolane as solvent, attempts at all aromatic semicrystalline PEK materials yielded only low molecular weight products, similar to the results from the EAS routes. Low reactivity of the 4,4'-dihydroxybenzophenone did not accelerate the formation of this PEK. Amorphous PEK's with extra ether or aliphatic spacers along the backbone were prepared in a very similar manner to the PES as illustrated in Scheme 15. Also, Radlmann [103] synthesized amorphous PEK's via nitro displacement polycondensation of 4,4'-dinitrobenzophenone with alkali metal salts of bisphenols.

Amorphous PEK's have been studied in many of the same areas of their PES counterparts. Similar to the PES prepared in Table 1 and Scheme 8, aliphatic substituted bisphenols were utilized in the synthesis of amorphous soluble PEK's as illustrated in Scheme 15 [104, 105]. Ultraviolet radiation initiated crosslinking of these materials through radical formation at either the carbonyl carbon or aliphatic carbon was observed for only PEK systems. Additionally, controlled molecular weight, controlled functionality amorphous PEK's were prepared by methods completely analogous to the PES routes. For example, carboxy [106] and amine ended [107, 108] PEK's have been reported. The amine terminal PEK's were further reacted with maleic anhydride to give maleimide end-groups, which were valuable in post-curing processes with bismaleimides [108].



Scheme 14. Early EAS mechanism polyacylations yielding aromatic PEK's.

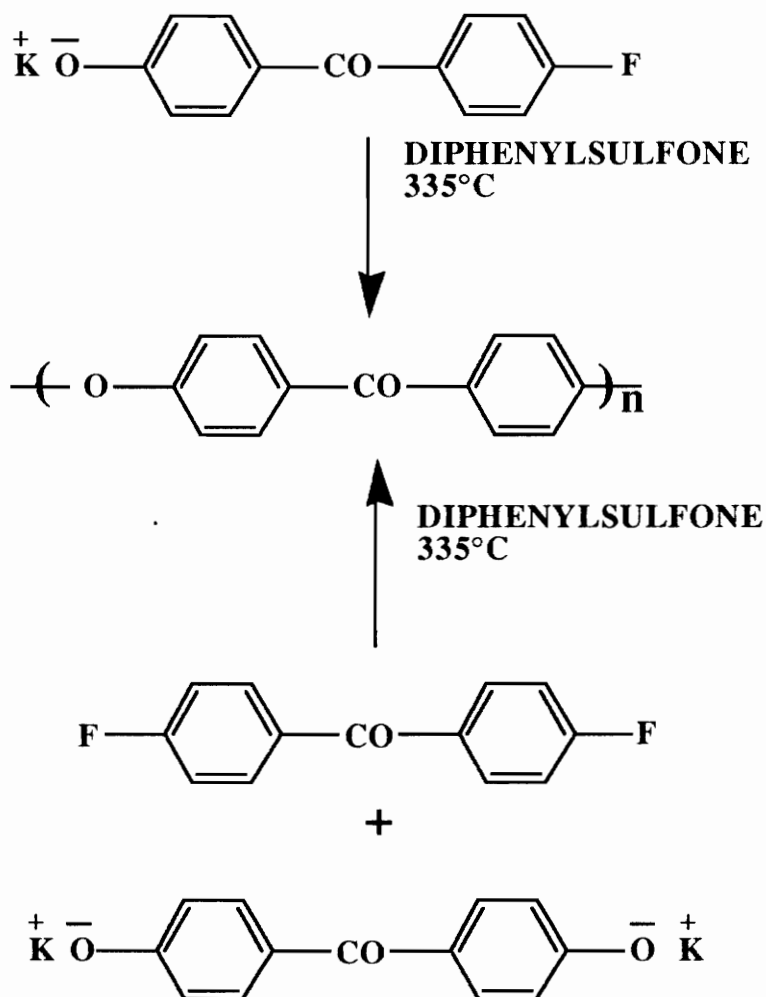
**BISPHENOL****T<sub>g</sub>, (°C)****Bis A****155****150****205****175****Bis A +****165**

Scheme 15. Amorphous PEK's prepared by Johnson in DMSO.

Later, both DuPont [109] and Raychem [110] workers found processes which could be run at room temperature for the polyacylations illustrated in Scheme 14. Utilizing hydrofluoric acid as a carbonyl protonating solvent and molar amounts of boron trifluoride as catalyst, high molecular weight structures were developed. However, owing to the extremely corrosive nature of the solvent/catalyst systems, along with the fact that a suitable nucleophilic route was soon discovered, these processes were discontinued in the 1970's.

The breakthrough in semicrystalline all aromatic PEK's came in the mid to late 1970's when ICI patented a process utilizing diphenylsulfone as a very high boiling dipolar aprotic solvent for the NAS polycondensations [111]. By carrying out homo- or copolymerizations (Scheme 16) in this solvent at 290-335°C, high molecular weight tough semicrystalline solvent resistant linear polymers were prepared with little or no degradation of the solvent [112, 113]. Kinetic studies of the AABB route using preformed salts of the bisphenol showed excellent agreement with second order kinetics. [114]. Commercial success was not accomplished by this route, however, since neither the AB monomer nor the carbonyl containing bisphenol were easily prepared or purified.

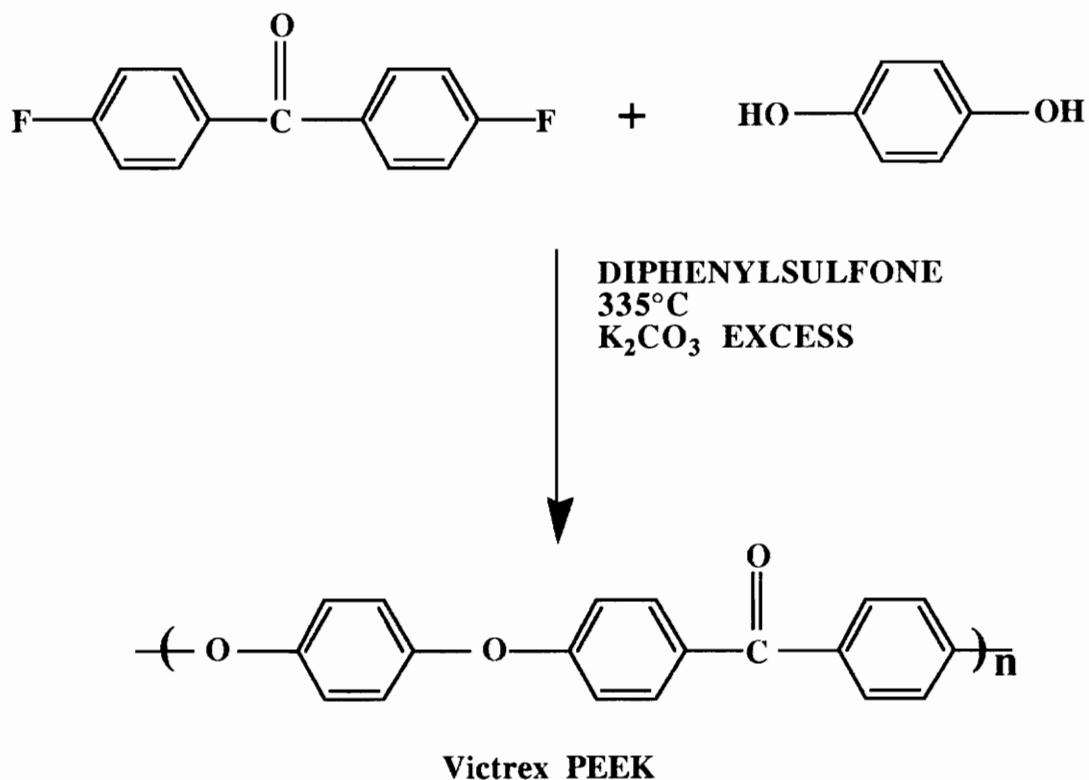
Soon, the application of potassium carbonate as discussed previously for PES was realized, and a new polymer, poly(arylene ether ether ketone) Victrex PEEK, was created [115]. By polymerizing hydroquinone with 4,4'-difluorobenzophenone (DFB) in the presence of excess potassium carbonate and utilizing diphenylsulfone as solvent at 335°C, high molecular weight linear macromolecules were developed



Scheme 16. Preparation of all aromatic semicrystalline PEK's by NAS.

(Scheme 17) with many desirable properties [116].

Kinetic investigations of this route have not been carried out as it was for the preparation of PES via the potassium carbonate/DMAC route. However, by the initial preparation of the disodium or potassium salt of hydroquinone in diphenylsulfone, model reactions investigated by ICI [117] showed approximate second order kinetics, with deviations explained in terms of phenolate association effects. The glass transition temperature of PEEK was somewhat low at 145°C, but



Scheme 17. PEEK synthesis via potassium carbonate/diphenylsulfone route.

the crystalline melting transition occurred around 345°C. These materials possessed good thermal, chemical, flame and radiation resistance. Several reviews were helpful in summarizing much of the work which has been performed in this field [91, 118, 119].

In the 10 years which have passed since the discovery of PEEK, the primary advancements which have been made in the field were new synthetic methods and modifications of the final polymer itself. Efforts to reduce the high reaction temperature and/or increase the low T<sub>g</sub> of PEEK have been the principle areas of research in this field. At least three different types of approaches have been taken to alleviate these

problems. These methods include new polycondensation processes, copolymerization techniques, thermal physical or solution blending procedures and chemical modification of PEEK.

As with the synthesis of PES, Kricheldorf developed a method for the polymerization of silylated bisphenols with several isomeric difluorobenzophenones in the melt with the volatile trimethylsilyl fluoride as the side product [120-123]. The electrophilic routes to aromatic PEK's have been reinvestigated in phosphorus pentoxide/methanesulfonic acid mixtures [124, 125] and in trifluoromethanesulfonic acid alone [126]. Also reported has been the use of N-cyclohexyl-2-pyrrolidone (CHP) as a very efficient solvent for the preparation of PEEK at 290°C in one hour; moreover, this solvent reportedly gave high molecular weight poly(phenylene ketone sulfide) from the reaction of DFB with sodium sulfide in CHP at 290°C for 30 minutes [127]. Finally, similar to PES formation by nickel-catalyzed coupling of aromatic chlorides, Ueda investigated the synthesis of amorphous PEK by this route; however, since the requirement of solubility in DMAC at 80°C was required, no crystalline PEK's could be prepared [128].

Copolymerization techniques were employed by two different groups [129, 130] who prepared PEEK-PES copolymeric materials, in which sulfone and ketone moieties were randomly or statistically dispersed throughout the polymer backbone. These procedures utilized the nucleophilic aromatic substitution polycondensation method developed by Johnson, et al. [34], which had been modified by both Attwood, et al.



[113] and Mohanty, et al. [45]. Basically, the procedure involved copolymerizing hydroquinone with varying ratios of 4,4'-dichlorodiphenylsulfone (DCDPS) to 4,4'-difluorobenzophenone (DFB) in the presence of a weak base, potassium carbonate, and a very high boiling solvent, either sulpholane or diphenylsulfone, used to keep the growing semicrystalline chains in solution. Research in this area showed that as the ratio of DCDPS:DFB increased, the solubility and  $T_g$  increased while the  $T_m$ , if any, decreased relative to pure PEEK. More recently [131], investigators have found that the incorporation of polydimethylsiloxane segments into the PEEK chain decreased the  $T_m$  of the resulting copolymer while giving a microphase separated material, but solubility was not enhanced due to the striking differences in the polarities of siloxane and PEEK.

In the past two to three years, much effort has been put forward to combine the favorable qualities of two different high performance polymers by preparing polymer blends. Included in these compositions are PEK/PEK [132, 133], PEK/polyetherimide (PEI) [134, 135], polybenzimidazole/PI [136-139], and PEK/PES [140, 141] combinations. While the scientific meanings of miscible and compatible blends are not always clear in the literature, the usual definition of miscible polymer blends is to consider them as molecular level mixed systems which therefore show a single  $T_g$  calculable from the Fox equation. On the other hand, compatible blends are products from mixing polymers of similar structure which are not macrophase separated and give tough coherent films from solution or melt, but show two  $T_g$ 's.

PEEK/engineering thermoplastic (ETP) blends have been found to be miscible when the ETP component is 27-57 % ketone content PEK or for certain polyimides, but compatible when the other component is PES. Variations on this theme include miscible blends of phenolphthalein based PEK with PES [142] and miscible sulfonated PEEK with PEI [143]. Miscible blends of PEEK had  $T_g$ 's which could be controlled by the amount of the other component (PEI or PEK) added, while compatible blends exhibited higher modulus after the  $T_g$  of the PEEK phase during mechanical testing.

Chemical modification of the monomers used to synthesize PEEK or of PEEK itself by protection or modification has been investigated by several groups in hopes of finding methods for synthesizing PEEK type precursors with milder conditions, and later removing the modifiers giving the desired semicrystalline PEEK materials. These procedures include the use of t-butylhydroquinone [144-146], acetal protected [147] and ketimine protected [148-152] DFB monomers. An interesting alteration on these procedures was the sulfonation of PEEK in concentrated sulfuric acid [153-155] which gave amorphous material with higher  $T_g$  that was later [143] found to be miscible with PEI and a poly(amide imide). Additionally, by the combination of several of the methods discussed thus far, Mohanty, et al. found a novel method for crosslinking PEK materials [156, 157]. Amine terminated PEK's could be crosslinked from the ketimine or Schiff base reaction between the in chain ketone groups and the terminal amine groups, yielding relatively tough, solvent resistant networks.

### 2.1.3 Other Advancements in Poly(arylene ether) Synthesis

When Johnson *et al.* discovered successful polymerizations of dihalides activated by sulfone and ketone moieties [34], they realized other groups were appropriate for this type of process. Such groups as azo, sulfoxide and oxadiazole properly activated aromatic rings to nucleophilic displacement under the correct conditions and with fluoride leaving groups. Table 2 summarizes this work.

In 1977 Hashimoto *et al.* discovered a new activating group for NAS polymerizations, the phenyl phosphine oxide moiety [158]. Also shown in Table 2, this group is much bulkier than other groups available for these types of monomers. Additionally, the availability of a new, perhaps more thermally stable material had been exposed, although high molecular weight was not accomplished. This procedure will be expanded upon later in the section dealing with phosphorus containing engineering thermoplastics.

Aryl cyano groups were found to sufficiently activate chloro or fluoro groups to aromatic displacement by the alkali metal salts of bisphenols in NMP [45]. As shown in Table 2, very fast polycondensations resulted in linear high molecular weight materials with lower  $T_g$ 's than their polysulfone counterparts probably due to the ortho substitution required for acceptable activation.

Finally, several heterocyclic containing activated dihalides and bisphenols have recently been reported from several workers in the field to undergo NAS polymerizations [159]. As illustrated in Tables 2 and 3,

these heterocyclic moieties include imides [50], phenylquinoxalines [160-166], imidazoles [167, 168], 1,3,4-oxadiazoles and 1,2,4-triazoles [169], benzoxazoles [161, 162, 170, 171], pyrazoles [172] and pyridine [173]. Except for the phosphorus containing dihalide, all of the dihalides or bisphenols illustrated in Tables 2 and 3 gave high molecular weight linear poly(arylene ether)s via either the NMP or DMAC routes with potassium carbonate. These groups were attractive as electron withdrawing moieties or bisphenol links due to their known high thermal stability and chemical resistance in other polymeric systems.

#### 2.1.4 Characteristics of Poly(arylene ether)s

This section will briefly cover some of the more common features of the poly(arylene ether)s, and then expand on some of the literature regarding the unique properties of this set of polymers. Generally, poly(arylene ether)s have been known as a tough, rigid, thermo-oxidatively stable family of macromolecules in the engineering plastics field [174]. This field of polymers offers chemical resistance, good mechanical and electrical properties, and processability above the glass transition temperature or melting temperature [28, 90, 175-178]. Certain characteristics differ between PEK and PES materials, since most PEK's have been found to be semicrystalline. Thus, PEK's are usually more chemically and solvent resistant than PES, but are also more difficult to process.

Impact resistance of polymeric materials has long been of interest for many commercial applications. Basically, in order for a material to

Table 2. Various other activated dihalides utilized in the synthesis of poly(arylene ether)s

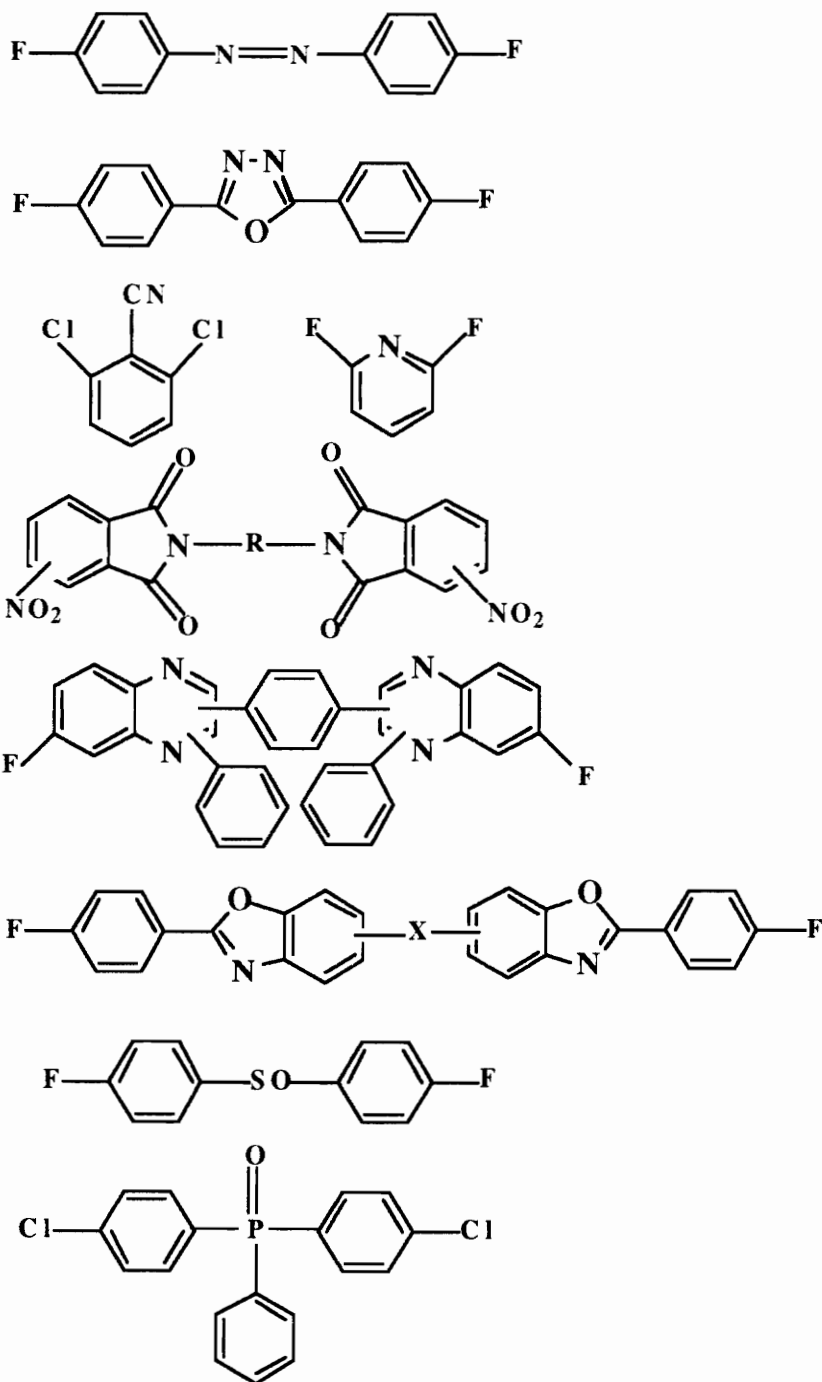
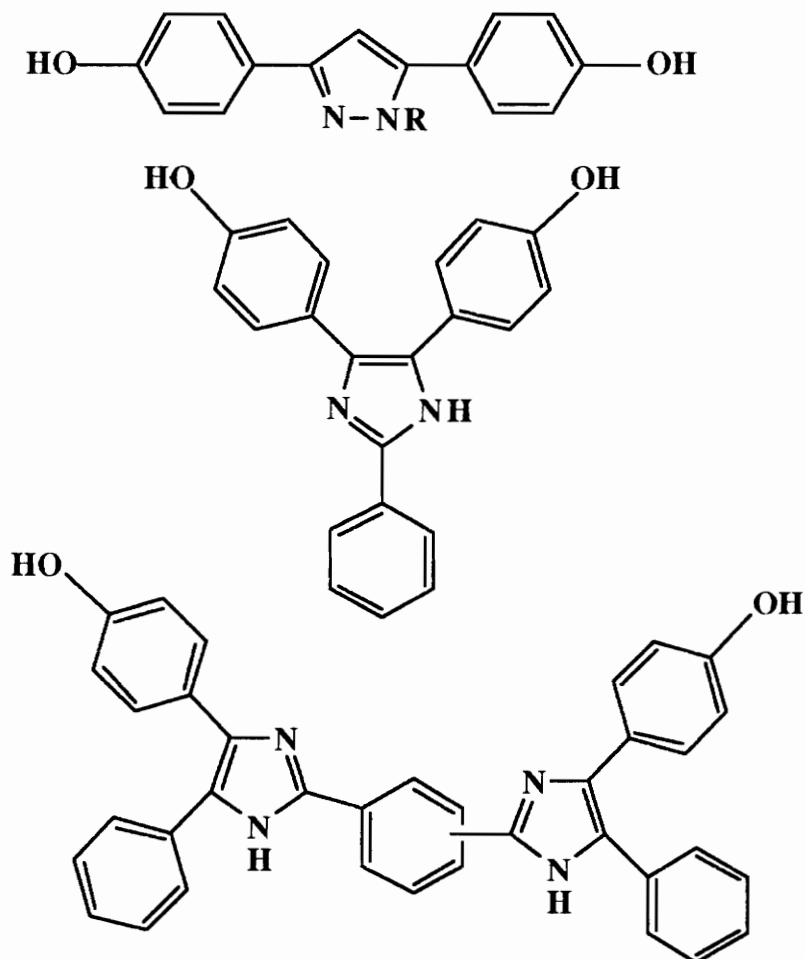


Table 3. Various bisphenols utilized for the preparation of poly(arylene ether)s



possess impact resistance, it must have some type of mechanism available to it for the dissipation of the energy of impact at a specified temperature. Heijboer noted in 1968 [179] that impact strength could be dependent on main chain secondary motions occurring at temperatures much below  $T_g$ . Side chain motions had no effect upon impact strength. Because secondary motions within the chain must also contribute to large scale

cooperative motions at  $T_g$ , any large deformation of chains will occur more easily if a mechanism along the chain can distribute the energy of deformation. For poly(arylene ether)s, a major secondary relaxation around  $-80^\circ\text{C}$  had been observed for many years and was quite a mystery until the mid-1980's. This controversial area has been reviewed [180] and has now been clarified by Dumais et al. [181]. The molecular basis for the secondary relaxations in poly(arylene ether)s was found to be due to  $180^\circ$  ring flips around the aryl ether bond, undoubtedly related to the low barrier to rotation of ethers discussed at the beginning of this introduction.

Finally, some studies as to the effect of molecular weight on poly(arylene ether) properties have appeared [182] and showed typical behavior for amorphous linear polymers, as illustrated in Figure 1. A number of mechanical properties have correlated well with this type of curve, with region I at less than 20,000 g/mol, region II at 20,000 - 30,000 g/mol and region III at greater than 30,000 g/mol. In region I, undesirably low mechanical properties were observed due to the lack of chain entanglements at this low molecular weight. In region II, entanglements are just beginning to occur, with acceptable values for tensile properties, while region III shows only a slight increase in properties with large increases in molecular weight. Therefore, it is not always advantageous to prepare polymers of very high molecular weights to obtain acceptable properties; in fact, molecular weights which are too high can often result in undesired difficulties in processing materials. The control of molecular weight as discussed

earlier in this introduction is therefore of prime concern with many engineering polymers. Appendix 1 will elaborate on the theoretical calculation and control of molecular weight of poly(arylene ether)s which can be applied to other linear step-growth polymers.

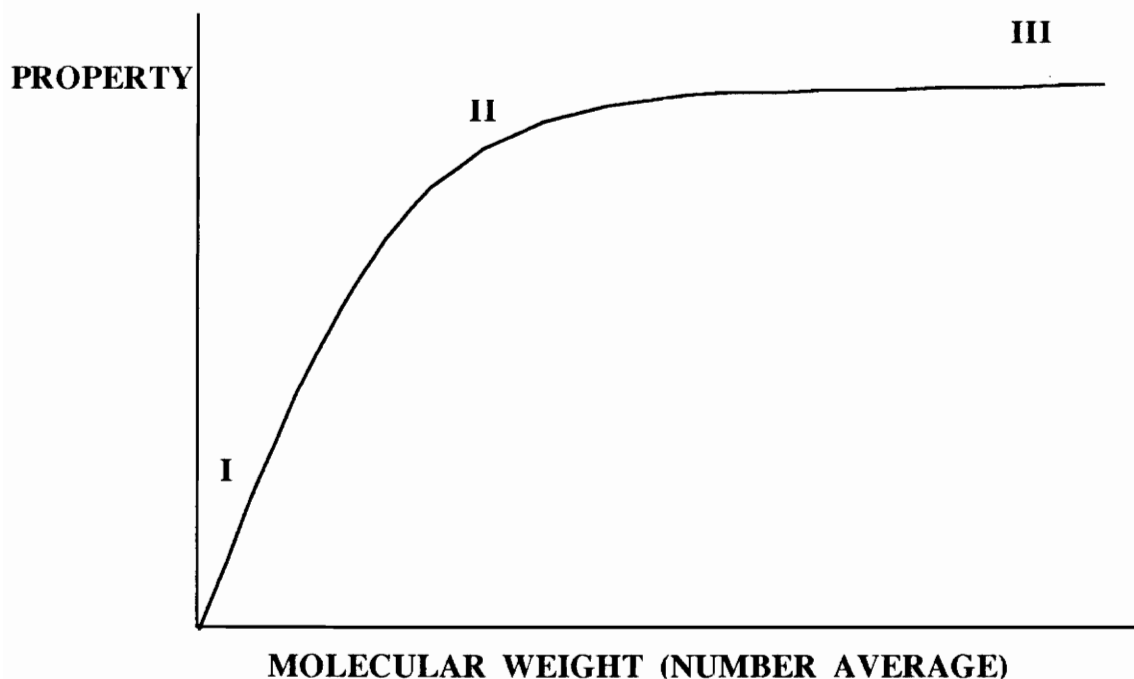


Figure 1. General property versus number average molecular weight for linear step-growth polymers [60].

## 2.2 PHOSPHORUS CONTAINING ENGINEERING THERMOPLASTICS

### 2.2.1 Terminology of Phosphorus Linked Polymers

The utilization of phosphorus into otherwise all organic polymers has been of interest to polymer scientists for many years due to some of the similarities between the carbon and phosphorus atoms (preferred coordination number of 4, electronegativity similar), while imparting



several other important properties, most namely fire-resistance [183]. Therefore, chemically linked incorporation of phosphorus into organic polymers does not drastically change most of the general features of the macromolecules. Several forms of organophosphorus links have been available to the chemist for incorporation into polymers, but the history of phosphorus containing polymers is relatively short and only sparse references to engineering polymers containing phosphorus can be found. The purpose of this introduction is first to introduce briefly the terminology of organophosphorus compounds, and then critically survey the available literature on phosphorus containing engineering polymers.

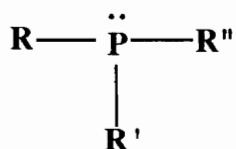
Table 4 illustrates the most common forms of organophosphorus compounds useful to the polymer scientist. From phosphorus in its lowest state of oxidation, the phosphine, to its highest state of oxidation, the phosphate, all of these types of molecules have eventually found ways into the polymer literature. As should be obvious, those polymers with phosphorus in its low states of oxidation (lone pair of electrons on phosphorus) have been found to be more prone to oxidation, as are the low molecular weight monomeric analogues. Not included in this set of molecules are the phosphorus-nitrogen polymers, since these types of macromolecules, such as the polyphosphazenes, were not concentrated upon in this work. Of more interest were those polymers containing phosphorus carbon bonds along the backbone. From Table 4, this would include all of the types of organophosphorus compounds except the phosphites and phosphates; however, description of these types of polymers with carbon-

oxygen-phosphorus bonds along the backbone will be briefly described in order to compare properties with those with phosphorus-carbon bonds along the backbone. Typically, phosphorus-carbon main chain bond containing polymers have been more hydrolytically stable materials, similar to the poly(arylene ether)s, while the phosphorus-oxygen bonds can be hydrolyzed by water, similar to polyesters.

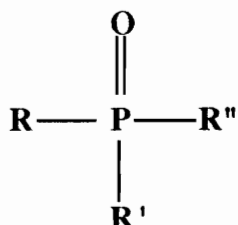
#### 2.2.1.2 Critical Survey of Phosphorus Containing Engineering Thermoplastics Literature

Many polymerization mechanisms have been found not suitable for the incorporation of phosphorus, mostly due to undesired side reactions which severely limit molecular weight of these materials. Included in these unsuccessful efforts have been chain polymerizations of phosphorus containing unsaturated organic compounds [184, 185] and step polymerizations involving formation of phosphorus-oxygen or phosphorus-carbon bonds [186]. Since these very comprehensive reviews nearly twenty-five years ago, high molecular weight linear phosphorus containing polymers from step- or chain-growth mechanisms have been difficult to locate. Those polycondensations forming phosphorus-oxygen bonds have been plagued by hydrolysis problems. An example of polyphosphonate synthesis is illustrated in Scheme 18. Although many techniques have been utilized for the preparation of these potentially important materials, the recurring problem has been the limits on useful molecular weights obtainable. Whether these reactions were run using melt [187], interfacial [188], solution [187, 189] or phase transfer

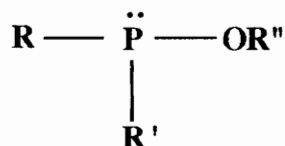
Table 4. Types of organophosphorus moieties.



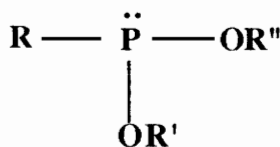
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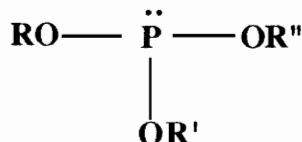
PHOSPHINE OXIDE



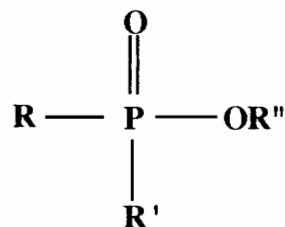
PHOSPHINITE



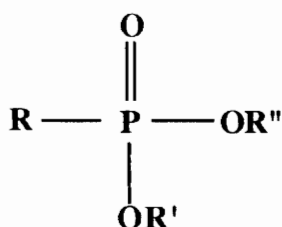
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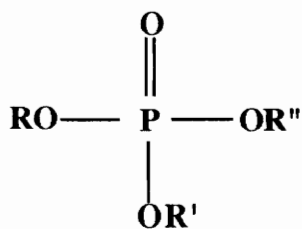
PHOSPHITE



PHOSPHINATE



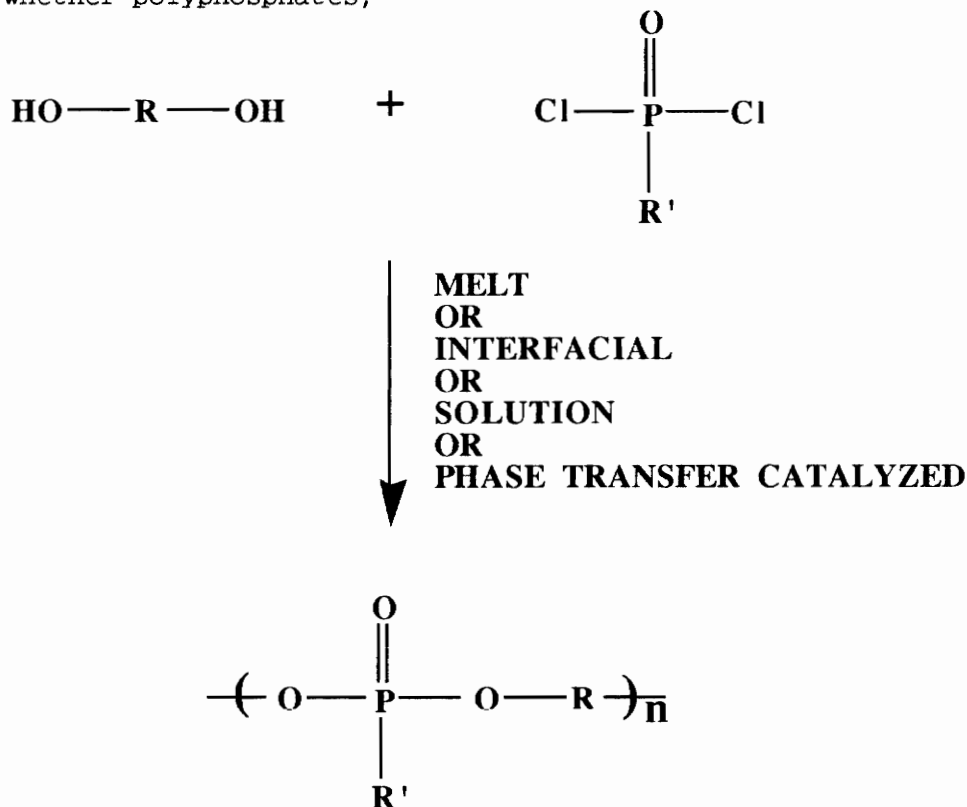
PHOSPHONATE



PHOSPHATE

techniques [187, 190, 191], high molecular weight has been difficult to obtain. Due to this fact, along with the findings that even these low molecular weight materials were noncombustible, most polyphosphonates have been investigated for use as oligomeric flame-retardant additives for other production polymers such as polyamides or polyesters. Most of these compositions have been reported in patent literature and much of it as foreign disclosures [187]. An additional concern has been with the

hydrolytic stability of such materials. The problems detailed above affect all of the polymers containing the phosphorus-oxygen (single) bond, whether polyphosphates,



Scheme 18. Polyphosphonate synthesis [187-191].

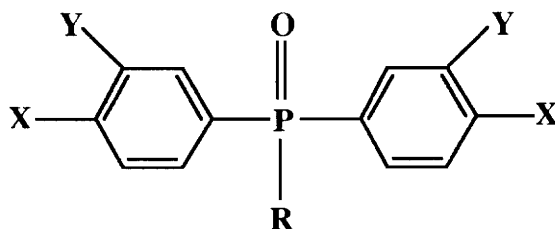
polyphosphites, etc. [192]. As mentioned above, polymerizations involving formation of phosphorus-carbon bonds has also been limited due to the lack of appropriate step-growth mechanisms available for this synthesis.

Therefore, it should be apparent that successful incorporation of phosphorus-carbon bonds along the main chain of an engineering thermoplastic can only occur through the classic step-growth mechanisms with phosphorus-carbon bond containing monomers. However, this approach

to phosphorus containing engineering thermoplastics also has its disadvantages, with the major problems being preparation of appropriate monomers for classical condensation polymerizations. The remainder of this section will discuss the successful attempts at both monomer and polymer formation of products containing the P-C bond, typically phosphine oxide materials.

Phosphine oxide containing monomers have been attractive in the literature for the outstanding thermal stability they should offer otherwise all organic polymers. From the knowledge that triphenyl phosphine oxide is a stable material at 700°C [193], it is surprising that even more research has not been conducted on these types of monomers for engineering polymers. Monomers of the generic type illustrated in Figure 2 would be desirable for inclusion into polyesters, polyamides, polycarbonates, poly(arylene ether)s, polyimides and other heterocyclic polymers.

Morgan and Herr [194, 195] first recognized the potential importance of these types of monomers in the early 1950's. Efforts were put forth to develop polyester fibers based on the phosphine oxide moiety by polymerizing bis(4-carboxyphenyl)phenyl (or methyl) phosphine oxide (or the esters thereof) with alcohols yielding the desired polyester. Scheme 19 illustrates this process, along with the synthetic methods developed for the preparation of the diacids. Either 1) Grignard or 2) decomposition of quaternary phosphonium salts routes were utilized to prepare the bis(4-methylphenyl)phenyl and methyl phosphine oxides,



**X = F, OH, COOH, NH<sub>2</sub>, COO**

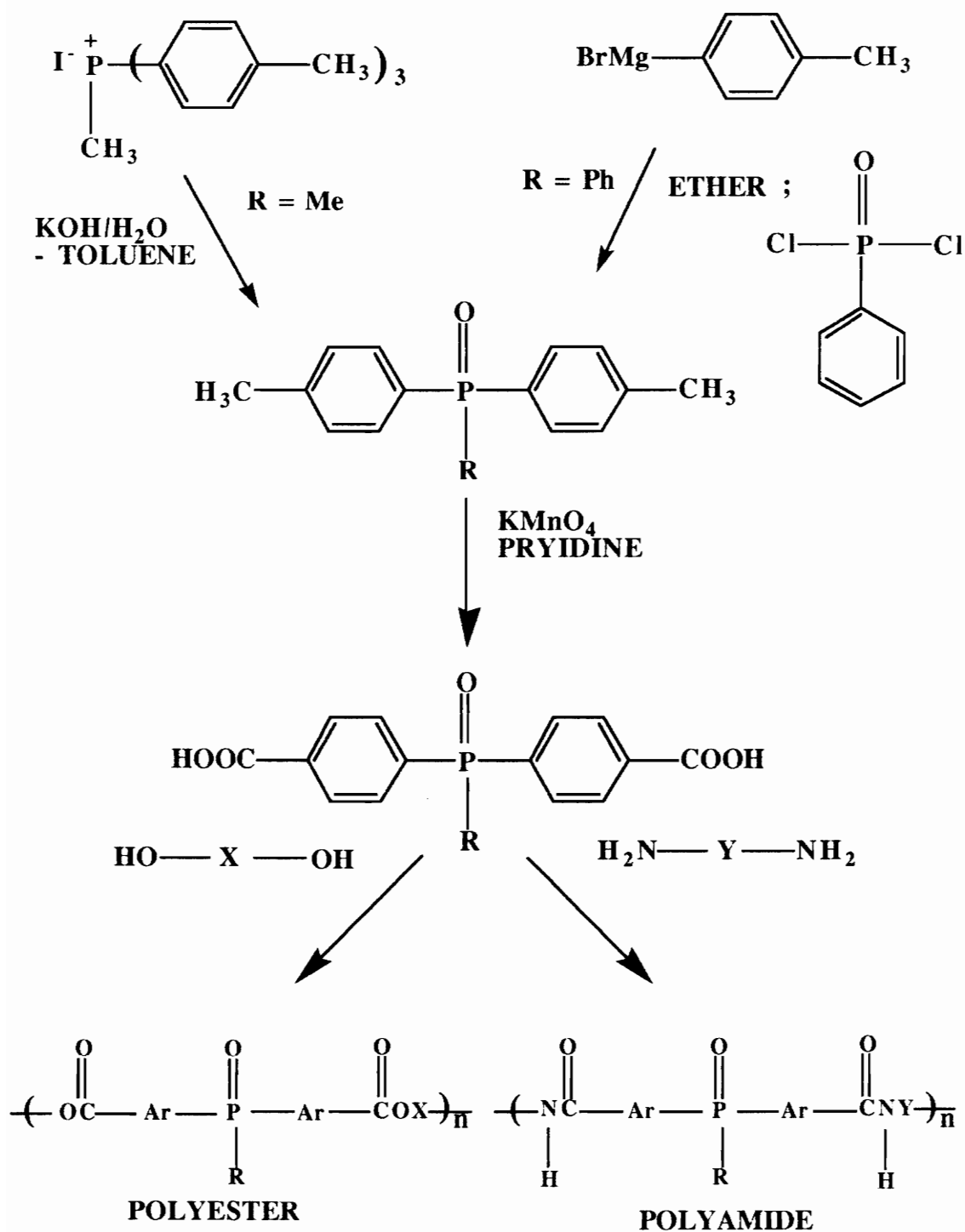
**Y = H, OH, NH<sub>2</sub>, COOH, CO**

**R = ALIPHATIC, AROMATIC  
TYPICALLY CH<sub>3</sub> OR Ph**

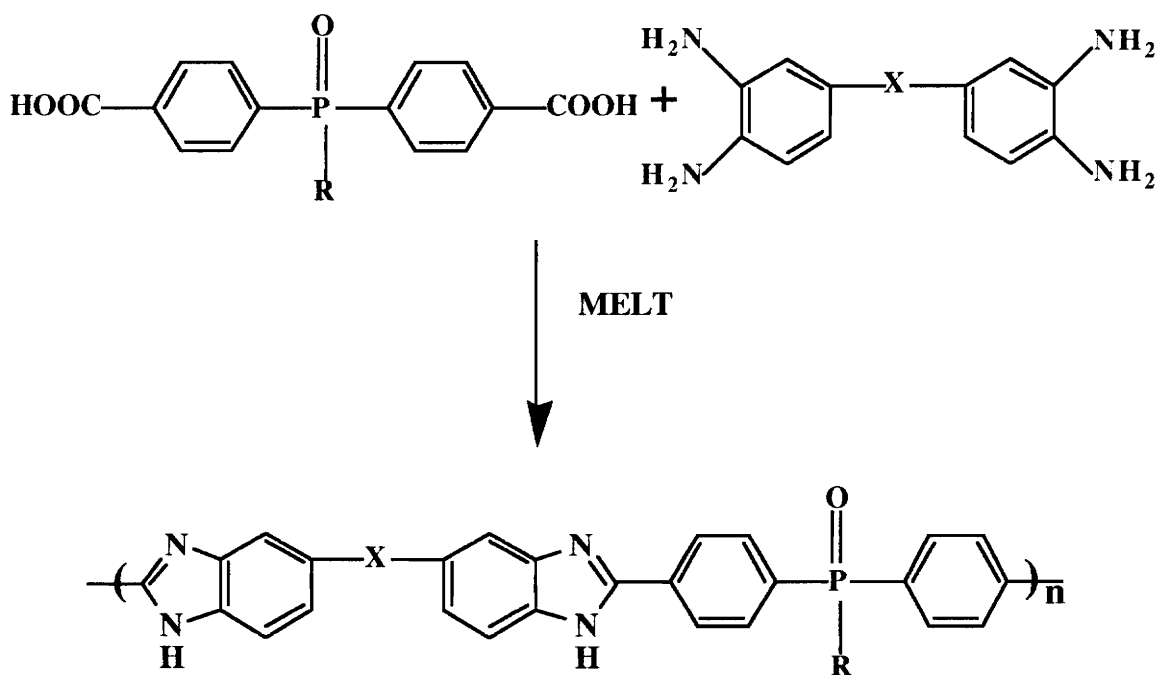
Figure 2. General phosphine oxide containing monomeric form desirable for incorporation into engineering polymers.

respectively. These products were then oxidized by standard aqueous potassium permanganate/pyridine methods, producing good yields. By conventional polymerization techniques at that time [195], transesterification and melt polycondensation techniques were utilized giving acceptable molecular weights and satisfactory fibers when spun. Other workers have also investigated these polyester [196, 197] and polyamide materials [197-200]. Since the mid-1960's, no reports of these types of polymers have been located in the open literature.

Also in the mid-1960's, several publications appeared describing the melt synthesis of low molecular weight polybenzimidazoles (PBI) from these aromatic diacids (or esters thereof) and aromatic tetraamines [201-203]. As illustrated in Scheme 20, these polymers were highly rigid with enhanced thermal stability and solubility properties relative



Scheme 19. Polyester and polyamide formation from diacids containing the phosphine oxide moiety [194, 195, 198-200].



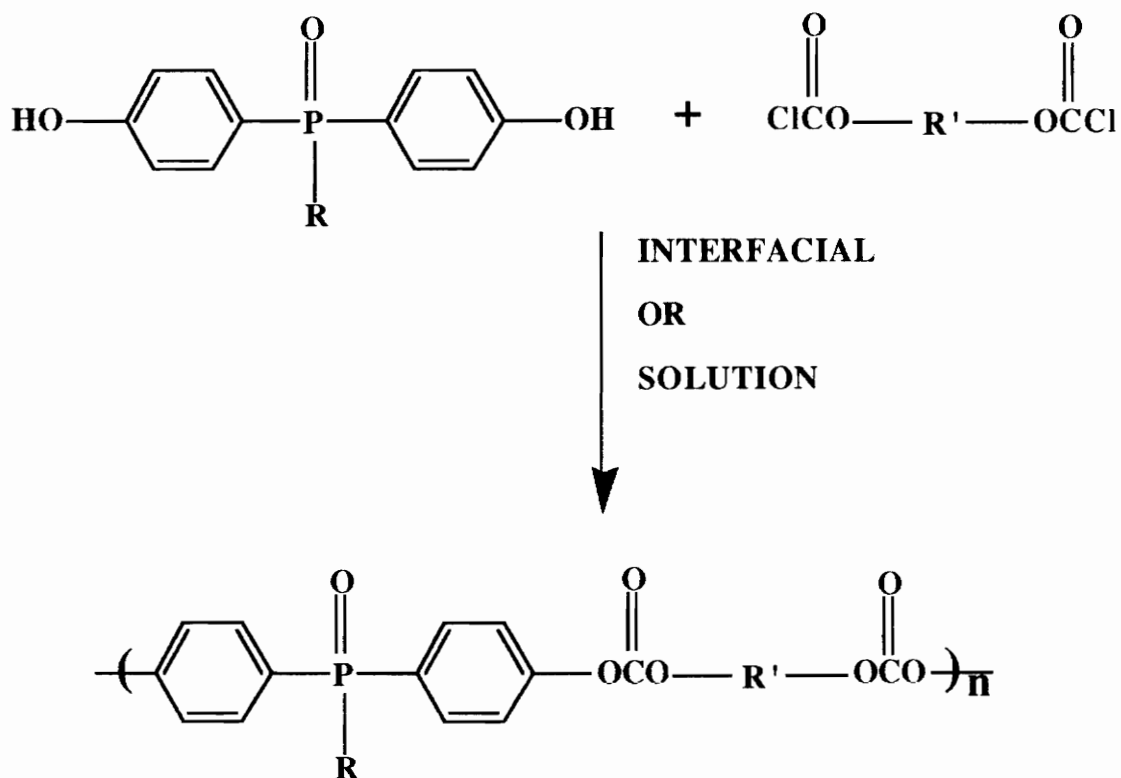
Scheme 20. Polybenzimidazole preparation from phosphine oxide containing diacid [201-203].

to other PBI's due to the presence of the bulky phenyl phosphine oxide unit. Later, these procedures were modified to give polybenzimidazoles and polybenzoxazoles of moderate molecular weight by solution polycondensation techniques [204, 205].

The bisphenol of the phosphine oxide structure shown in Figure 2 was also prepared in the 1950's [206] and its possible use in polymeric structures (epoxy formation) was recognized in the early 1960's [207]. Also utilizing a Grignard route for the formation of P-C bonds, this process gave bis(4-hydroxyphenyl)phenyl phosphine oxide in good yield by hydrolysis of bis(4-methoxyphenyl)phenyl phosphine oxide. Basically, the preparative method is identical to those in Scheme 19 with the exception



that the aromatic methyl groups were replaced by methoxy groups. Additionally, the dimethoxy compound was hydrolyzed by hydrobromic acid in acetic acid. This monomer was later used in the preparation of polyarylates [208] as shown in Scheme 21.



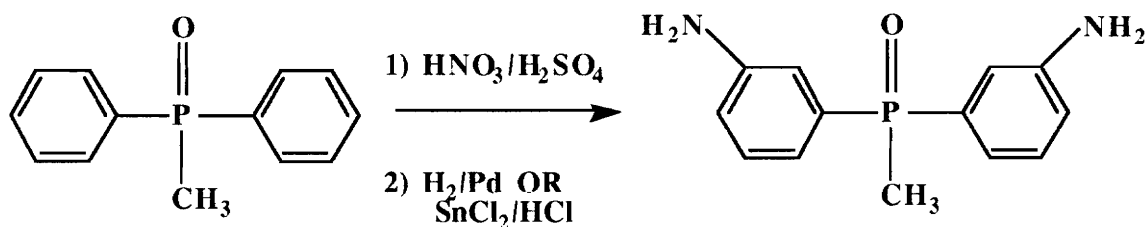
Scheme 21. Polyarylate synthesis with phosphine oxide containing bisphenol [208].

Although only moderate molecular weights were formed due to either inactivity of the bisphenol or purity considerations, the films which were formed containing phosphorus adhered very well to glass and metal and had improved self-extinguishing behavior relative to Bis-A based polyarylates. These polymers also were more soluble and displayed lower

"melting" temperatures, probably referring to  $T_g$ 's.. This bisphenol was also utilized in the preparation of poly(arylene ether)s, as will be covered later in this introduction. However, very few other attempts at polymerizing this monomer have been reported.

Phosphorus incorporation into polyimides would perhaps be an area in which polymer chemists would most like to observe the effects of the bulky phosphine oxide unit upon solubility and thermal stability. Polyimides have been well known for their outstanding thermal properties, but also for the ability to be very difficult to process. Preparation of polyimides has normally been carried out through the polycondensation of aromatic diamines with aromatic dianhydrides to give poly(amic acid) materials in solution. Next, either in the solid state or in solution, the imide rings are closed via chemical or thermal means. Therefore, for the monomers in Figure 2, the diamine and dianhydride functional groups would be desired in synthesis.

The first reported preparation of a diamine of the phosphine oxide family was in 1963 [198, 209] by the nitration of diphenylmethylphosphine oxide followed by reduction to the diamine. As shown in Scheme 22, this procedure gave good yields for the methyl substituted phosphine oxide; however, polyimides were not reported until almost twenty years later [210], and even then only low molecular weight polymers were prepared by a bulk thermal ring closing mechanism. This diamine monomer was utilized for the preparation of polyamides [198, 209] of acceptable molecular weights which reportedly could be spun into fibers. High softening temperatures



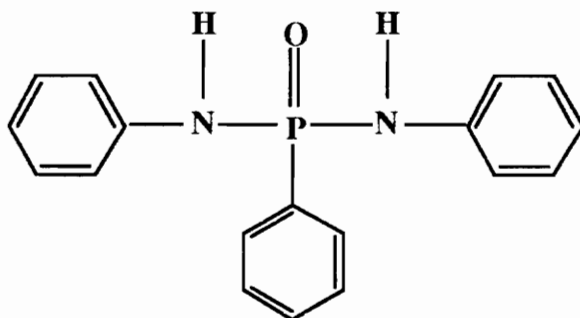
Scheme 22. Bis(3-aminophenyl)phenyl phosphine oxide synthesis.

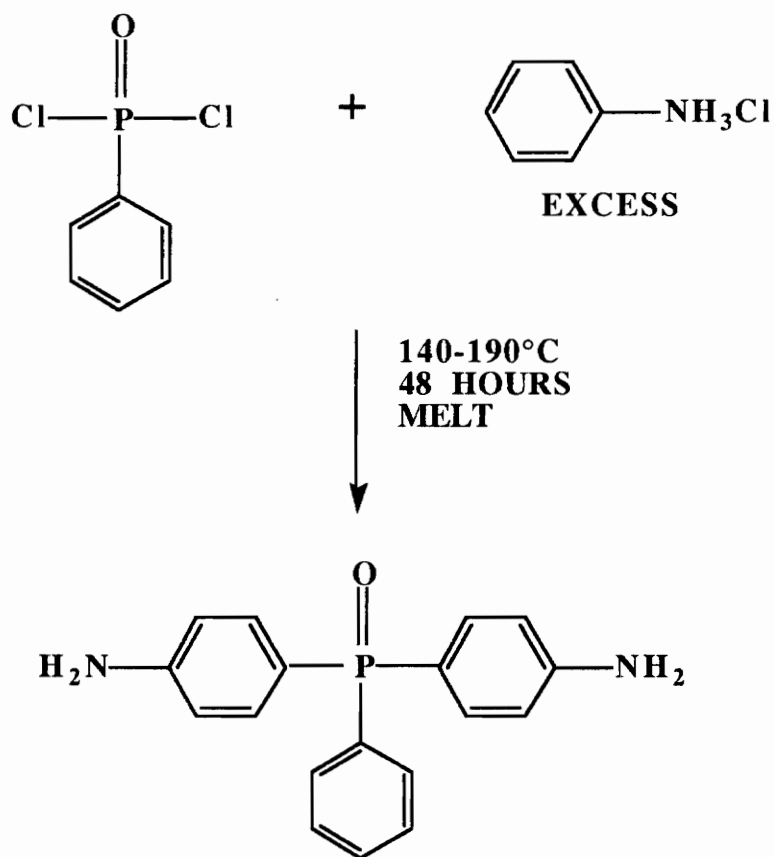
and nonflammability were claimed, with very high molecular weights in optimized cases.

Diamine functional phenyl substituted phosphine oxides were more scarce in the literature than any other phosphine oxide containing monomer, due to the nature of P-C bond formation. As discussed earlier, Grignard techniques could be used for the preparation of triphenyl phosphine oxide unit containing monomers, but amine or nitro group substitution on an aromatic ring render the Grignard route useless without special protective groups. Another process for P-C bond formation in these types of compounds is a Friedel-Crafts process with phosphine sulfides (P=S); these materials can then be oxidized back to the corresponding phosphine oxides [211]. However, again the problem existed with nitro inactivation of aromatic compounds to Friedel-Crafts type catalysts. A final possible method, nitration of triphenylphosphine oxide, followed by reduction [212, 213], was unacceptable due to several isomeric forms which were obtained; these were separable only by precise chromatographic procedures. Therefore, other methods were sought to prepare this highly desirable monomer.

A very laborious low yield route was carried out by Schiemenz in

1971 yielding the bis(3-amino) compound. Also in 1971, Russian workers claimed to have made the bis(4-aminophenyl)phenyl phosphine oxide via a simple one step route [214, 215] illustrated in Scheme 23. In the presence of excess aniline hydrochloride at high temperatures, phenylphosphonic dichloride was alleged to undergo a Friedel Crafts type reaction giving the polymer grade diamine in low yields after recrystallization from ethanol. However, the polyimides prepared from such diamines [216, 217] were always brittle and much less thermally stable than other polyimides synthesized with the same methods without phosphorus [218]. No other reports of the preparation of this diamine by this route exist in the literature, and we were not able to repeat the work. Therefore, it was likely the monomer these workers claimed was incorporated into polyimides was actually not a diamine, but rather the diamide formed from the reaction of aniline with phenylphosphonic dichloride as shown below the scheme. Our studies always yielded this compound, as evidenced by nuclear magnetic resonance studies and the proximity of melting points to the known diamide compound [219]. Note that elemental analysis studies in this case were not helpful due to the identical masses of the two compounds (diamide and diamine).



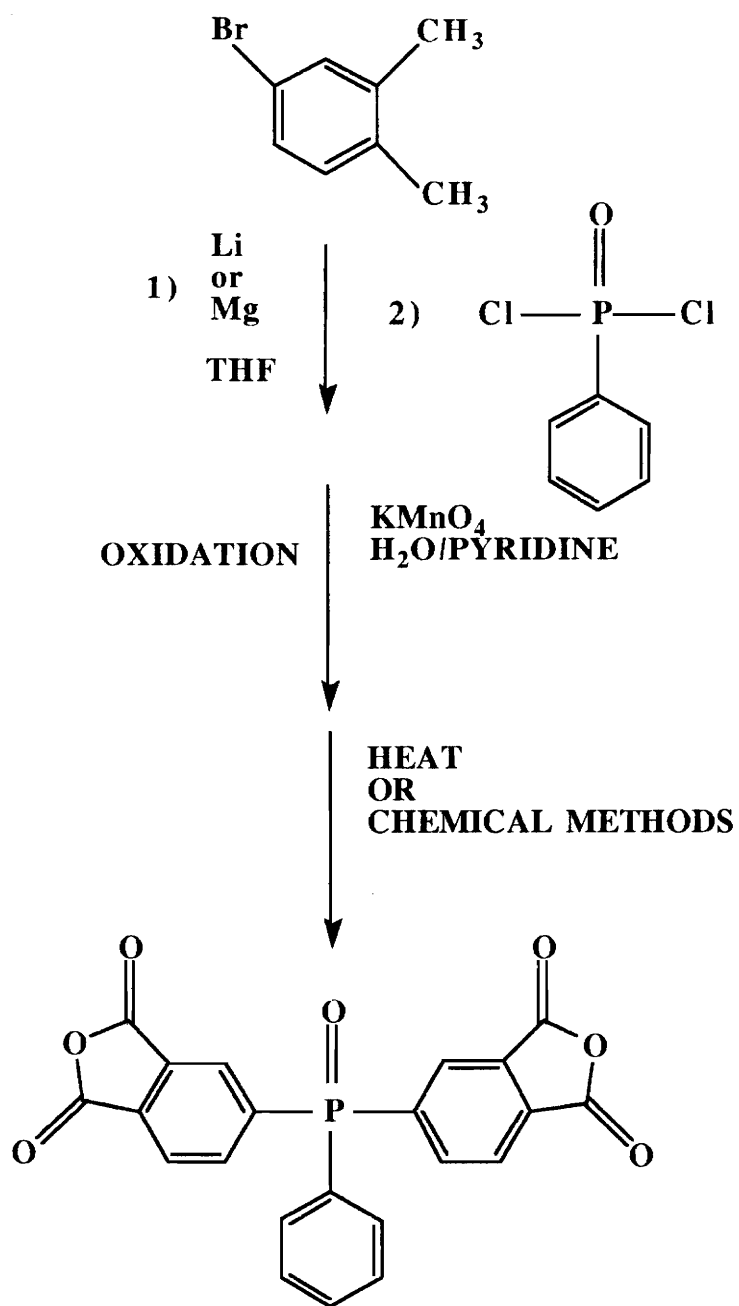


Scheme 23. Claimed preparation of bis(4-aminophenyl)phenyl phosphine oxide [214, 215] .

Schiemenz soon published [220] a more feasible route to the 4, 4'-dinitro compound but never reduced the nitro groups to obtain the diamine. From the displacement reaction of bis(4-fluorophenyl)phenyl phosphine oxide (discussed herein later) with lithium nitrite-semihydrate in HMPT at 150°C for nine hours, the bis(4-nitrophenyl)phenyl phosphine oxide was prepared in 26% yield. This work will certainly be continued to find an inexpensive high yield route to this desirable diamine.

Several thermosetting resins have been developed based on the nitrated triphenyl phosphine oxide [210, 221-224]. By reducing tris(3-nitrophenyl) phosphine oxide to the corresponding triamine, and reacting it with different stoichiometric ratios of maleic or nadic anhydride, several maleimide containing amines were asserted to be formed. Some of these diamines were then reacted with various ratios of other diamines and dianhydrides giving polyimide materials capable of being crosslinked. Alternatively, the maleimide materials were cured in the monomeric form and flame retardant properties were investigated.

Another route to polyimides containing the phosphine oxide group in the backbone was by synthesizing the triphenyl phosphine oxide tetracarboxylic dianhydride shown in Scheme 24 [225-229]. By reacting either the 4-lithiated *ortho*-xylene or the Grignard reagent of 4-bromo-*ortho*-xylene with phenylphosphonic dichloride in THF, followed by oxidation of the tetramethyl compound, the tetraacid of the phosphine oxide containing monomer was isolated in approximately 30% yields. Quantitative ring closure procedures resulted in the desired dianhydride. Reported enhanced solubility and increased thermal stability would make this route an attractive one to study by modern imidization techniques. In order for this method for polyimide synthesis to take on higher proportions, oxidative routes to the tetraacid must be optimized for better yields. Also, 4-bromo-*ortho*-xylene is not commercially available in pure form, as it forms an azeotropic distillation with the 3-bromo isomer; however, the pure 4-bromo isomer can be prepared from the available 4-amino-*ortho*-xylene by diazotization



Scheme 24. Preparation of dianhydride containing phosphine oxide [225-229].

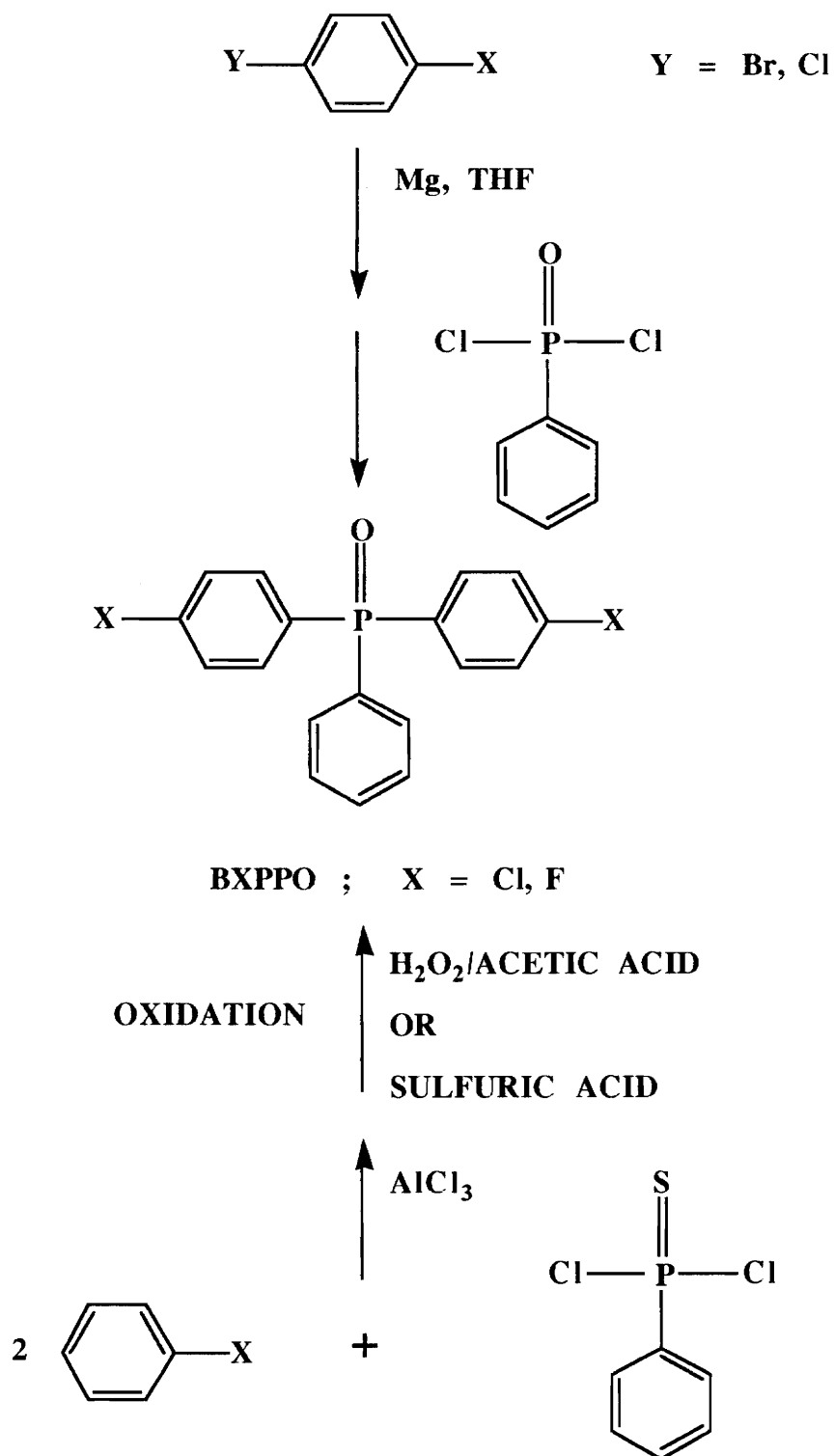
reaction followed by treatment of the diazonium salt with CuBr.

In the late 1970's, another phosphine oxide containing monomer was

introduced, along with polymerization procedures for preparing poly(arylene ether phosphine oxide) (PEPO) [158]. As briefly discussed in section 2.1.3 of this dissertation, the polycondensation of the sodium salt of bisphenol-A with bis(4-chlorophenyl)phenyl phosphine oxide (BCPPO) in DMSO gave low molecular weight PEPO with enhanced solubility characteristics relative to polysulfones. Synthesis of BCPPO was carried out as illustrated in Scheme 25 by the Grignard route utilizing p-dichlorobenzene and phenylphosphonic dichloride. The bis(4-fluorophenyl) (BFPPO) analogue was never investigated by these workers, but should have been the reasonable alternative due to the effects of leaving groups discussed previously.

Several other workers have investigated the synthesis of bis(4-halophenyl)phenyl phosphine oxides by either of the pathways illustrated in Scheme 25 [230-236]. This compound was even known for its ability to combat certain insects [237]. Either route to this important monomer seemed satisfactory. The Grignard process was simpler and only one step was required once the Grignard reagent was formed; however, this method was not preferred industrially due to the expense and danger of large quantities of ether or tetrahydrofuran. Synthesis of bis(4-halophenyl)phenyl phosphine oxide via a Friedel-Crafts type process, as shown in the bottom half of Scheme 25, also proceeded smoothly, but needed two steps to complete conversion to the phosphine oxide. Phenylphosphonic dichloride has been found not to give products when utilized under the same conditions as the phosphine sulfide. No clear reason has ever been cited in the literature



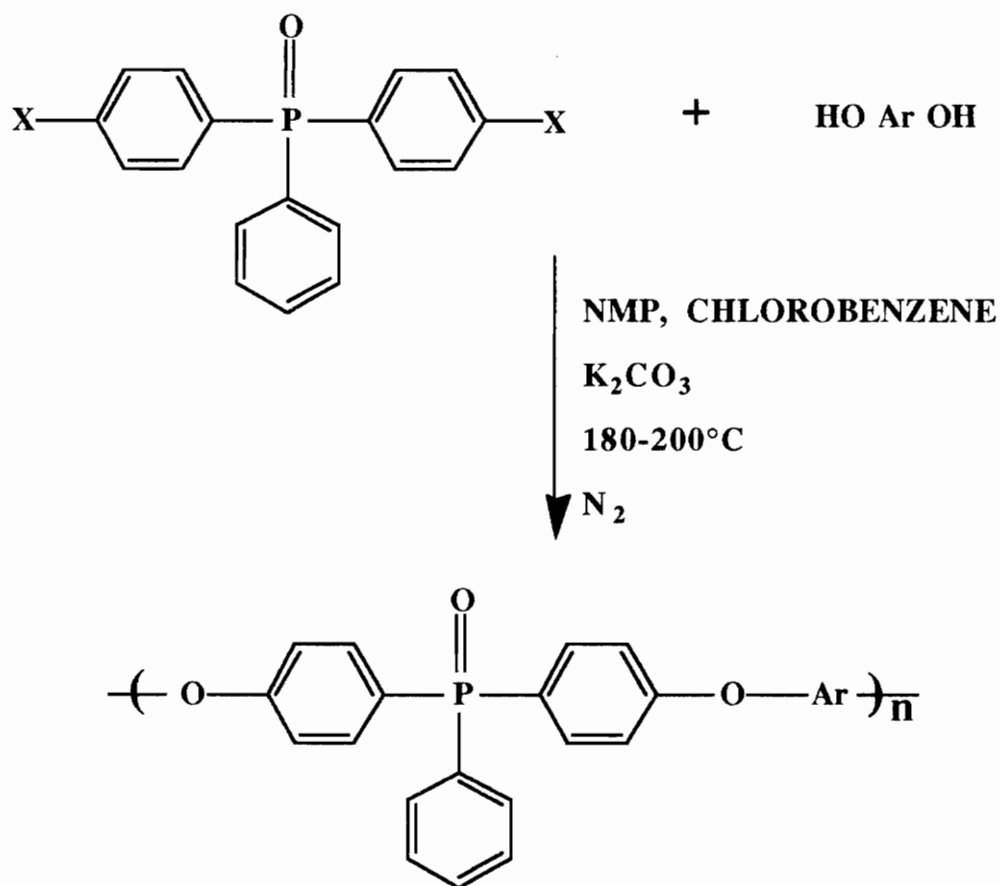


Scheme 25. Preparation of bis(4-halophenyl)phenyl phosphine oxide [230-236].

for this effect, but some theories can be made from our experiences, as will be discussed in the Results and Discussion section of this thesis. Both yields and monomer purity were reduced for the Friedel-Crafts method of preparation, due to isomeric impurities which form from the reaction of halobenzenes with phenylphosphothionic dichloride.

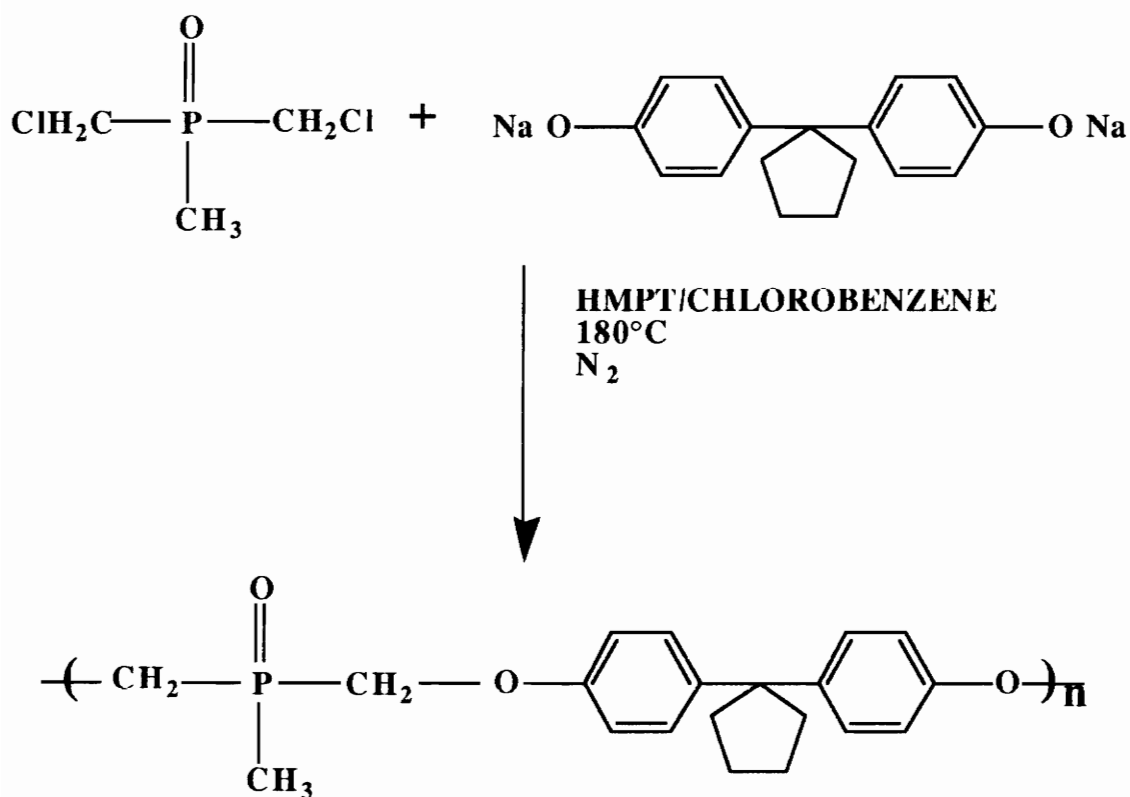
Eventually, reasonably high molecular weight poly(arylene ether phosphine oxide)s were prepared (Scheme 26) from the nucleophilic displacement polycondensation of bis(4-halophenyl)phenyl phosphine oxide with aromatic bisphenols in dipolar aprotic solvents [238-242]. The fluoro substituted monomer was the preferred monomer to utilize for this polymerization, as use of the chloro substituted dihalide resulted in low molecular weights unless polyfunctional halides typical aromatic bisphenols, although higher molecular weights were still achievable if conditions had been optimized [241]. All of these materials were reported to be thermally stable, self-extinguishing polymers with  $T_g$ 's in the range 150-260°C.

An interesting variation to this type of polymer is illustrated in Scheme 27, from the polycondensation of bis(chloromethyl)methyl phosphine oxide with sodium salts of cardiac type bisphenols in HMPT at 150-180°C [243]. Of course, this polymer was not formed by nucleophilic aromatic substitution, but probably by a conventional  $S_N2$  mechanism. were coreacted [239]. Acceptable molecular weights were formed from These materials were also flame retardant with acceptable molecular weights formed under the conditions specified.

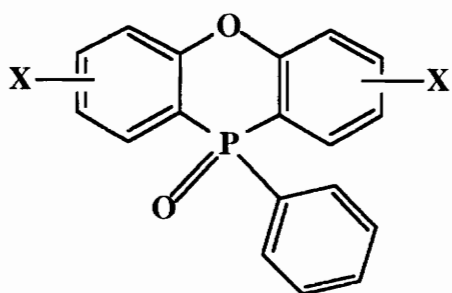


Scheme 26. Poly(arylene ether phosphine oxide) synthesis [238-242].

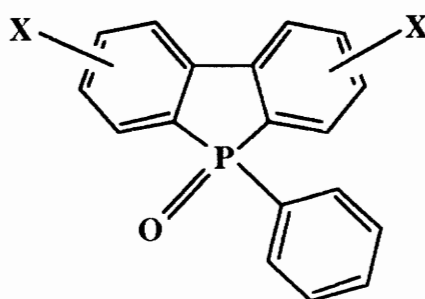
As final examples of phosphorus containing high performance polymers, this background will consider those materials with double strand phosphine oxide containing units along the backbone, such as phenoxaphosphine oxide or dibenzophosphole. As illustrated below, these structures could behave in much the same way other double stranded polymers (polyimides, PBI's, etc.) do, with such characteristics as high thermal stability, chemical and solvent resistance and high thermal transitions. Synthetic aspects on forming the phenoxaphosphine oxide



Scheme 27. Example of cardiac bisphenol based methylene group containing poly(arylene ether phosphine oxide).



**PHENOXYPHOSPHINE OXIDE**



**DIBENZOPHOSPHOLE**

ring were first developed in 1961 [244] and further refined later in the 1960's and early 1970's [245-247]. Basically, the procedures for the synthesis of phenoxaphosphine oxide containing monomers involved the *ortho* lithiation of substituted diphenyl ethers, followed by reaction with phenylphosphonic dichloride. Thus, these monomers were eventually prepared containing X groups of acids or acid chlorides [248-255] and tetraacids or dianhydrides [254, 256]. These phenoxaphosphine containing monomers were then incorporated into polyamides [248, 249], polyesters [250, 255], polybenzimidazoles and polybenzoxazoles [251, 253], polyoxadiazoles [252], polyimides [256] and polyamide-imides [254]. For the dibenzophosphole derivative, 2,2'-dibromo-5,5'-dimethoxydiphenyl was lithiated, reacted with phenylphosphonic dichloride and hydrolyzed to give the compound above where X was -OH [257]. This bisphenol was utilized in the preparation of low to moderate molecular weight polyesters which were more soluble, fire-resistant and stable to UV radiation, as were the phenoxaphosphine containing polymers.

#### 2.2.2.1 General Characteristics of Phosphorus Containing Thermoplastics

Several generalizations can be made from the prior discussion on the history of the synthesis of phosphorus containing high performance materials and are summarized as follows:

1. Phosphorus containing engineering thermoplastics tend to be much more flame-retardant than their non-phosphorus containing counterparts.
2. High molecular weight phosphorus containing engineering polymers have

been difficult to prepare.

3. Reduction in thermal stability does not occur when phosphorus was incorporated into otherwise highly thermally stable polymers.

High molecular weights have generally not been achieved for most cases in the literature probably due to purity considerations, but possibly also due to reactivity or choice of polymerization techniques. Most of the monomers which have been prepared are quite bulky in nature and do not crystallize well from solution, and were therefore often simply precipitated with nonsolvents.

The resistance of polymeric materials to burning has been a subject of interest for many years, especially in view of the large number of consumer applications for macromolecular systems [258, 259]. The mechanism of phosphorus containing polymers' resistance to burning and char formation has been in doubt for these many years, however several studies have begun to "clear the smoke" which has covered these complex areas of polymer and fire science. The next section will briefly comment on the available arguments attempting to define this topic, since these investigations will again be considered in the results part of this thesis.

#### 2.2.2.2 Fire Retardancy Aspects of Phosphorus Containing Polymers

Two broad methods exist for the preparation of fire resistant (used interchangeably with flame retardant) polymeric materials: a) the incorporation of fire resistant additives into a combustible organic

polymer or b) the chemical insertion of monomeric materials into a macromolecular system which will also retard ignition and combustion in the final product. This background will briefly comment on the first approach, when important to the discussion, and will also attempt to elaborate on the latter technique of producing "inherently" flame retardant polymers. First, however, a short summary of some basic features of combustion will be presented.

Several workers have reviewed flammability aspects of polymeric materials in general [258-266] and specifically for high performance polymers [267-269]. When macromolecular systems burn, several mechanisms operate simultaneously as illustrated in Figure 3. The material of interest first must acquire sufficient energy from the environment ( $-Q_1$ ) to begin to pyrolyze. The thermal decomposition products from this pyrolysis can be in one of three forms: nonflammable gases, flammable gases or carbonaceous char. Finally, those flammable gases can ignite affording the final combustion products and also releasing energy ( $+Q_2$ ), which can further feed the pyrolysis process. Fire resistant materials or flame retardant additives can be described in terms of how they alter this mechanism. In order to impart flame resistance, a system must have a high  $Q_1$  value and a low  $Q_2$  value.

Therefore, for flame retardant systems, large amounts of energy for bond breakage to occur are required and low amounts of flammable gases must be evolved. Stronger main chain chemical bonds that are resistant to radical chain cleavage will result in higher  $Q_1$  numbers, while high amounts of nonflammable gases and/or carbonaceous char will result in

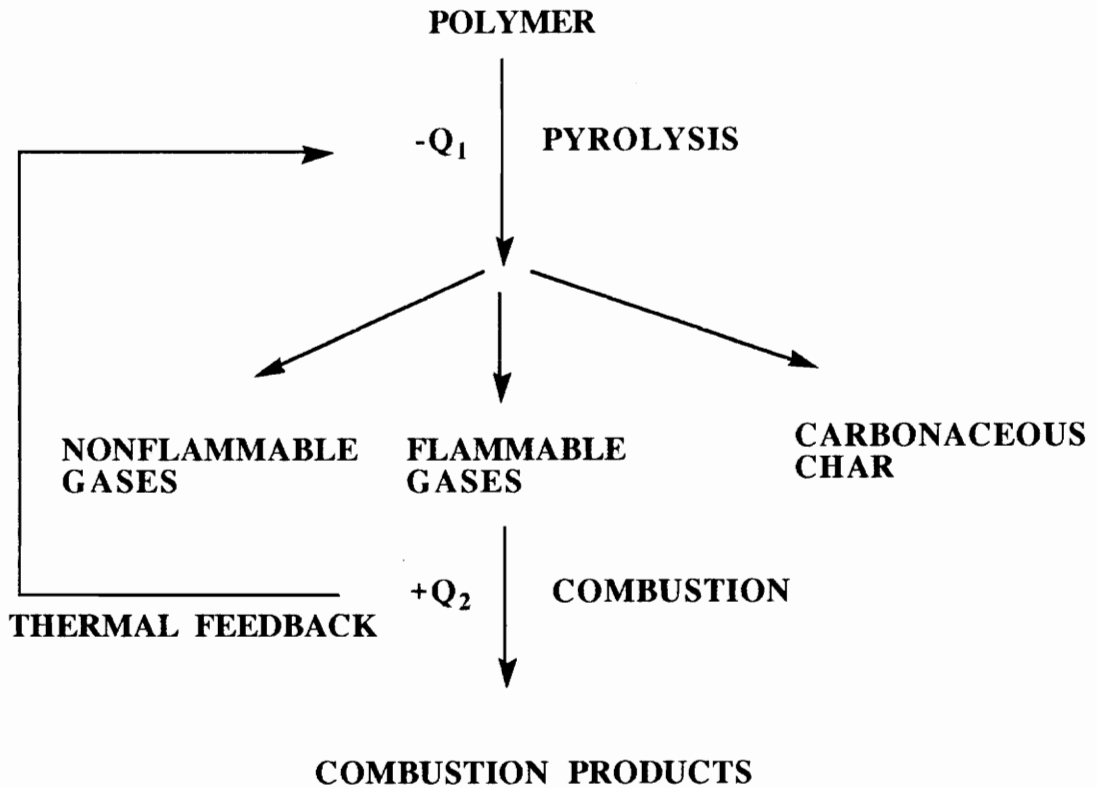


Figure 3. Burning mechanistic cycle representation [260, 261].

low  $Q_2$  values. These are basically the mechanisms by which polymeric flame retardant additives operate. Thus, either they scavenge radicals formed in the solid state, limiting chain cleavage and promoting char, or they volatilize to nonflammable vapors, severely diluting the flammable gases formed.

Additives which can provide flame retardancy to macromolecular systems must normally conform to several requirements, such as stability under polymer processing temperatures and times, compatibility with the polymer structure while not detracting from mechanical properties and retaining flame retardant properties over long periods of time.



Additionally, the additive must not generate large amounts of poisonous fumes when burned, as smoke inhalation is arguably the primary culprit for deaths during fires. Typical additives include metal oxides such as antimony oxide, phosphorus ester containing materials, halogenated compounds and others [258], many of which have been patented and reviewed in detail [270].

Inherently fire resistant polymers can be very desirable because they may avoid the disadvantages listed for utilization of additives. For example, halogenated polysulfones have numerous appearances in the patent literature [271] as flame retardant engineering plastics; however, the fact that burning these materials releases generous amounts of toxic gaseous acids which may be more harmful than the fire itself is often overlooked. Nevertheless, those polymers addressed above as possessing high  $Q_1$  values are in the thermally stable or high-temperature [272] family of macromolecules. Typically, these polymers require large amounts of energy for the scission of main chain aromatic bonds prior to volatilization. The following review will concentrate only on those so-called single strand polymers as opposed to double strand materials such as PBO's, etc.

Polysulfones were initially studied in order to determine the flammability compared to other known engineering thermoplastics [267, 268, 273, 274]. These neat resins were termed nonflammable due to their limiting oxygen index (LOI) of around 30-40. The LOI is that percent oxygen in a controlled continuously changing oxygen/nitrogen atmosphere which a material will sustain candle-like burning [275,

276]. Any material with LOI greater than 26 has been termed "nonflammable" [260]. Udel type Bis-A based PSF had lower LOI values than the Victrex PES due to the partial aliphatic character of the Bis-A polysulfone. Additionally, char yields of these, along with many other engineering polymers, have been correlated with the limiting oxygen index, with higher char yields giving higher LOI's [260, 267, 268, 277-279] due to the low  $Q_2$  value in Figure 3. This generalization does not hold for halogen containing polymers due to their activity in the gas phase and not the condensed phase.

Mechanistic studies of such systems have been utilized to determine the route which PES degrade. Typically, pyrolysis of a polymeric material followed by gas chromatography and/or mass spectrometry has been employed to determine which low molecular weight compounds were formed upon heat treatment [33, 280]. From the identities and amounts of the degradation products, some statements can be made concerning the route by which PES materials degrade. In nitrogen atmospheres, it was assumed that only thermal degradation mechanisms were operating and free radical reactions occurred which led to small low molecular weight volatile compounds. By assigning bond dissociation energies of each group along the polymer chain, workers have been able to design possible routes by which radical reactions leading to polymer degradation were likely to take place. For polysulfones, Figure 4 illustrates possible pathways by which these polymers decomposed.

As is easily recognizable from this sketch, several products can be explained from one of many routes. For example, phenols, toluene,

benzene, biphenyls, diphenyl ether, sulfur dioxide and methane were just some of the products observed. The products were somewhat simplified when the all aromatic PES were pyrolyzed due to the absence of aliphatic compounds [280]. Additionally, the temperature at which the materials were pyrolyzed had an effect on the amounts and identities of each compound from the degradation. No studies have been performed to quantitatively determine the kinetics of this decomposition process. These studies gave similar results for the poly(arylene ether ketone)s [281].

The role phosphorus plays in preventing the burning of polymeric materials has been investigated mostly in terms of additives [282-287] and very slightly in phosphorus containing polymers [288]; even when investigated in polymers, only those polymers with phosphorus- oxygen bonds have been studied. The literature contains no information on the mechanism of fire retardancy of phosphorus-carbon bond containing homopolymers, probably due to the low success rate at which these polymers have been synthesized. Phosphorus compounds, when used as additives, have been shown to be active in both the gaseous phase and the condensed phase, depending on polymer and additive structure [259]. Generally, oxygen containing polymers with volatile phosphorus containing additives were inhibited to burning due to solid phase reactions (char formation), while for hydrocarbon polymers, these additives reduced combustion due primarily to gas phase reactions. The major reason proposed for condensed phase flame retardancy mechanisms

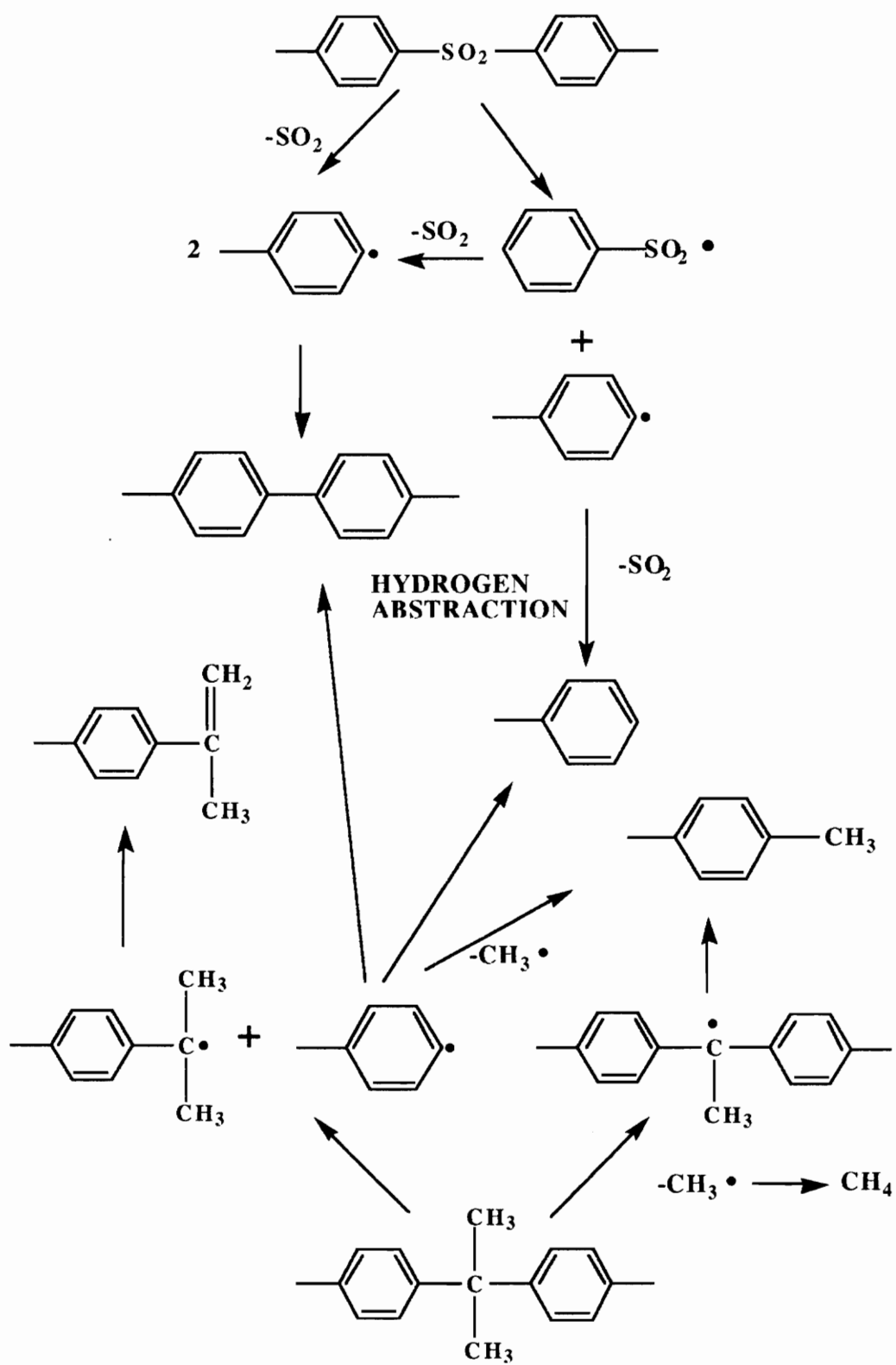


Figure 4. Possible pathways for degradation of Bis-A PES [33].

has been through the formation of nonvolatile phosphorus containing acid formation. When no substrate phase reactions could give phosphoric acid type inhibitors, the phosphorus additive mode of action was typically due to gas phase reactions after volatilization. Examples of vapor phase reactants which yield enhanced flammability characteristics include triphenylphosphine oxide and triphenyl phosphate.

Thus, it should be readily seen that many conflicting views exist on both the mechanism of phosphorus compound flame retardance as additives in organic polymers [289], and even less is known concerning the presence of phosphorus along a polymer chain. Condensed phase and vapor phase retardation mechanisms have been studied in quite some detail for additives, but almost nothing is known about the mechanism of flame inhibition when phosphorus compounds have been chemically linked in a macromolecular chain.

### 2.1.3 Research Logic

From this background section, one may conclude that it should be advantageous to prepare high molecular weight thermooxidatively and hydrolytically stable polymers containing a thermooxidatively stable phosphorus monomers. The poly(arylene ether phosphine oxide) materials are an example of such a system that has all of the desirable features listed above. High molecular weight has not routinely been obtained in the literature; however, by utilizing modern methods, preparation of high molecular weight linear macromolecules should be possible. The triphenyl phosphine oxide group would then be chemically bound in the polymer chain and not be able to volatilize out of the system as it would as an additive. Note that the carbon-phosphorus bond energy is 70-75 kcal/mol (phosphorus to aromatic carbon) or about 66 kcal/mol (phosphorus to aliphatic carbon) [211], and the phosphine oxide bond energy is about 128-138 kcal/mol [211]. Since the low molecular weight compound triphenyl phosphine oxide was reported to be stable at 700°C [193], incorporation of this group along a poly(arylene ether) would not be detrimental to thermooxidative stability. The geometry of the pendant phenyl phosphorus bond would be expected to encourage amorphous morphologies.

### 3.0 EXPERIMENTAL

#### 3.1 PURIFICATION OF SOLVENTS AND GENERAL REAGENTS

Table 5 summarizes information regarding chemical structures, boiling points, acronyms and sources of many of the dipolar aprotic solvents utilized throughout this research.

##### 3.1.1 N-Methylpyrrolidone (NMP)

Vacuum distillation at around 70°C using a water aspirator after stirring over calcium hydride and storage in an anhydrous environment yielded sufficiently pure and dry solvent for the polycondensation reactions. Typically, NMP was stored in a round bottom flask fitted with a septum under anhydrous nitrogen pressure.

##### 3.1.2 N,N-Dimethylacetamide (DMAC)

Vacuum distillation at around 60°C using a water aspirator over calcium hydride was utilized to purify and dry this solvent and it was stored as was NMP.

##### 3.1.3 Diphenylsulfone (DPS)

Diphenylsulfone was obtained as 99% material from Aldrich, and was recrystallized from acetone with a small amount of charcoal. Filtration while hot through celite, followed by concentration to just before the cloud point and slow cooling at room temperature gave DPS as large white

crystals. Filtration and air drying, followed by crushing in a mortar and pestle and drying in a vacuum oven at 60°C afforded solvent grade material.

#### 3.1.4 Sulfolane

This solvent, also known as tetramethylene sulfone, was vacuum distilled over calcium hydride at about 100°C using a water aspirator, giving a slightly yellow distillate, which was stored in anhydrous conditions.

#### 3.1.5 Dimethylsulfoxide (DMSO)

After vacuum distilling at around 80°C using a water aspirator over calcium hydride and storage in a rubber septum covered flask under nitrogen pressure, this solvent was adequately dry and pure for use.

#### 3.1.6 Chlorobenzene

Chlorobenzene was vacuum distilled over calcium hydride near 35°C using a water aspirator and stored under a nitrogen atmosphere.

#### 3.1.7 Tetrahydrofuran (THF)

Careful distillation of this ether solvent from sodium/benzophenone purple complexes afforded acceptably dry solvent for Grignard syntheses.

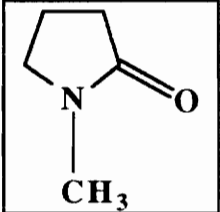
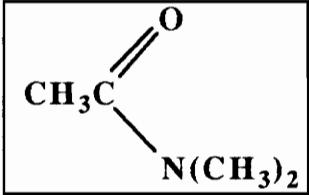
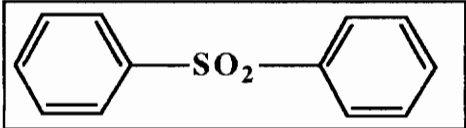
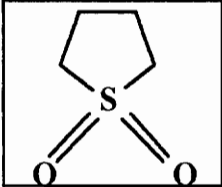
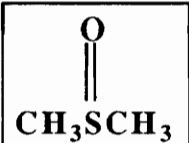
#### 3.1.9 General solvents and Reagents

Anhydrous potassium carbonate (Fisher) was crushed and dried at



100°C in a forced air oven and stored in a screw cap jar in a dessicator.

Table 5. Dipolar aprotic solvents utilized for the preparation of poly(arylene ether)s

<u>SOLVENT(ACRONYM)</u>	<u>SOURCE</u>	<u>BOILING POINT</u> (1 ATM, °C)
N-METHYLPYRROLIDONE (NMP)	FISHER	202
		
N,N-DIMETHYLACETAMIDE (DMAc)	FISHER	165-6
		
DIPHENYLSULFONE (DPS)	ALDRICH	379
		
SULFOLANE	ALDRICH	285
		
DIMETHYLSULFOXIDE (DMSO)	FISHER	189
		

The following solvents were used as received from Fisher : toluene, methanol, acetone, methylene chloride, chloroform, anhydrous ethyl ether, pyridine, ethanol and hexanes. General reagents such as potassium hydroxide, concentrated sulfuric acid, concentrated hydrochloric acid, magnesium turnings, metal halide salts, aluminum chloride, potassium permanganate and others were purchased and used as received from Fisher Scientific.

Obtained from Aldrich Chemical were the following reagents which were used without further purification : phenylphosphonic dichloride (97%), methyl phosphonic dichloride, p-bromofluorobenzene, p-bromotoluene, aniline hydrochloride, fluorobenzene, and phenyl phosphothionic dichloride.

### 3.1.9 Other Commercial Engineering Resins Utilized

Several commercially available engineering thermoplastics were utilized for comparison purposes in this investigation. The structures, properties and sources are outlined in Table 6.

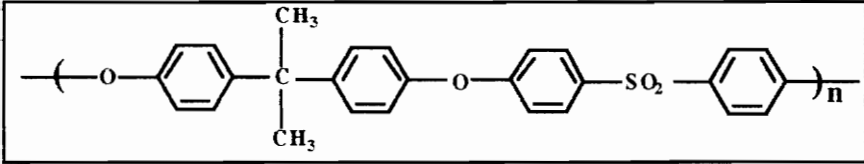
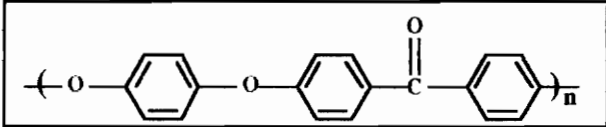
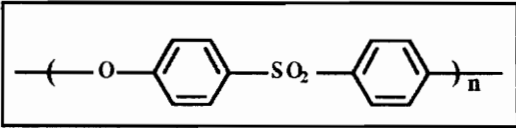
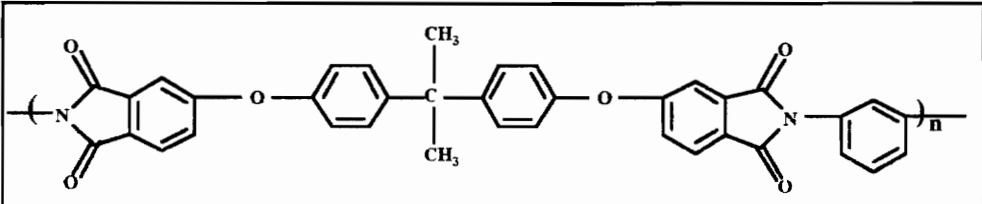
## 3.2 PREPARATION AND PURIFICATION OF MONOMERS

Table 7 summarizes monomers which were important throughout this investigation, including their formulas, acronyms, supplier (if any) and melting points.

### 3.2.1 Bisphenol A (BIS A)

Monomer grade BIS A was generously supplied by DOW Chemical and

Table 6. Commercial engineering resins utilized in this research.

<u>POLYMER</u>	<u>SOURCE</u>	<u>T<sub>g</sub>(°C)</u>
<b>UDELM POLYSULFONE</b> 	<b>AMOCO</b>	<b>190</b>
<b>PEEK</b> 	<b>ICI</b>	<b>145</b> (T <sub>m</sub> = 345)
<b>VICTREX POLYSULFONE</b> 	<b>ICI</b>	<b>230</b>
<b>ULTEM</b> 	<b>GENERAL ELECTRIC</b>	<b>218</b>

normally needed no further purification (only drying under vacuum prior to use). If desired, it could be recrystallized from concentrated toluene solution to give white needles and dried under vacuum at 60°C.

### 3.2.2 Hydroquinone (HQ)

Similar to BIS A, two sources were used for this monomer, and depending on the quality, recrystallization may be used. If 99+% gold label monomer was utilized from Aldrich, only drying *in vacuo* at 40°C was needed prior to use. However, from other sources, careful recrystallization from nearly saturated deoxygenated acetone gave satisfactory results, followed by drying in a vacuum oven at low temperatures to remove any excess acetone.

### 3.2.3 Biphenol (BP)

Biphenol was received as 97% pure monomer from Aldrich Chemical Co. It had to be recrystallized similar to hydroquinone, from saturated deoxygenated acetone giving large white crystals, which were dried over a nitrogen flow, crushed in a mortar and pestle, and dried under vacuum at 50°C.

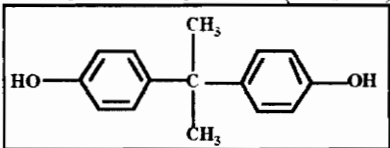
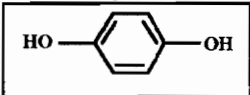
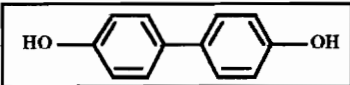
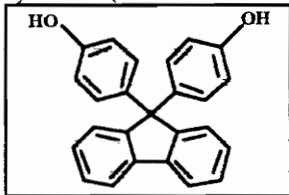
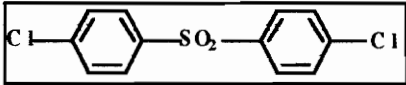
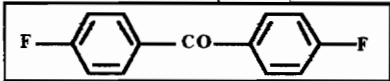
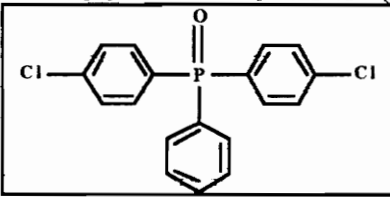
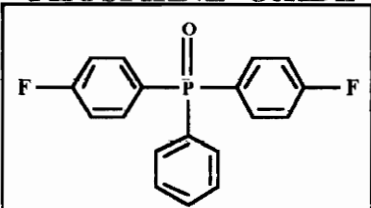
### 3.2.4 9,9-Bis(4-hydroxyphenyl)fluorene (FL)

This specialty monomer was donated as monomer grade material by NASA Langley workers and needed no further purification.

### 3.2.5 m-Aminophenol (mAP)

An agent for functionally terminating poly(arylene ether)s, this material had to be treated as if it were also a monomer for step-growth polymerizations. Therefore, the 98% pure material from Aldrich was vacuum sublimed around 130°C using a mechanical pump at about 1 torr and

Table 7. Monomers used throughout this research.

<b>MONOMER (ACRONYM)</b>	<b>SOURCE</b>	<b>MELTING POINT (°C)</b>
<b>BISPHENOL A (BIS A)</b> 	<b>DOW</b>	<b>156-7</b>
<b>HYDROQUINONE (HQ)</b> 	<b>ALDRICH (99+%)</b>	<b>172-3</b>
<b>BIPHENOL (BP)</b> 	<b>ALDRICH (97%)</b>	<b>278</b>
<b>9,9-BIS(4-HYDROXYPHENYL)FLUORENE (FL)</b> 	<b>NASA, LANGLEY</b>	<b>222-224</b>
<b>4,4'-DICHLORODIPHENYLSULFONE (DCDPS)</b> 	<b>AMOCO CHEMICAL</b>	<b>147-48</b>
<b>4,4'-DIFLUOROBENZOPHENONE (DFB)</b> 	<b>ICI</b>	<b>106-107</b>
<b>BIS(4-CHLOROPHENYL)PHENYL PHOSPHINE OXIDE (BCPPO)</b> 	<b>AKZO CHEMICAL</b>	<b>105-7</b>
<b>BIS(4-FLUOROPHENYL)PHENYL PHOSPHINE OXIDE (BFPPPO)</b> 	-----	<b>124-26</b>

stored under nitrogen in a dessicator.

### 3.2.6 4-tert-butylphenol (tBP)

Also a monofunctional endcapper, this chain terminator was utilized to confirm polymer molecular weights from integration of the t-butyl methyl protons in  $^1\text{H NMR}$ . The 99% purity compound from Aldrich was sublimed once and stored in a dessicator.

### 3.2.7 4,4'-Dichlorodiphenylsulfone (DCDPS)

Similar to BIS A, purification procedures depended on the quality received. As monomer grade material from Amoco Chemical, drying at about  $60^\circ\text{C}$  under vacuum for 4 hours gave sufficiently pure DCDPS. From other sources, this monomer needed to be recrystallized from a concentrated toluene mixture using some charcoal. For example, four liters of a very concentrated solution of DCDPS in boiling toluene was prepared. Next, one liter of toluene was added, along with enough activated charcoal to just darken the mixture. This solution was stirred with refluxing for 2 hours, after which a generous amount of Celite was added to this mixture. Filtration through a Celite pad is not suggested due to crystallization of DCDPS in the funnel. Therefore, another 6 liter Erlenmeyer flask was set up covered with aluminum foil. A large powder funnel was placed into the mouth of this funnel and about 200 ml toluene was added; into the powder funnel was placed a fluted piece of filter paper. The small amount of toluene was refluxed into the powder funnel, and the mixture of DCDPS/Celite/charcoal/toluene was slowly filtered

through this hot funnel. The resulting clear, uncolored toluene solution was reduced to just above the cloud point, then slowly cooled to room temperature. After sitting overnight, large white DCDPS needles or crystals were filtered off, air dried, and vacuum dried at 60°C after being crushed.

#### 3.2.8 4,4'-Difluorobenzophenone (DFB)

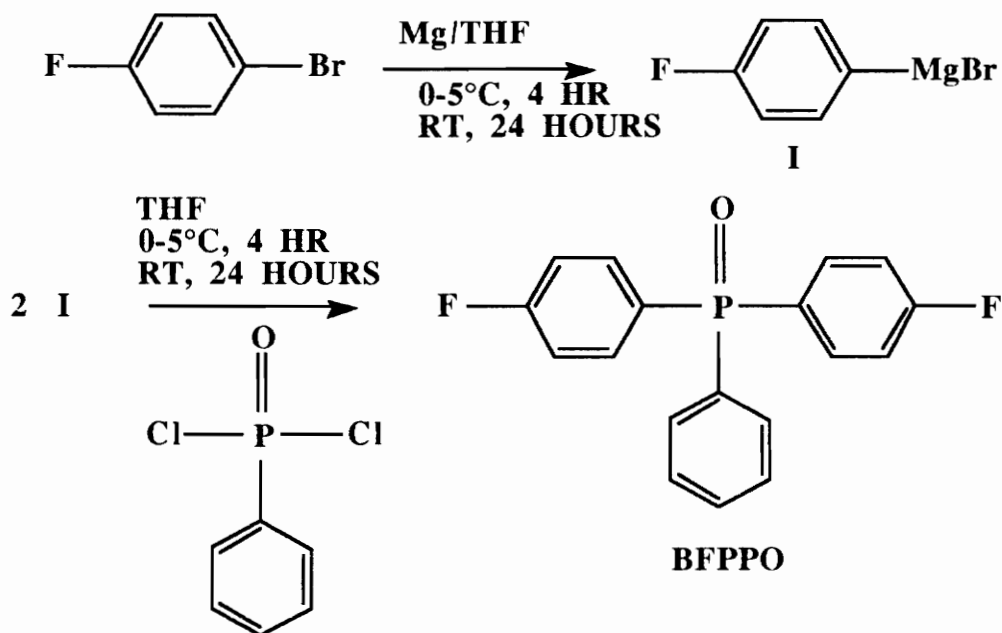
A monomer similar to most of the others discussed thus far, quality depended on source. If monomer grade material was supplied from ICI, only drying at 60°C under vacuum for 4 hours was necessary. However, from any other source, this material had to be carefully recrystallized from mixtures of ether/petroleum ether. The monomer would not crystallize from ether solution alone, so petroleum ether was added to the hot ether solution until a cloud point was reached, followed by addition of just enough ether to clarify the mixture. The solution was slowly cooled to room temperature and allowed to crystallize. Cooling the room temperature mixture further in a refrigerator facilitates crystallization.

#### 3.2.9 Bis(4-chlorophenyl)phenyl Phosphine Oxide (BCPPO)

Acquired as a white powder from Akzo Chemicals, this monomer was reported to be monomer grade. No acceptable purification routes (crystallization, distillation, sublimation) could be determined.

## 3.2.10 Bis(4-fluorophenyl)phenyl Phosphine Oxide (BFPPPO)

Bis(4-fluorophenyl)phenyl phosphine oxide (BFPPPO) was prepared by a variation of known Grignard techniques [241], and purified as



Scheme 28. Preparative method utilized for BFPPPO.

illustrated in Scheme 28. For example, to a flame dried 5l 4-neck round bottom flask fitted with an overhead mechanical stirrer, an addition funnel and a nitrogen inlet were added 85.1g (3.5 mol) magnesium turnings (Aldrich, 99%) and 3.5l dry THF. This solution was cooled with an ice water bath. To this stirred solution was added dropwise at or below 5°C 618.7g (3.5 mol) p-bromofluorobenzene (Aldrich, 99%) over 3-4 hours. This mixture was stirred at room temperature overnight to give a gray slightly cloudy solution. Next, 351.8g (1.75 mol) phenylphosphonic



dichloride (97%) was added dropwise at 5°C over 3-4 hours and this solution was allowed to stir at room temperature overnight to give a yellow clear solution. Enough 10% aqueous sulfuric acid was added to make the solution acidic and about 1 liter of water was added, yielding a homogeneous golden yellow mixture. Diethyl ether was added in order to separate the solution into organic and aqueous phases. The aqueous layer was washed well with ether/THF solutions and all organic layers were combined. This organic solution was washed well with 10% sodium bicarbonate, followed by water washings. The ether solvents were stripped off to give wet product, which was dissolved in toluene and azeotroped for several hours over activated charcoal. This dry solution was filtered through a celite pad and enough toluene removed to give 50% or greater solids by weight. After sitting at room temperature overnight, the large crystals were filtered off, air dried, crushed with a mortar and pestle and dried under vacuum at 70°C. Kugelrohr distillation at 160-70°C and about 1 torr gave a white solid which could be removed from the receiving flask in one of two ways : melting with a heat gun or refluxing toluene through the receiving flask as shown in Figure 5. The crystals were collected and redistilled, typically giving overall yields around 70-80% of monomer grade material with melting point of 124-26°C.

Several refinements in this technique have been found which will save time and use of much ether solvents. After running the reaction as described before, if the correct amount of water was added to the reaction mixture after hydrolysis, two layers would form, thus saving

much time in extractions. For example, in a 2.56 mole preparation of BFPPO (5l THF used), after the reaction, exactly two liters of water were added, whereupon the mixture separated into two layers after stirring, probably due to the high ionic content of the aqueous phase.

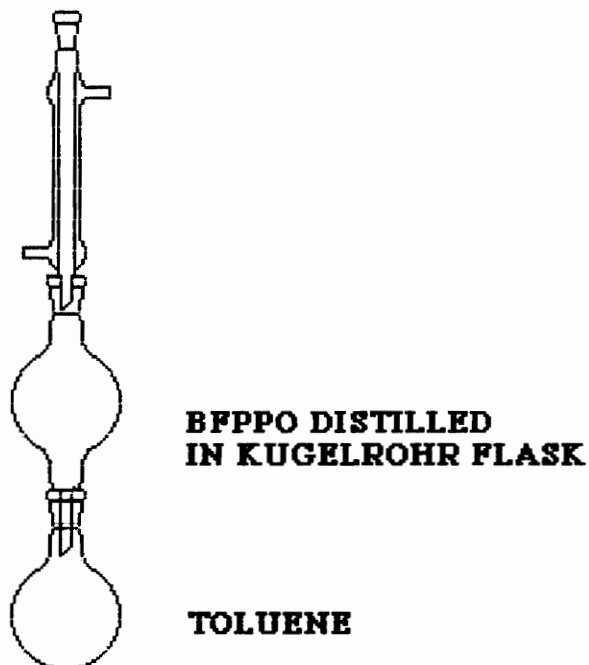


Figure 5. One method used for removal of BFPPO from Kugelrohr flask.

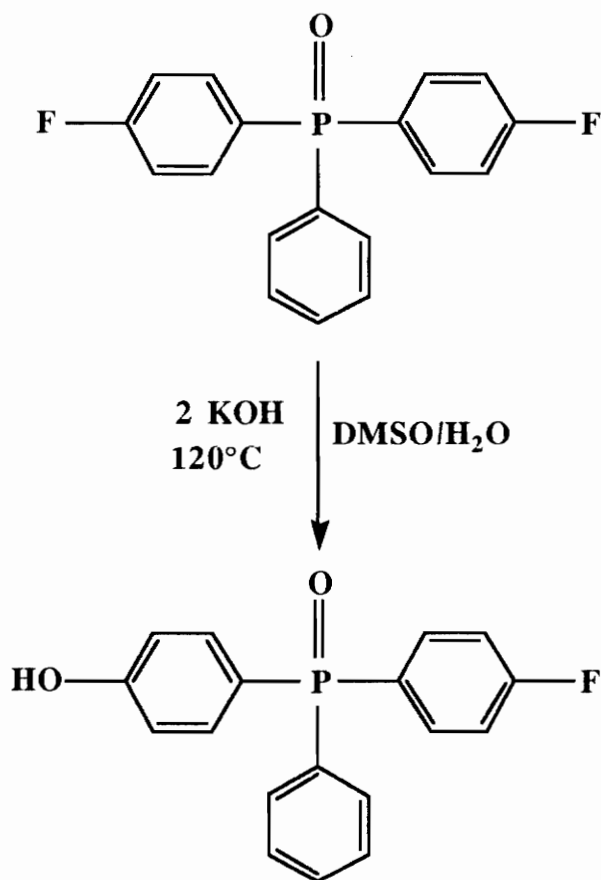
Thus, the THF layer was decanted, the water layer washed well with ether/THF mixtures, and all organic layers combined. Also, no further washings of the organic phase were necessary. After azeotroping off the water from the wet toluene mixture and removing all of the toluene, it was found that the impurities did not interfere in the distillation of the crude monomer, as they stayed behind. The most efficient way of removing BFPPO from the Kugelrohr receiving flask was by melting the material and allowing it to drip onto a large sheet of teflon.

### 3.2.11 Bis(4-fluorophenyl)methyl Phosphine Oxide (BFMPO)

This product was prepared in exactly the same manner as BFPPPO, with one major exception. After one distillation, it was found that this monomer sublimed quite nicely around 100°C and 1 torr giving white crystalline materials in about 60% yields. The melting point was 112-14°C.

### 3.2.12 4-Hydroxyphenyl-4'-fluorophenyl Phenyl Phosphine Oxide

A monomer of the AB type, this compound was prepared from BFPPPO in aqueous DMSO and potassium hydroxide, similar to procedures reported for 4,4'-difluorodiphenylsulfone [38] yielding 4-fluorophenyl-4'-hydroxyphenylsulfone. As illustrated in Scheme 27 below, this process required the use of aqueous concentrated KOH solutions with DMSO. Excess KOH can be utilized due to the "bridge effect" discussed earlier in the background [29]. For example, 10 g (0.0318 mol) BFPPPO, 30 ml DMSO, and 3.8 g of a 50 weight % aqueous solution of KOH were added to a 3 necked 100ml round bottom flask equipped with a condensor, a thermometer and a nitrogen inlet. A magnetic stir bar was added and the reaction was run at 120°C. This substitution reaction was conveniently followed by thin layer chromatography (TLC), using 50% ethyl acetate/ 50% toluene as the mobile phase. Typically, the disappearance of BFPPPO was followed by this method by taking very small samples from the mixture over time and running this TLC together with a BFPPPO control. If complete reaction had not occurred after about 6-8 hours, another 3.8 g of the 50% KOH solution was added.



Scheme 29. Synthetic process used for the preparation of 4-hydroxyphenyl-4'-fluorophenyl phenyl phosphine oxide.

When no more BFPPPO was observed by TLC, the mixture was poured slowly over 250 g ice and allowed to stir until room temperature was reached. Any small amounts of unreacted BFPPPO precipitated in water and could be removed by filtration through a fairly thick pad of Celite. Next, the mixture was slowly acidified to pH 5 to precipitate the fluorophenol. White flakes readily formed upon addition of 25% aqueous HCl. The white precipitate was filtered off and washed with generous

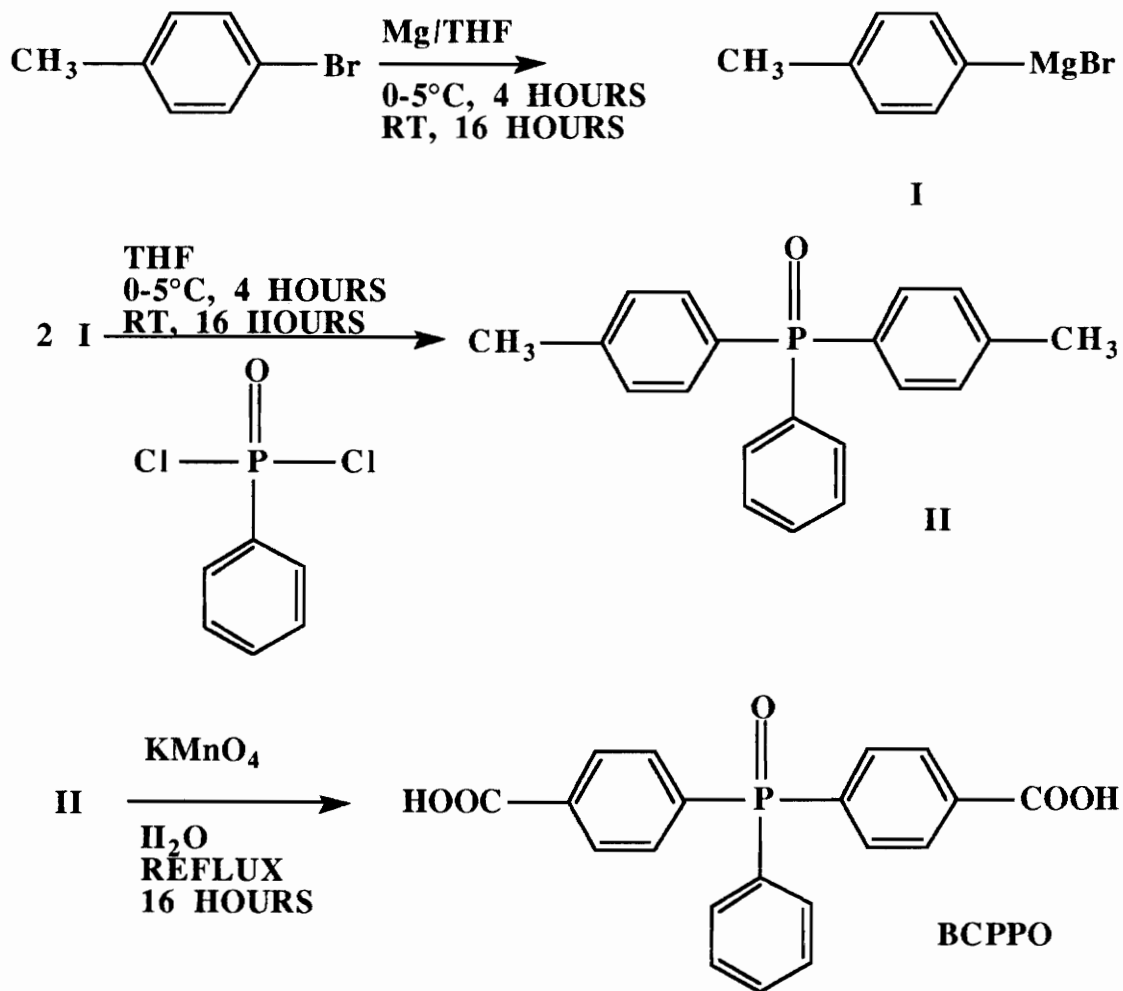
portions of water. This product was vacuum dried at 100°C yielding 8.5 g (86%) of a white powder with a melting point of 195-208°C. Kugelrohr distillation of this product gave about 4 g of a white crystalline solid with melting point of 218-221°C. No literature melting point is available for this product.

### 3.2.13 Bis(4-carboxyphenyl)phenyl Phosphine Oxide

In order to prepare a sample polyester material containing the phosphine oxide moiety, a phosphine oxide containing diacid was prepared. Using a procedure similar to that of Morgan and Herr [194], the diacid was synthesized according to Scheme 30. A Grignard procedure identical to that for BFPPPO was utilized for the preparation of bis(4-methylphenyl)phenyl phosphine oxide, **II**, with the use of *p*-bromotoluene. The resulting bismethyl substituted material could also be purified according to the procedures used for BFPPPO, by Kugelrohr distillation at approximately 190°C and 1 torr. Only upon sitting undisturbed for long periods of time would this dimethyl product crystallize, as it distilled as a very viscous slightly yellow oil/glass. Addition of this material to hexanes and stirring caused some solidification, but the material was still at best a waxy solid. Yield of distilled oil was nearly the same as BFPPPO, about 75%.

Oxidation of this oil by classic basic aqueous potassium permanganate procedures was then carried out as follows. To a one necked 2 liter round bottom flask were added 28g (0.0914 mol) bis(4-methylphenyl)phenyl phosphine oxide, 1.4 liters H<sub>2</sub>O, 8.0g NaOH, and

121.5g  $\text{KMnO}_4$  (0.81 mol). This purple mixture was refluxed overnight to give a dark brown solution, which was cooled and filtered through celite



Scheme 30. Preparation of phosphine oxide containing diacid by Grignard route followed by oxidation.

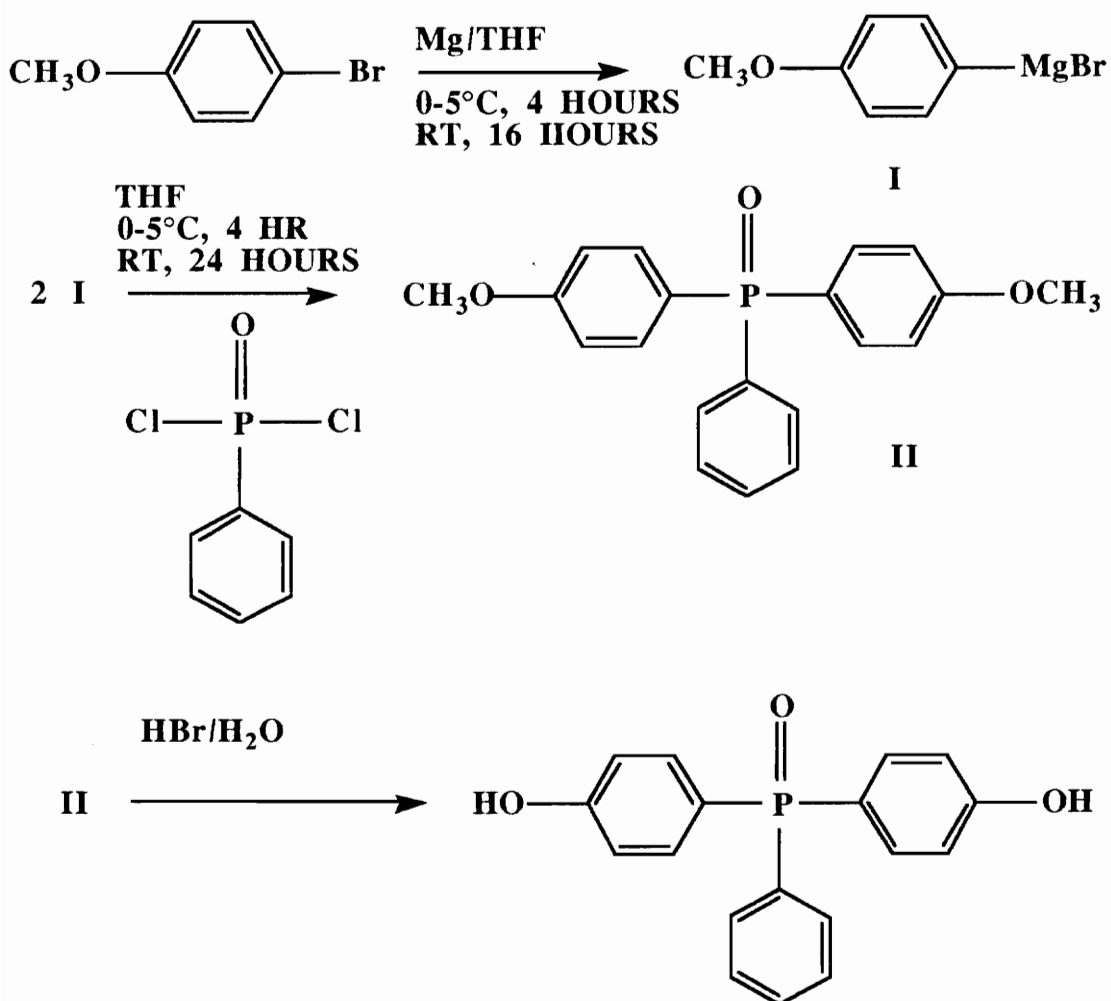
to remove the  $\text{MnO}_2$ . The Celite pad was washed with generous portions of hot water. This basic solution was slowly acidified with 15% aqueous  $\text{HCl}$ . A peach colored solid (17g) was isolated and washed well with

water. An additional 6g could be recovered by reduction of the mother liquor for a total yield of 70%. Yields of 80% could be obtained by the use of pyridine/water cosolvents in the oxidation procedure. These compounds were vacuum dried at 100°C. The melting point of this monomer was 324-26°C as compared to 335°C from the literature [194].

#### 3.2.14 Bis(4-hydroxyphenyl)phenyl Phosphine Oxide (BHPPPO)

Another route for the synthesis of poly(arylene ether phosphine oxide)s was to prepare a bisphenol containing the phosphine oxide moiety. Utilizing procedures discussed in the background [206-7] and illustrated in Scheme 31, a Grignard process giving the dimethoxy compound followed by acid hydrolysis to the bisphenol was a tedious method to produce this diphenol in monomer grade purity due to crystallization difficulties. Nevertheless, a procedure is given below.

Similar to BFPPPO and BCPPPO, the initial carbon-phosphorus bond forming step was via a Grignard procedure between PPD and p-bromoanisole. Each step for the preparation of the bismethoxy compound was identical to that of the bisfluoro compound, however, distillation failed due to excessive foaming. Crude yield was about 90%. Hydrolysis was performed as follows. The unpurified oil was taken up in a ten fold excess of aqueous hydrobromic acid and refluxed for at least 24 hours. This mixture was slowly poured over ice water and the product filtered off. After several washings with water and drying, a tan to yellow powder was obtained. Recrystallization from methanol three times gave a nearly white crystalline solid with melting point of 233-36°C.

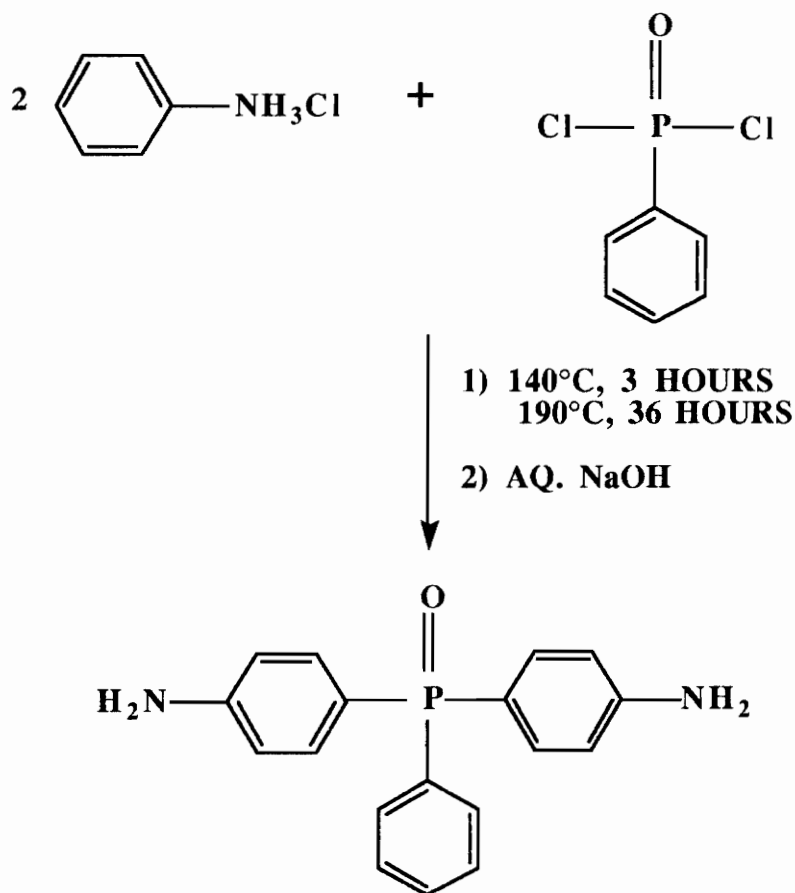


Scheme 31. Synthesis of BHPPO.

## 3.2.15 Attempts at Bis(4-aminophenyl)phenyl Phosphine Oxide (BAPPO)

As discussed in the background, a simple reported procedure [214] for the preparation of this diamine was attempted as shown in Scheme 32. A direct translation was utilized for this procedure. Into a 100 ml two necked round bottom flask were added 25g (0.1282 mol) phenylphosphonic dichloride and 38.2g aniline hydrochloride (0.295 mol). Under a constant stream of nitrogen, the reactants were heated with stirring to 140°C for four hours, then at





Scheme 32. Reported synthesis of BAPPO [214].

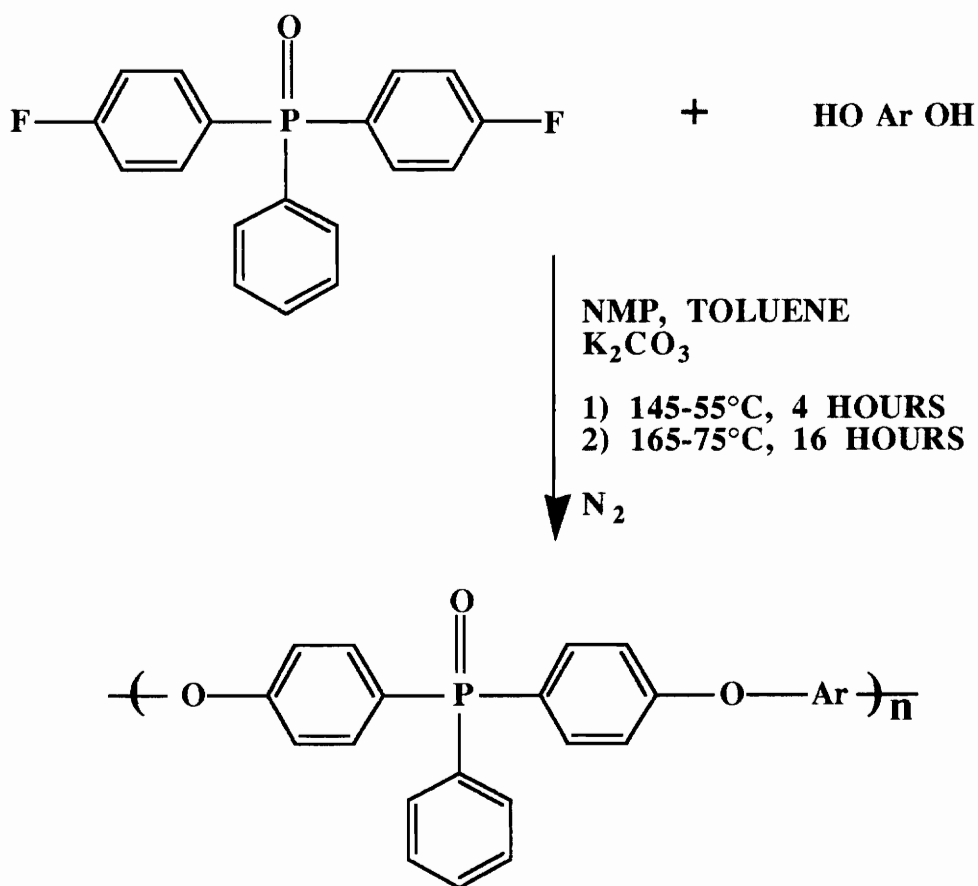
190°C for 35 hours. The resulting brown viscous melt was cooled, crushed and stirred with aqueous sodium hydroxide. Washing with water and drying under vacuum at 100°C yielded a tan powder (25g, 50%). Next, this solid was dissolved in just enough boiling 95% ethanol to dissolve it (about 400-425 ml), treated with charcoal, filtered through Celite and reduced to 200 ml. Crystallization of a solid material (7.5 g) followed which was filtered and dried. A second crop afforded about 2.5 g, for a total yield of crystallized monomer of 40%. The dried monomer had a melting point of 212-14°C (lit. [214] 220-21°C). As will be discussed in the

results section, this material was later unfortunately found to be the diamide from the simple addition of aniline to phenylphosphonic dichloride.

### 3.3 SYNTHESIS OF POLYMERS

#### 3.3.1 High Molecular Weight Poly(arylene ether phosphine oxide)

The preparation of a high molecular weight BIS A based poly(arylene ether phosphine oxide) will be used to illustrate (Scheme 33) representative procedures employed. A 250 ml 4-necked round bottom flask, equipped with an overhead stirrer, a nitrogen inlet, a Dean-Stark trap with condenser, and a thermometer, was charged with 5.707g (0.025 mol) BIS A and 7.856g (0.025 mol) BFPPPO. The teflon coated pans from which the monomers were transferred were rinsed well into the flask with NMP, for a total volume of 90 ml NMP. A 15% excess of  $K_2CO_3$  (4.15g, 0.03 mol) and 45 ml toluene were added to the reaction mixture. A constant purge of nitrogen was maintained and the temperature was controlled by a high temperature silicone oil bath. The water and toluene azeotrope formed at about 150-155°C and the system was allowed to dehydrate about eight hours. Next, the temperature of the mixture was raised to 170°C and held there for about sixteen hours. The solution was a dark brown viscous mixture with a white inorganic salt suspension. Finally, the mixture was allowed to cool until just warm, diluted with chloroform, and filtered through a Buchner funnel to remove the inorganic salts. Glacial acetic acid was



Scheme 33. Preparative route to high molecular weight PEPO.

utilized to neutralize the solution to afford a viscous clear brown to amber mixture. This solution was precipitated in a 80:20 methanol:water mixture in a high speed blender to yield a nearly white highly fibrous material. The polymer was dried at 100°C in a vacuum oven overnight, redissolved in chloroform, filtered, neutralized, reprecipitated in methanol and dried again under the same conditions. This polymer was soluble in chloroform, methylene chloride, tetrahydrofuran and dipolar aprotic solvents.

### 3.3.2 Controlled Molecular Weight Poly(arylene ether phosphine oxide)

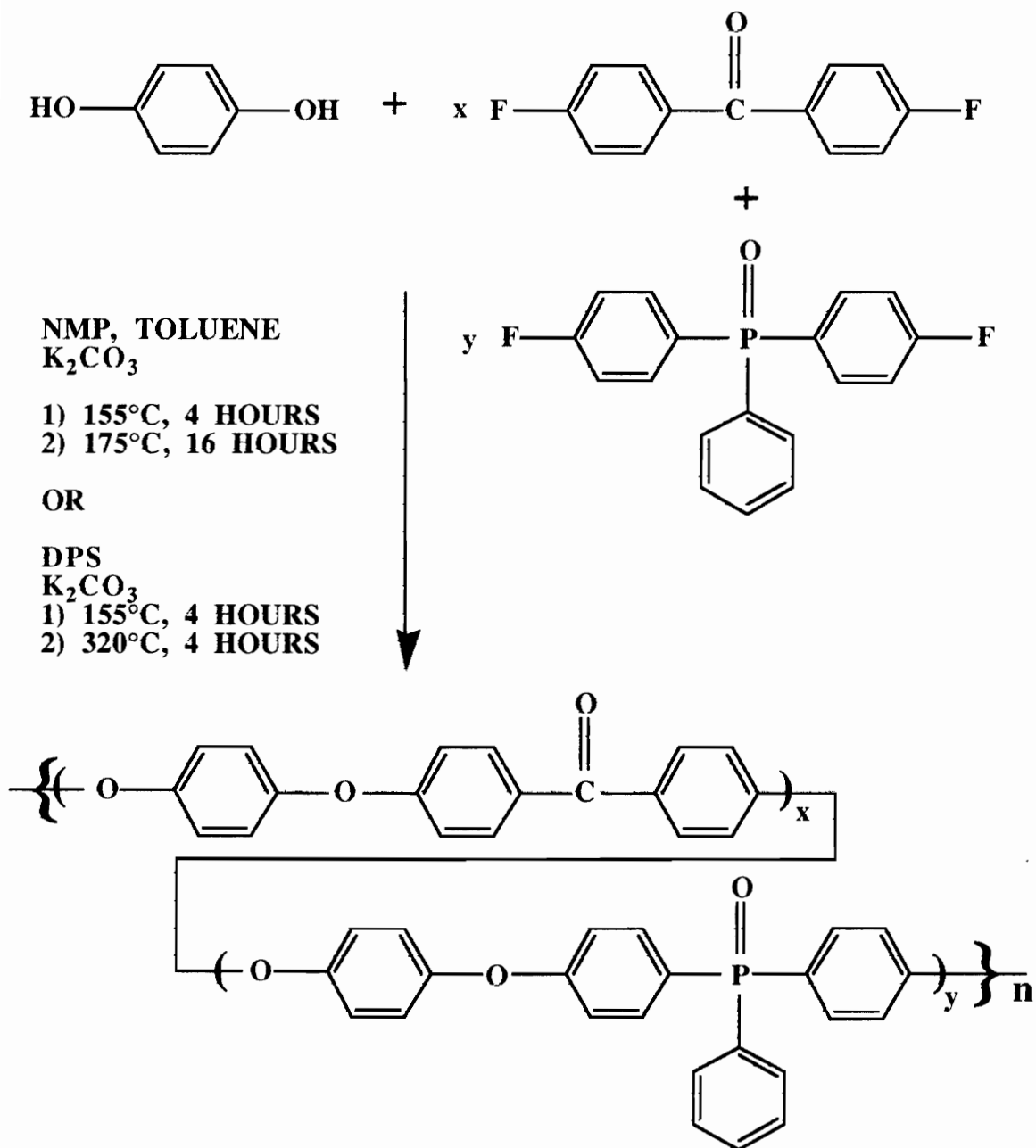
From Appendix 1, the control of molecular weight was most conveniently performed by addition of a monofunctional endcapper, typically a substituted phenol. For example, if amine functionality was desired, *m*-aminophenol was utilized. A series of *t*-butyl terminated poly(arylene ether phosphine oxide)s were prepared to confirm molecular weight control via  $^1\text{H}$ NMR measurements. The procedure for preparing these controlled molecular weight oligomers was identical to that for the synthesis of high molecular weight PEPO, with the only exception being addition of a calculated amount of end-capper, as described in Appendix 1. The list below gives amounts of biphenol (BP) and *t*-butylphenol (*t*-BP) calculated from the equations in Appendix 1 used in the synthesis of a series of biphenol based PEPO materials using a constant 3.0000g (0.0095456 mol) BFPPPO. According to the same procedure above, 33 ml DMAc and 20 ml toluene were utilized as the solvent system, while 1.52g  $\text{K}_2\text{CO}_3$  was added.

<u>MOLECULAR WEIGHT THEORY (<math>M_n</math>)</u>	<u>r</u>	<u>moles BP</u>	<u>moles t-BP</u>
5000 g/mol	0.9119602	0.0087052	0.001763
10000 g/mol	0.95499	0.009116	0.0008796
15000 g/mol	0.969766	0.009257	0.0005863
20000 g/mol	0.977239	0.0093283	0.0004396

### 3.3.3 High Molecular Weight Random Copolymer

Some crystallinity could be incorporated into PEPO materials by the

copolymerization with 4,4'-difluorobenzophenone (DFB), BFPPPO and either biphenol or hydroquinone as the bisphenol, as Scheme 34 illustrates. These materials could be prepared in NMP with HQ up to the 50:50 mole ratio between DFB:BFPPPO, past which diphenylsulfone was utilized as the solvent. Procedures for these copolymers were slightly different than for the PEPO homopolymers due to solubility differences between the homo- and copolymers. Thus, as an example of copolymer synthesis, the preparation of a 50 mol% DFB/50 mol% BFPPPO material will be described. A 250 ml four necked round bottom flask was fitted with an overhead mechanical stirrer, a nitrogen inlet, a Dean-Stark trap with condenser and a thermometer. Into this flask were added via teflon coated aluminum weighing pans 3.0000g (0.00955 moles) BFPPPO, 2.0829g DFB (0.00955 moles), 2.1022g HQ (0.0191 moles), 3.04 g  $K_2CO_3$  (0.0191 moles plus 15% excess), 60 ml N-methylpyrrolidone (NMP) and 45 ml toluene. The reaction flask was quickly heated to reflux temperature ( $150^{\circ}C$ ) with a high temperature silicone oil bath and a water/toluene azeotrope formed. The water was collected in the Dean-Stark trap over a period of at least four hours, in which the reaction mixture changed from a clear yellow color to a gray color. Next, the temperature of the reaction was brought to about  $175^{\circ}C$  with removal of toluene and kept at this temperature at least 16 hours to yield a very viscous brown solution. Enough NMP was added to the solution to transfer it from the reaction flask to a high speed blender containing about 1.5 L of a 80:20 (by volume) methanol:water mixture. The polymer precipitated as thick fibers which were gray to tan in color. This material was washed well with methanol,



Scheme 34. Preparation of random poly(arylene ether ketone)-poly(arylene ether phosphine oxide) copolymers.

then added to 1 L hot water and stirred for three hours. Much of the brown color extracted into the water over this period of time, along with any inorganic salts from the reaction byproducts. Drying at 120°C in vacuo overnight yielded fibers which were soluble only in boiling NMP and insoluble in chlorinated solvents and ethers.

The procedures for the other compositions were the same except for the different relative amounts of reactants. Note that any composition richer than 50 mole % DFB must be prepared in the high boiling solvent diphenylsulfone. If this is the case, similar workup procedures to those described above were employed, except the mixture was poured, while still melted, into 50/50 methanol/water, filtered, washed with ample amounts of methanol. Next the material was stirred in hot water for several hours, filtered, washed with water, and stirred again in warm methanol to remove diphenylsulfone. Finally, the polymer was filtered and washed with methanol, then dried at 100°C in a vacuum oven. If any diphenylsulfone was noted to be subliming on the oven window or in the drying dish, the washing steps above were repeated.

#### 3.3.4 Polymerization of the AB Monomer

These types of polycondensations presented a much simpler reaction "recipe" with only one monomer being present. As illustrated in Scheme 35, the reactions of the halogenophenols of both the sulfone and phosphine oxide families were quite similar except for one important difference, that of reactivity. The salt formed from the AB sulfone monomer has been reported to not be reactive enough in NMP to give high

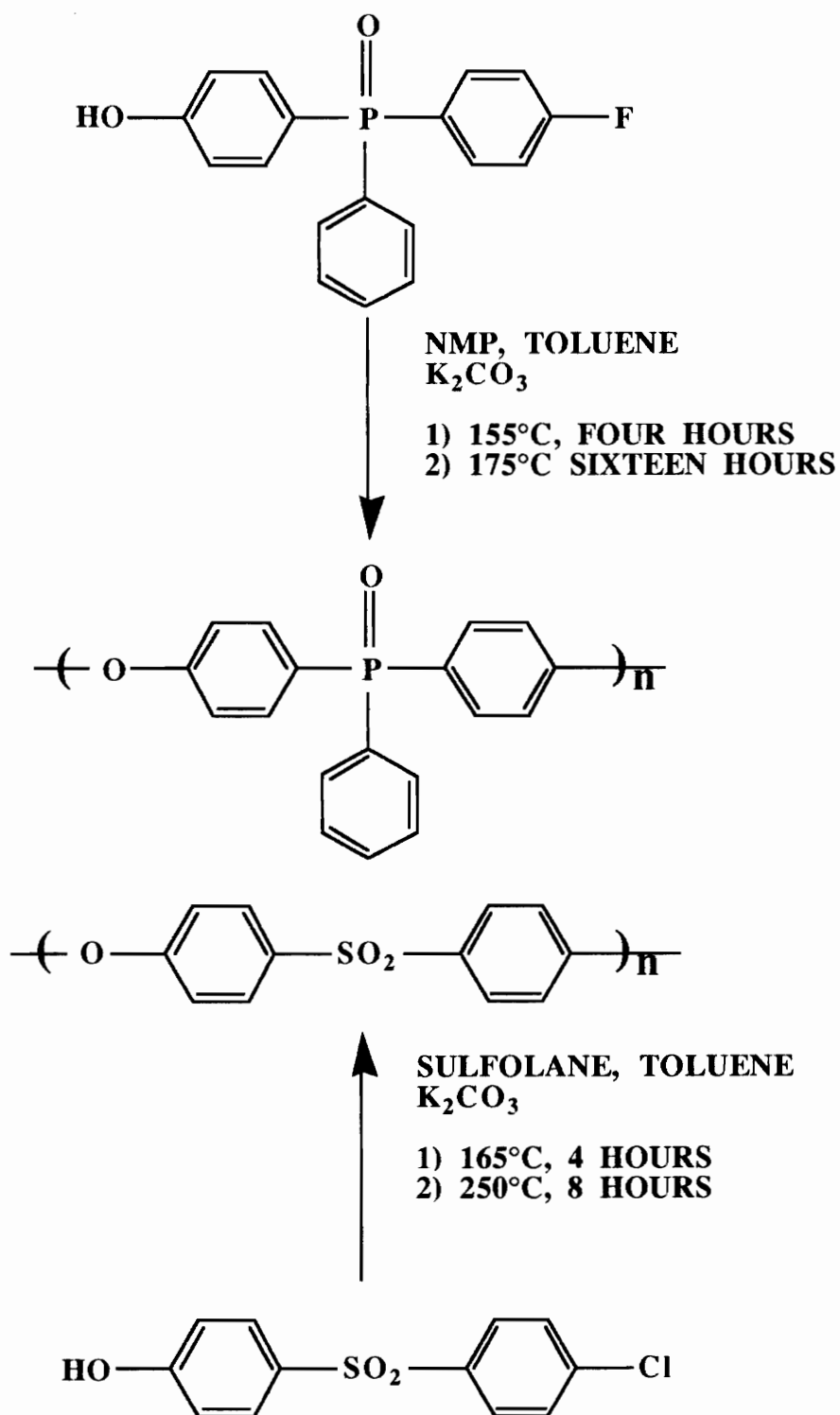
polymer, while the material from the phosphine oxide containing monomer was reactive in this lower boiling solvent. Thus, either DMAC or NMP could be applied as solvents for the phosphine oxide system. A representative procedure is described for the PEPO material.

Into a 250 ml 4-necked round bottom flask were added 5.0000g (0.016 mol) 4-fluorophenyl-4'-fluorophenyl phenyl phosphine oxide, 33 ml NMP, 20 ml toluene and 1.3g  $K_2CO_3$  (0.0092 mol). This mixture was heated to azeotrope temperature (about 155°C) and held there four-six hours. Next, the temperature was raised to 175°C for sixteen hours. Workup was identical to that previously discussed for the high molecular weight materials, yielding off white fibers which were dried at 100°C in a vacuum oven. This material (intrinsic viscosity 0.2 dL/g in methylene chloride) was soluble in aprotic dipolar solvents and chlorinated solvents.

### 3.3.5 Melt Transesterification Polycondensation

As shown in Scheme 36, a polyester derivative containing the phosphine oxide moiety was desired for comparative reasons. Thus, 5.00g (0.01365 mol) bis(4-carboxyphenyl)phenyl phosphine oxide and 4.69g (10 mol% excess due to sublimation) Bisphenol A diacetate were added to a melt reactor with high torque overhead stirrer, nitrogen inlet and condensor. Ten ml chlorobenzene was added to homogenize the mixture at 220°C for 24 hours; however, the diacid was not soluble in chlorobenzene and considerable bumping occurred. Slowly, chlorobenzene was allowed to escape the reaction, in order to keep most of the diacetate from



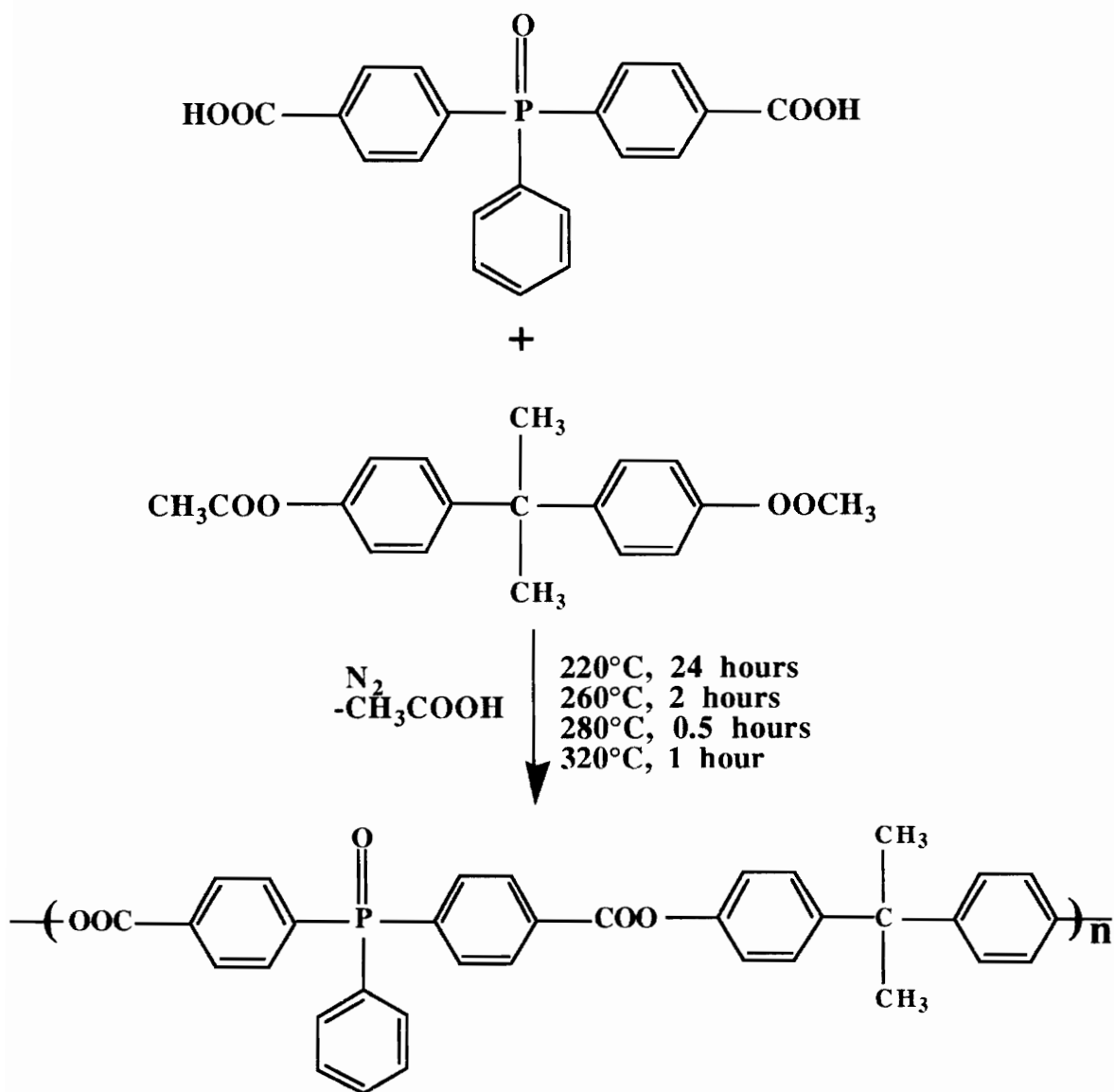


Scheme 35. Polymerization of AB monomers.

subliming. Once a homogeneous melt was formed, the reaction temperature was raised to 260°C for two hours. Soon after this temperature increase, the material solidified and the temperature was raised to 280°C and a vacuum was applied. The polymer again solidified, so again the temperature was raised to 320°C for one hour with vacuum. A very viscous brown mixture resulted, which was cooled and taken out of the flask. The brittle brown glassy solid was soluble in many solvents and was of low molecular weight (intrinsic viscosity of 0.1 dL/g in methylene chloride).

#### 3.4 PREPARATION OF POLYMER BLENDS

For the blending studies, the PEPO materials were prepared as described previously. Both the PEEK and PEPO polymers were dried at 120°C for at least 48 hours in vacuo prior to blending. Melt blends were prepared in a Haake-Buchler Rheomix blender. The two components were quickly weighed and transferred to the preheated blender (360°C). After seven minutes of intensive shear mixing, during which time the temperature exothermed to 400-425°C, the melt was rapidly removed and placed in a preheated (360°C) hydraulic press between clean ferrotype plates treated with high temperature release agent. The material was allowed to flow under no pressure for about 15 minutes, after which 10 ksi pressure was applied and kept for 10 minutes. Films, still between ferrotype plates, were quenched into ice water to give clear amber films which were amorphous in nature.



Scheme 36. Transesterification polycondensation of phosphine oxide containing aromatic diacid with Bis A diacetate.

### 3.5 PREPARATION OF METAL COMPLEXED POLY(ARYLENE ETHER PHOSPHINE OXIDE) FILMS

Once the desired composition of metal to polymer ratio was determined, the appropriate materials were weighed into a clean vial by the following equation for the amount of metal halide to use.

$$\frac{(\text{Mass of polymer used})}{(\text{Molecular weight of PEPO repeat unit})} * \frac{(\text{Mole \% metal desired})}{(100)} * \text{Formula weight metal halide} = \text{grams metal halide to use}$$

For example, for 30 mole %  $\text{CuCl}_2$  in PEPO, the following compounds were weighed into a cleaned 20 ml vial: 1.0 g 20,000g/mol t-butyl endcapped BP PEPO (molecular weight repeat unit = 460.472 g/mol) (1 g = 0.002172 moles P=O units), 0.111 g  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.00065 mol), and 7.5ml DMAC (15% solids). This solution was stirred until homogeneous, then poured onto an appropriate surface for casting thin films (glass plate, aluminum pan, etc.) and placed in a room temperature vacuum oven. A vacuum was applied at room temperature for several hours until degassing was complete (no more bubbles). Slowly, the temperature was raised over eight hours to 150°C, and kept there sixteen hours to yield clear yellow/green films with the same visible properties as the unmodified PEPO film prepared by the same method. The other metal modified films were prepared in analogous procedures. Sulfone containing polymers did not give good quality films, as the metal salts appeared to precipitate from the solvent mixture and many bubbles and voids were formed.

### 3.6 CHARACTERIZATION METHODS

#### 3.6.1 Infrared Spectroscopy

Fourier transform infrared spectra were obtained with a Nicolet MX-1 instrument. Polymer spectra were taken as films on KBr windows while monomers were taken from windows prepared by grinding the monomer of interest with dry powdered KBr, and appropriately pressing into pellets in a FTIR window apparatus.

### 3.6.2 Nuclear Magnetic Resonance Studies

#### 3.6.2.1 Proton NMR

Proton ( $^1\text{H}$ ) NMR spectra were taken on a Varian 400 MHz instrument normally in  $\text{CDCl}_3$  or deuterated DMSO when necessitated by solubility. All spectra were referenced to tetramethylsilane (TMS) at 0 ppm.

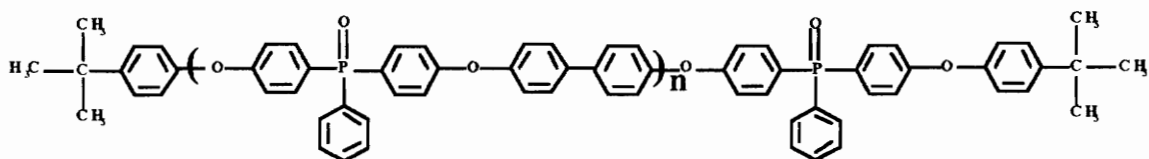
This method was also used to calculate the number average molecular weight ( $M_n$ ) of t-butyl terminated BP based PEPO materials as follows. In  $\text{CDCl}_3$ , the endgroup methyl protons fall between 1.3 and 1.4 ppm, while the polymer and endgroup aromatic protons appear between 7.0 and 7.8 ppm. These sets of peaks were integrated, with special precautions taken to exclude from the integration process the peak at 7.24 ppm corresponding to the chloroform proton. The equations below can be utilized for the calculation of  $M_n$ .

Integrated Aromatic Region #/Integrated Aliphatic Region # =

# Aromatic Protons per chain/# Aliphatic Protons per chain = # Aromatic Protons per chain/18

If  $n$  = # repeat units,  $Z$  = # aromatic protons in repeat unit and  $Y$  = #

aromatic protons in end groups, then for the polymer below



# Aromatic protons/18 = (Z\*n + Y)/18 = (21\*n + 21)/18 = ratio from NMR

Therefore, from the integrated values from  $^1\text{H}$ NMR, the number of repeat units can be solved for. Next, n was multiplied by the repeat unit molecular weight (460.472 g/mol) and the molecular weight of the endgroups (574.7 g/mol) was added to give the  $M_n$  of this polymer.

### 3.6.2.2 Carbon NMR

Carbon ( $^{13}\text{C}$ ) NMR spectra were taken in the same manner as the proton spectra were.

### 3.6.2.3 Phosphorus NMR

Phosphorus ( $^{31}\text{P}$ ) NMR spectra were also taken on the Varian 400 MHz instrument in a variety of solvents, since deuterated solvents need not be used ( $^{31}\text{P}$  is naturally occurring isotope) and solvent effects were not important. Nevertheless, when comparisons were needed, compounds were run in the same solvents. All spectra were referenced to  $\text{H}_3\text{PO}_4$  at 0 ppm.

### 3.6.3 Intrinsic Viscosities

Intrinsic viscosities were measured at 25°C in Ubbelohde viscometers, typically using methylene chloride as polymer solvent. Where solubility was a problem, NMP was utilized as the viscosity solvent. Procedures were as follows. Three polymer solutions of low polymer concentrations were prepared and the times measured for 1) the polymer solutions ( $t$ ) and 2) the pure solvent ( $t_0$ ) to pass through the viscometer path. Assuming  $t/t_0 = \eta/\eta_0$ , then the specific viscosity was defined as  $\eta_{sp} = (\eta/\eta_0) - 1$  and the reduced viscosity as  $\eta_{red} = \ln(\eta/\eta_0)$ . Next, both  $\eta_{sp}$  and  $\eta_{red}$  divided by concentration were plotted against concentration and extrapolated to zero concentration to give intrinsic viscosity  $[\eta]$ .

#### 3.6.4 Titration of Functional Oligomers

In efforts to determine the molecular weight of amine functional PEPO materials, a titration technique was utilized. A MCI GT-05 Automatic Titrator (COSA Instruments Corp.) was used with approximately 0.025M HBr solutions in glacial acetic acid. The HBr titrant was standardized with potassium hydrogen phthalate prior to use. In order to conserve titrant, titrations were set up to use approximately four to six ml HBr solution. At least three samples were titrated and the average molecular weight taken. The solvents used for amine end group titrations was chloroform or methylene chloride. To calculate the amount of polymer to use for 4-6 ml HBr, the following simple calculation was performed.

0.025 mol/L HBr = 0.00025 mol/ml; if four ml HBr use desired, then  
4ml \* 0.00025 mol/ml = 0.0001 mol titrant used in 4 ml; thus 0.0001 mol  
amine groups will titrate 4 ml; two amines per polymer chain, so 0.00005  
mol polymer will titrate 4 ml.

Thus, for a theoretical 5000 g/mol amine terminated PEPO,  $5000 * 0.00005$   
= 0.25g polymer used should titrate approximately 4 ml. Results agreed  
within  $\pm 1000$  g/mol Therefore another convenient method for the  
calculation of amine functional polymer number average molecular weight  
was available.

### 3.6.5 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed on a DuPont  
912 instrument. The reported glass transition temperatures ( $T_g$ 's) 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  
 $10^\circ\text{C}/\text{min}$  and the reported  $T_g$  values were from the second run, after a  
quench cool from the first run, unless otherwise noted. This procedure  
insures little effect of prior thermal history on the  $T_g$ 's.

### 3.6.6 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out on a DuPont 951  
instrument routinely utilizing heating rates of  $10^\circ\text{C}$  per minute in air,  
unless otherwise noted. When comparisons were made between samples,  
similar sample forms were compared. For example, powders were compared



to other powders, films to films, etc.

### 3.6.7 Thermomechanical Analysis (TMA)

Thermomechanical analysis (TMA) was performed on a Perkin-Elmer model TMA-7 instrument both in the expansion and penetration modes. Heating rates of 10°C per minute were utilized and 0-5 mN and 200-500 mN forces were used for expansion and penetration experiments, respectively. Coefficients of thermal expansion from expansion runs are reported in the low temperature range (30-60°C) while  $T_g$ 's are reported from both types experiments as the onset temperature determined from the computer.

### 3.6.8 Dynamic Mechanical Thermal Analysis (DMTA)

These investigations were measured on a Polymer Laboratories instrument at 1Hz and 5°C per minute on about 2 mil thick compression molded bars of the desired material, unless otherwise noted. The pressed bars were obtained by first heating to 50-75°C above the  $T_g$  between heated plates with Teflon interliners for release purposes, allowing the material to flow for about five minutes, then applying pressure to the material for approximately 10 minutes, followed by quench cooling of the sample. Storage moduli ( $E'$ ) and loss tangent ( $\tan \delta$ ) values were recorded.

### 3.6.9 Dielectric Thermal Analysis (DETA)

Dielectric thermal analyses experiments were also performed on a

Polymer Laboratories instrument. Frequencies of 1, 10 and 100 KHz at a heating rate of 3°C per minute using 22 mm electrodes on solution cast and dried thin films which were gold sputtered on the surfaces.

#### 3.6.10 Stress-Strain Measurements

Stress-strain analyses were carried out on an Instron Series IX Automated Materials Testing System on dogbone shaped samples which had been compressed into films at least 40°C above their T<sub>g</sub>. The crosshead speed was 0.1 in/min.

#### 3.6.11 Pyrolysis Studies

All samples were pyrolyzed in air at 600 and 700°C with a quartz tube/ furnace pyrolysis unit. Volatile pyrolysates were condensed at about -100°C at the front of a 30m DB-5 fused silica capillary column. The oven temperature, initially at -100°C for 3 minutes, was programmed at 20°C/min to 0°C and then 7°C/min to 300°C. Three minutes after the onset of pyrolysis, spectra covering a range of m/z 33 to 650 were obtained by scanning every second. Only the 600°C pyrograms are shown, the only difference between the 600 and 700°C pyrolysis being minor intensity differences in the different products formed. Product identities were confirmed based on substantial model compound studies at Philip Morris USA.

#### 3.6.12 Oxygen Plasma Conditions

A Plasmod plasma chamber from the Tegal Corp. was utilized as the

oxygen plasma atmosphere for the etching experiments. A 13.56 MHz radio frequency generated oxygen plasma operated at 50W of power and a pressure of approximately 1.2 torr were the specific parameters of this chamber.

### 3.6.13 Ellipsometric Studies of Thin Films and Etching Experiments

Ellipsometry was the technique used to measure the thickness of very thin spin coated polymer films on ferrotype plates before and during the plasma etching process. A Gaertner Dual Mode Automatic Ellipsometer Model L116A was utilized. The ferrotype (chrome plated steel from Thompson Photoproducts) plates were first cleaned by treatment in the oxygen plasma at the conditions listed above for 20 minutes to generate a stable oxide layer. Next, the plates were subjected to a deionized water and an acetone rinse. This plasma treatment followed by solvent scrubbing was repeated for each plate. The plates were then dried at room temperature under a nitrogen flow. Optical constants were then determined on the cleaned plates with ellipsometry. Spin coating techniques were employed to generate very thin films (ca. 800-1800Å) on the ferrotype plates from dilute solution, normally in the range 1-4% (w/v) from a variety of acceptable solvents, such as methylene chloride, chloroform, or chlorobenzene. Drying was accomplished in a vacuum oven at 50°C for the low boiling solvents and 100°C for chlorobenzene.

Film thicknesses were measured from at least four spots. Measurements were taken at 30°, 50° and 70° angles of incidence and reflection to guarantee that small refractive index changes on the

surface due to plasma treatment did not give rise to significant errors in measurements. The thin films were subjected to the oxygen plasma for different periods of time, initially for one minute, then an additional two, then three, etc., up to a five minute treatment; thus, each sample was in the plasma for a total of fifteen minutes. Between each plasma treatment, ellipsometry was used to measure film thickness. It was observed that any treatment in excess of about five minutes at one time gave rise to unacceptable heating effects of the ferrotype plate. Representations of the data were plotted as percent polymer film height remaining as a function of time, based on an initial height of 1000Å.

#### 3.6.14 X-ray Photoelectron Spectroscopy (XPS)

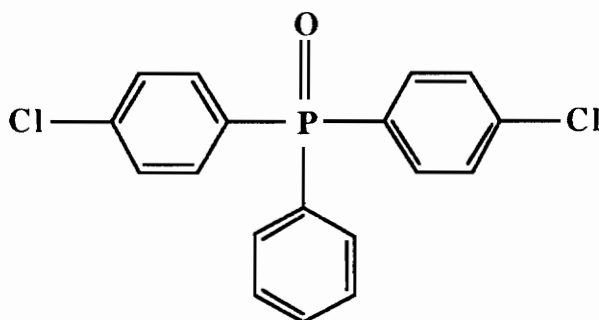
XPS analysis was performed using a Perkin-Elmer PHI 5300 spectrometer employing a MgK $\alpha$  (1253.6 eV) achromatic x-ray source operated at 15 KeV with a total power of 400 watts. Typical operating pressures were  $< 1 \times 10^{-7}$  torr and the surface area analyzed was either a 1 mm circular spot or a 1 x 3 mm rectangle. The spectrometer was calibrated to the 4f (7/2) photopeak of gold at 83.8 eV and the 2p (3/2) photopeak of copper at 932.4 eV, and all binding energies were referenced to the main C-H photopeak at 285 eV.

## 4.0 RESULTS AND DISCUSSION

### 4.1 MONOMER SYNTHESIS AND CHARACTERIZATION

#### 4.1.1 Bis(4-chlorophenyl)phenyl Phosphine Oxide (BCPPO)

The initial candidate for nucleophilic aromatic substitution polycondensations leading to poly(arylene ether phosphine oxide)s was bis(4-chlorophenyl)phenyl phosphine oxide. It was supplied in monomer grade purity from Akzo America [236] with a melting point of 105-107°C. This compound was investigated spectroscopically in order to obtain information which would be helpful in confirming polymer structure.



The FTIR spectrum of BCPPO taken as a compressed KBr disk is shown in Figure 6. Aromatic phosphine oxide stretching patterns are known to be somewhat complex [290, 291] and many different modes of vibrations have been assigned, however, only the most important constantly observed values will be discussed here [211]. Primary peaks in the FTIR spectrum corresponding to the 5 major stretches were found to be at 3063  $\text{cm}^{-1}$  (aromatic C-H), 1583, 1562

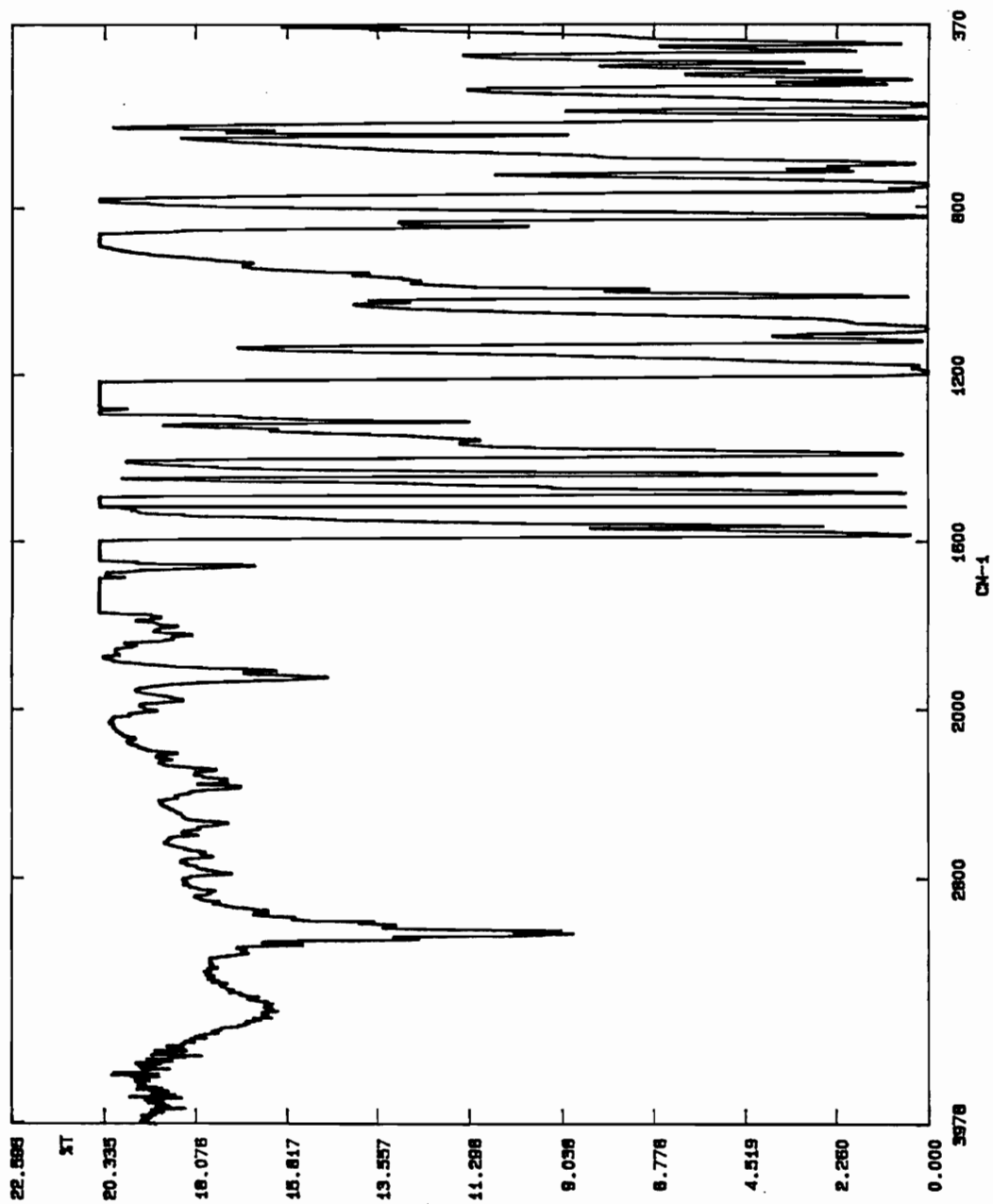


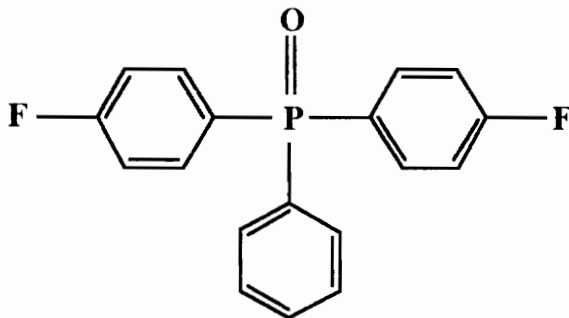
Figure 6. FTIR spectrum of BCPPO.

and  $1515\text{ cm}^{-1}$  (aromatic C=C),  $1093\text{ cm}^{-1}$  (aromatic C-Cl),  $1196\text{ cm}^{-1}$  (triaryl P=O) and  $752\text{ cm}^{-1}$  (C-P). In addition, several bending modes of action in this molecule were indicative of aryl carbon to phosphorus bonds including those peaks at  $1439$  and  $997\text{ cm}^{-1}$ . This data agrees with the structure of this monomer.

Proton NMR was utilized to further establish the structure of this activated dihalide. The spectrum of this monomer was identical to that of the difluoro derivative shown in the next section and will be discussed further in that section, as will the  $^{13}\text{C}$  and  $^{31}\text{P}$  spectra.

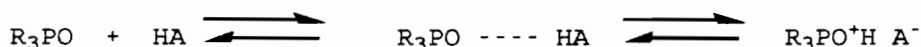
#### 4.1.2 Bis(4-fluorophenyl)phenyl phosphine oxide (BFPPPO)

As described in the experimental section, this monomer was prepared via Grignard routes involving p-fluorobromobenzene and phenylphosphonic dichloride [241]. These reactions proceeded smoothly at room temperature after initially holding 4 hours at  $0-5^{\circ}\text{C}$  as described previously (see Scheme 28) and afforded the desired monomer in yields typically ranging from 70-80% purified monomer grade material. The melting point was  $124-26^{\circ}\text{C}$ .



Structural confirmation through FTIR analysis (KBr disk) gave very similar results to the dichloro analogue, as shown in Figure 7. Again, the major peaks were identified and assigned as follows : 3062  $\text{cm}^{-1}$  (aromatic C-H), 1590 and 1498  $\text{cm}^{-1}$  (aromatic C=C), 1197  $\text{cm}^{-1}$  (P=O), 1164  $\text{cm}^{-1}$  (C-F) and 1438 and 998  $\text{cm}^{-1}$  (P-aryl carbon).

Proton NMR was another tool utilized for structure determination. Figure 8 illustrates both the entire spectrum for BFPPPO from 0 - 10 ppm and the expanded aromatic region between 7 - 8 ppm, relative to TMS at zero ppm. An observation which was made in the  $^1\text{H}$ NMR spectrum of all phosphine oxide containing polymers and monomers was the appearance of the water peak in deuterated chloroform at lower fields than the normal. Typically, the water peak in  $\text{CDCl}_3$  appears at about 1.7 ppm; however, in all phosphine oxide containing monomers and polymers investigated, the water peak was shifted downfield to around 2-2.5ppm. Undoubtedly, this phenomena is related to the strong hydrogen bonding capabilities of the phosphoryl moiety as described in detail in the literature [211].



This complexation results in a downfield shift of the normal water peak in  $\text{CDCl}_3$ .

An additional comment must be made regarding the spectra of phosphine oxide containing monomers and polymers, that of phosphorus-hydrogen atom coupling. Since  $^{31}\text{P}$  (100% of the natural abundance) has a



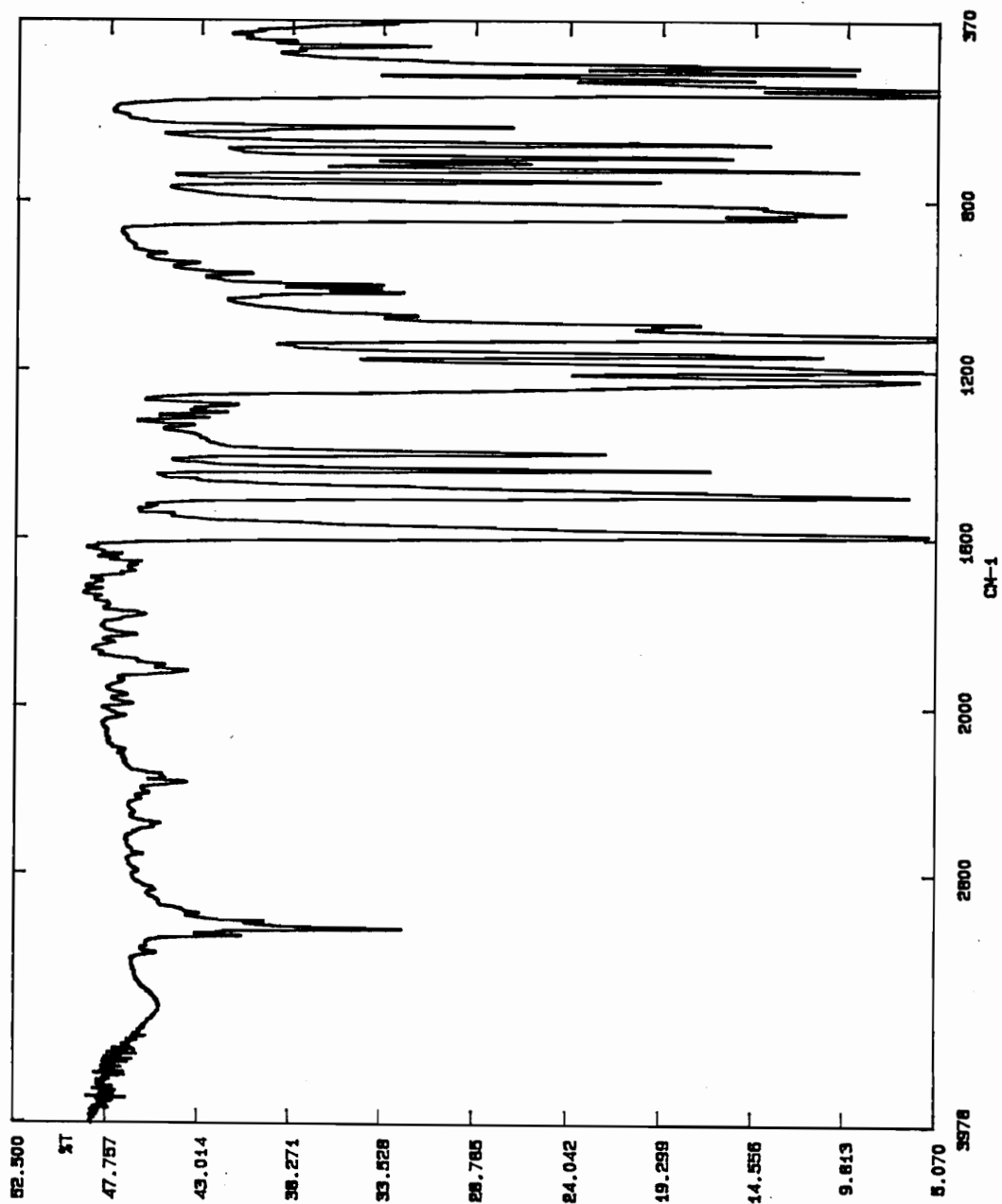


Figure 7. FTIR spectrum of BFPO.

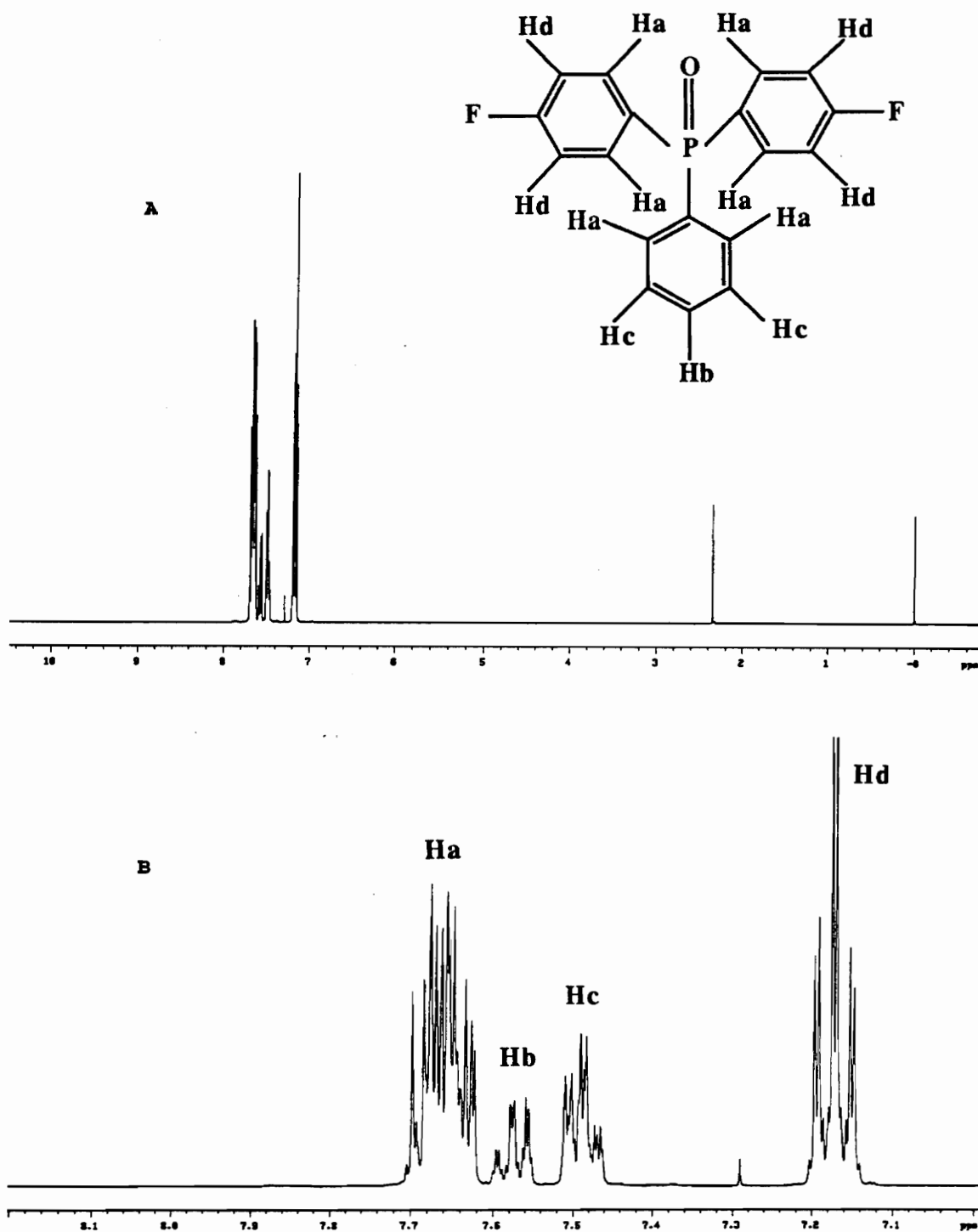
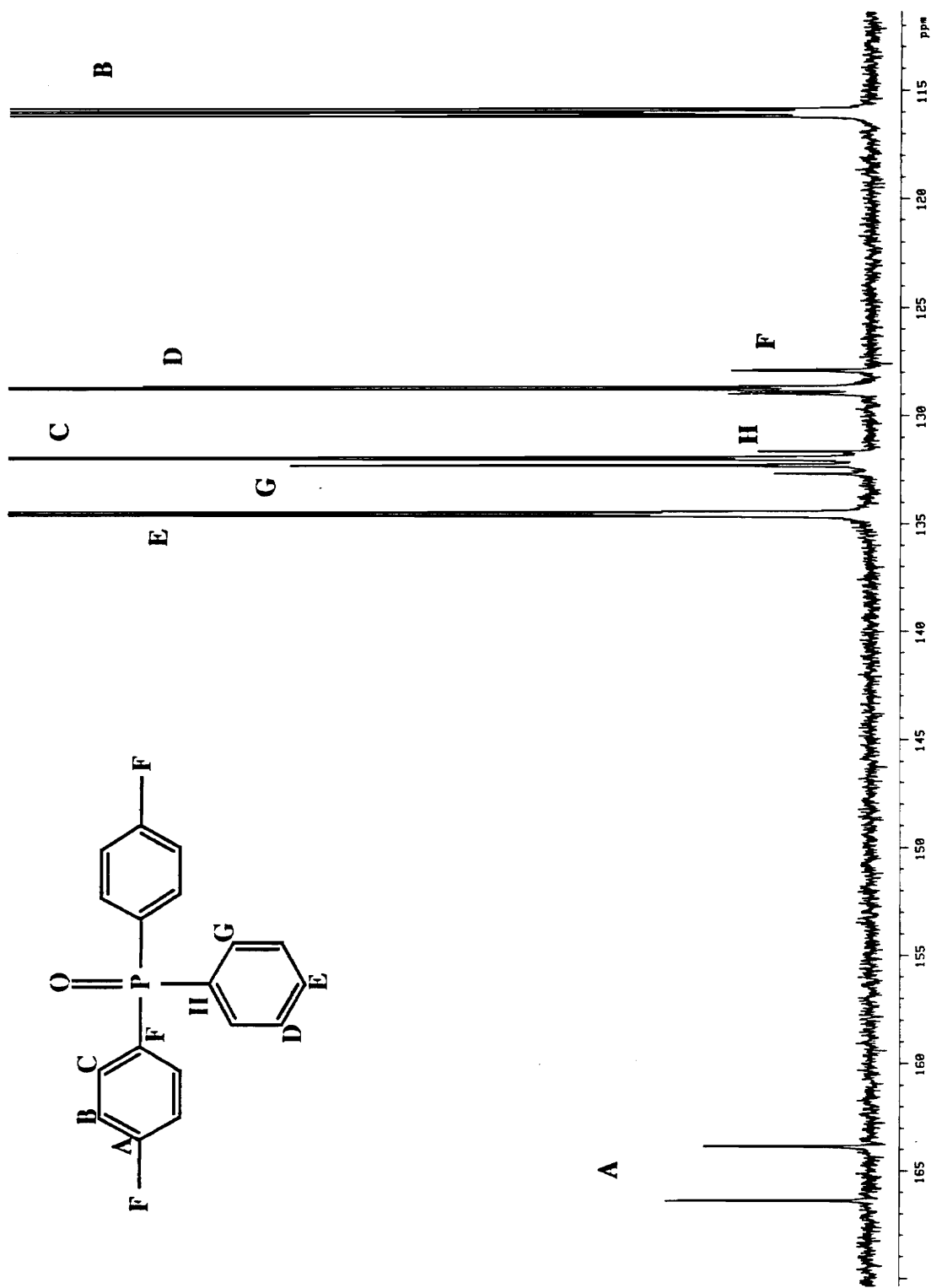


Figure 8.  $^1\text{H}$ NMR spectrum of BFPPPO : A) entire spectrum and B) expanded aromatic region.

nuclear spin of  $1/2$ , the same as the hydrogen atom, additional splitting patterns were observed in all  $^1\text{H}$ NMR spectra, giving rise to somewhat more complicated appearing spectra. It has been noted in the literature [292] that phosphine oxide group (phosphoryl group) containing aromatic systems exhibit unique behavior in  $^1\text{H}$ NMR. Protons which were ortho to the phosphoryl group were shifted downfield relative to those protons ortho to electron donating groups attached to aromatic rings, giving evidence for the electron accepting ability of the phosphine oxide group. This effect will be expanded upon shortly in comparison to other activated dihalides.

With this somewhat lengthy prologue to  $^1\text{H}$ NMR of phosphorus containing monomers, all of the major peaks can be identified and assigned as shown on the expanded spectrum. All six protons ortho to the phosphoryl group are basically equivalent and will be the most deshielded and furthest downfield centered near 7.66 ppm. The proton on the pendant phenyl ring para to the phosphine oxide group is also deshielded due to resonance and is the next splitting pattern upfield centered around 7.58 ppm. Splitting occurring around 7.5 ppm was assigned to those two protons meta to the phosphoryl group on the pendant phenyl ring, while the four protons meta to the phosphine oxide and ortho to the fluoro atoms had chemical shifts furthest upfield at 7.17 ppm. Integration of this spectrum gave the expected ratio of (moving from low to high field) 6:1:2:4.

Carbon NMR was helpful in confirming the structure of this monomer as well. Shown in Figure 9 is the  $^{13}\text{C}$ NMR of BFPPPO in  $\text{CDCl}_3$ . All of the

Figure 9.  $^{13}\text{C}$  NMR spectrum of BFPO.

peaks can be assigned with the typical equations used for benzenoid compounds and the following approximated values (calculated from estimates made from a combination of many 4, 4' substituted triphenyl phosphine oxides) for diphenylphosphine oxide substitution : Cl \* 5, ortho \* 1, meta \* -0.5, para \* 3. The data below summarizes the assignments.

<u>Carbon atom</u>	<u><math>\delta</math> experimental (ppm)</u>	<u><math>\delta</math> calculated (ppm)</u>
A	166, 164	165
B	116	116
C	132	132
D	129	129
E	132	132
F	134.5	133.5
G	132	131.2

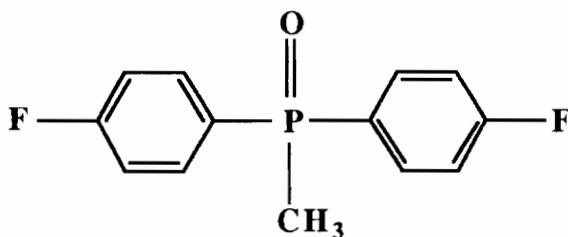
Phosphorus ( $^{31}\text{P}$ ) NMR was also used to check the purity and identity of BFPPPO. Since this isotope is 100% of the natural abundance, any solvent which dissolves the compound can be used in this spectroscopic method; however, one must be careful in comparing values of two different compounds in different solvents, since changing solvents also changes the phosphorus atom chemical environments. Literature values are almost always reported relative to 85%  $\text{H}_3\text{PO}_4$ . Downfield shifts from this standard are reported as positive values and upfield values are negative. Investigations of the  $^{31}\text{P}$ NMR spectrum of BFPPPO showed only a

single peak at 22.5 ppm in THF and 35 ppm in methanol. The downfield shift in methanol was due to the hydrogen bonding discussed earlier.

As a final method for the confirmation of monomer structure, mass spectral information was utilized in the electron impact mode. The results are shown in Figure 10. From other model compound mass spectral identifications [211], the nature of the decomposition products were assigned. Mass was confirmed (314.28 g/mol) as the -1 peak at 313 and the radical cation at 314. Benzene (77) and fluorobenzene (95) cations and the analogous phosphorus containing fragments (219 and 237) were the primary products formed. Additional fragments formed are shown in Scheme 37.

#### 4.1.3 Bis(4-fluorophenyl)methyl Phosphine Oxide (BFMPO)

As described in the experimental section, this monomer was synthesized by methods analogous to those used for BFPPPO and, in fact, was much easier to purify since it sublimed quite nicely.



The melting point was 112-14°C. Infrared analysis confirmed the structure with many of the same bands as BFPPPO. Important stretches are outlined below.

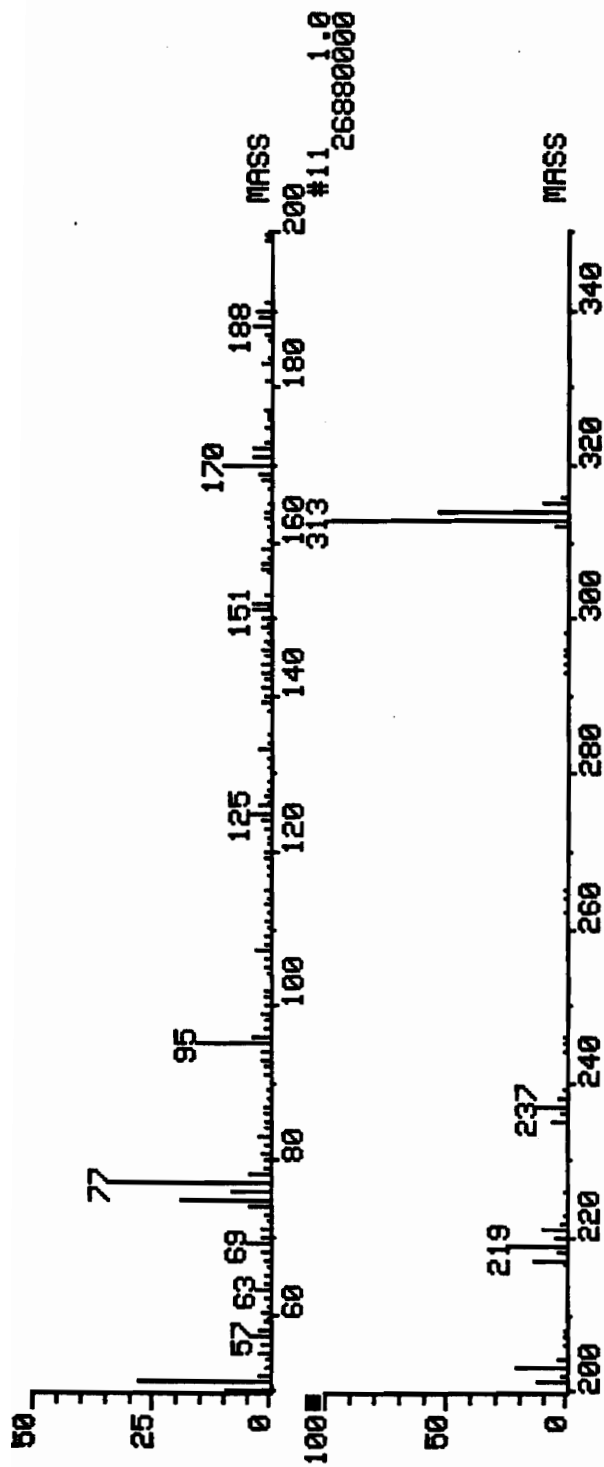
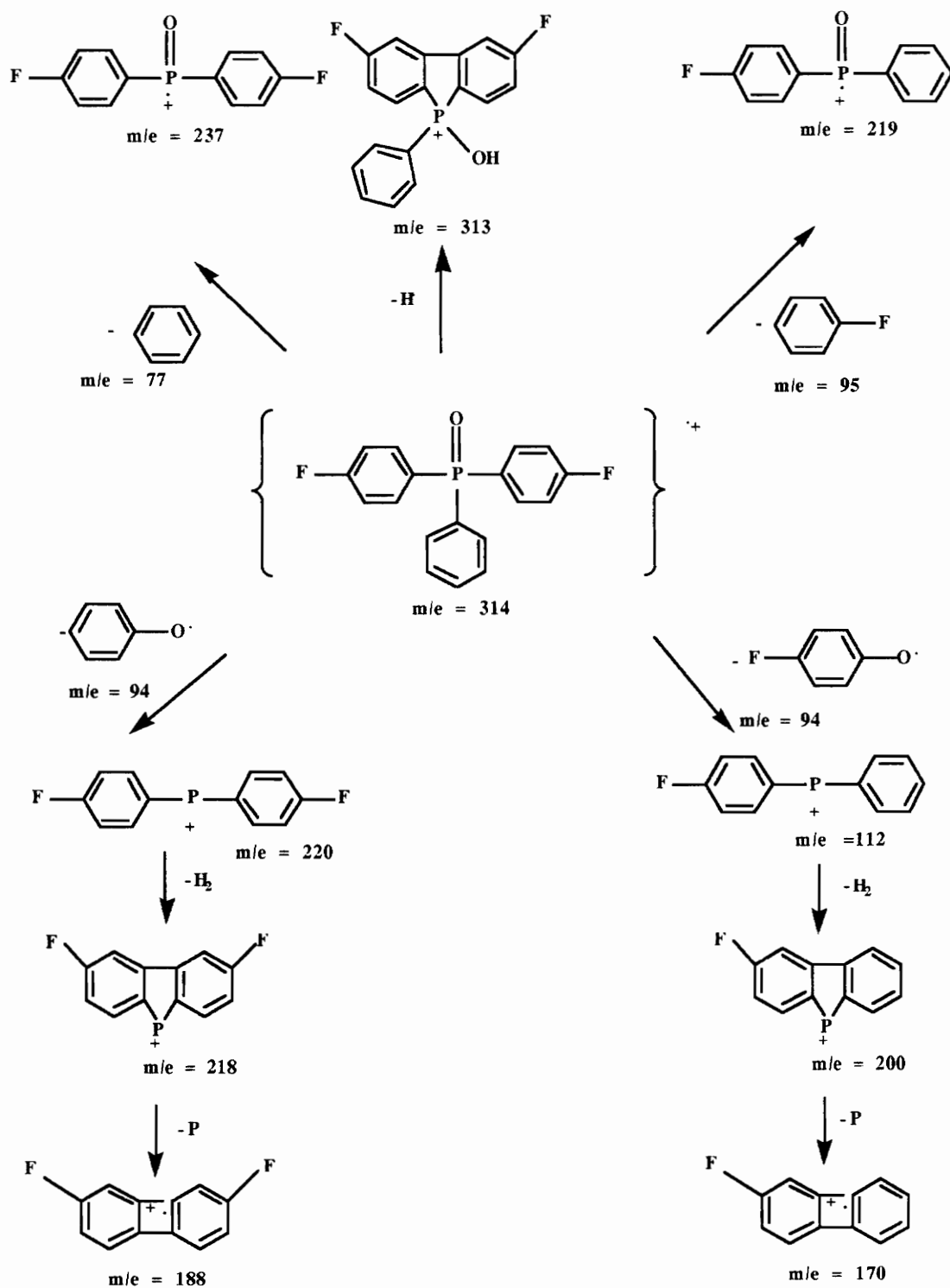


Figure 10. Mass spectral analysis of BFPO.



Scheme 37. Possible fragmentation routes of BFPPPO in mass spectrometry.



<u>FTIR Peak (cm<sup>-1</sup>)</u>	<u>Assignment</u>
3060	Aromatic C-H
1590, 1489	Aromatic C=C
1400, 1305, 885	P-CH <sub>3</sub>
1202	P=O

Proton NMR (Figure 11) also confirmed the structure of this methyl substituted monomer. As identified in the figure, all protons were assigned according to their chemical shifts as follows. The aromatic region was greatly simplified since only two equivalent types of protons were present in this compound. Aromatic protons ortho to the phosphoryl group (Ha) had chemical shifts further downfield centered around 7.72 ppm, while those protons meta to the phosphine oxide unit (Hb) appeared near 7.18 ppm. The methyl protons appeared as a doublet at 2.0 ppm due to splitting with the adjacent phosphorus atom. Additional structural evidence from <sup>13</sup>CNMR (Figure 12) where 5 types of carbon atoms were found, each corresponding to their calculated values (see above for BFPPPO). The methyl carbon chemical shift was 17 ppm.

#### 4.1.4 Proton Nuclear Magnetic Resonance Studies of Activated Dihalides

As a qualitative test to determine whether these phosphine oxide containing monomers would be capable of undergoing nucleophilic aromatic substitution polycondensations, <sup>1</sup>HNMR was used to observe the chemical shifts of the aromatic protons ortho to the electron withdrawing groups. The stronger the electron accepting ability of the central moiety, the

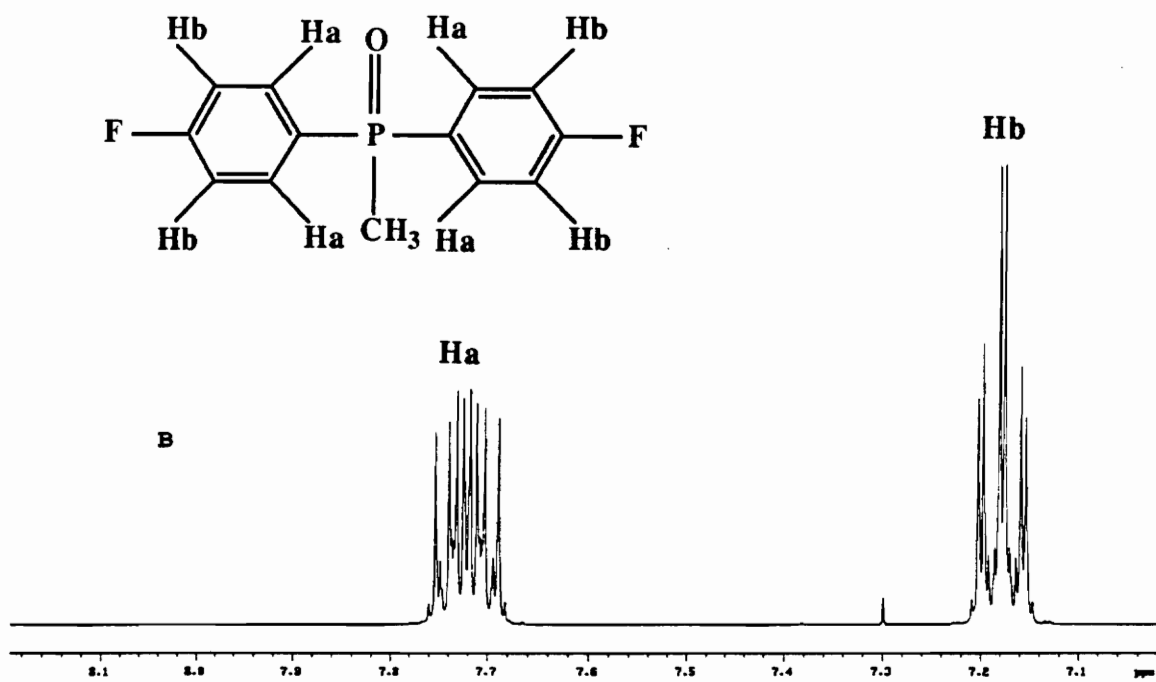
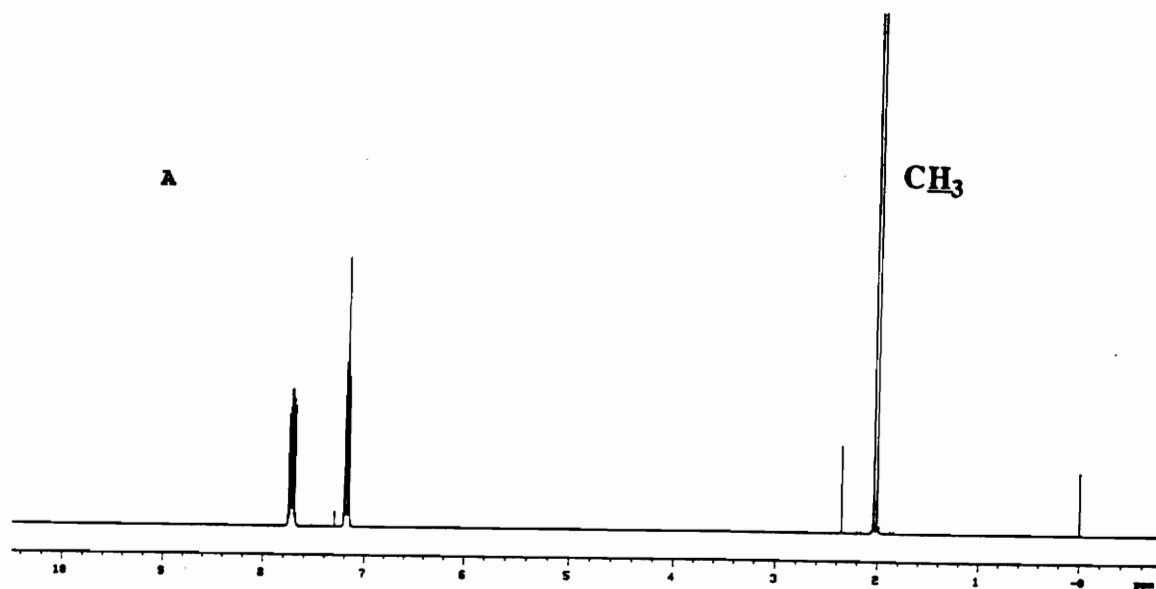
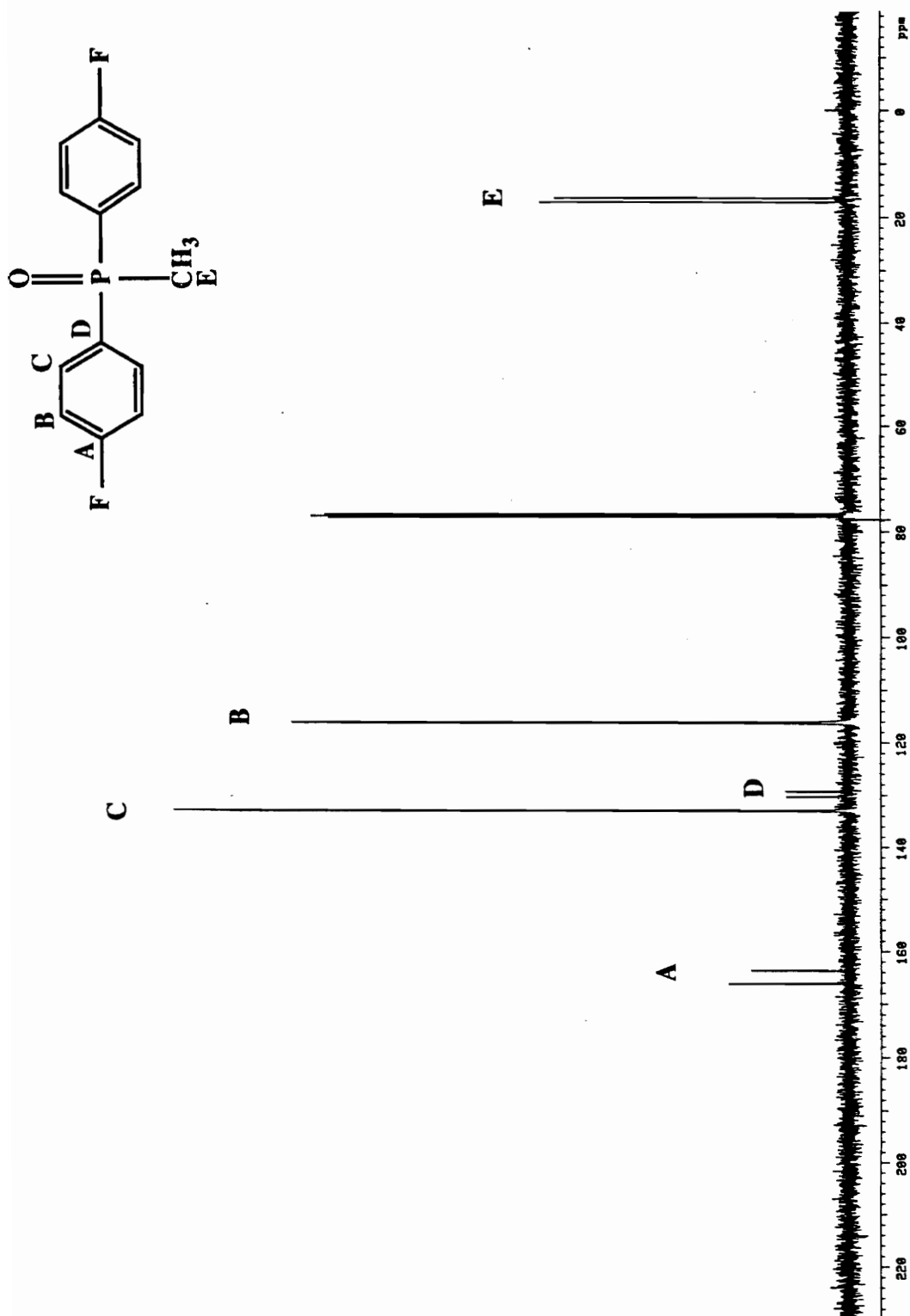


Figure 11.  $^1\text{H}$ NMR of BFMPO : A) Entire spectrum and B) Expanded aromatic region.

Figure 12.  $^{13}\text{C}$  NMR of BFMPPO.

more deshielded these ortho protons would be and therefore would appear further downfield. For comparison, 4,4'-difluorobenzophenone and 4,4'-difluorodiphenylsulfone were also run against BFPPPO and BFMPO. The results are tabulated in Table 8.

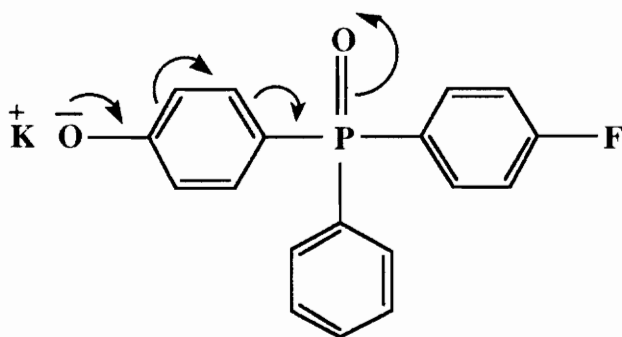
Table 8.  $^1\text{H}$ NMR chemical shifts of aromatic protons ortho to electron withdrawing groups.

<u>ELECTRON ACCEPTING GROUP</u>	<u>CHEMICAL SHIFT (PPM)</u>
$\begin{array}{c} \text{O} \\    \\ \text{S} \\    \\ \text{O} \end{array}$	7.96
$\begin{array}{c} \text{O} \\    \\ \text{C} \end{array}$	7.82
$\begin{array}{c} \text{O} \\    \\ \text{P} \\   \\ \text{CH}_3 \end{array}$	7.72
$\begin{array}{c} \text{O} \\    \\ \text{P} \\   \\ \text{C}_6\text{H}_5 \end{array}$	7.65

With the knowledge that the sulfone group is more capable of accepting electron density than the ketone group, it is not surprising that those aromatic protons on DFDPS ortho to the sulfone moiety appear much further downfield than the corresponding protons on DFB. From this NMR data, it appeared that the phosphoryl group was even less effective in accepting electron density; thus, the qualitative order of electron accepting ability was  $\text{SO}_2 > \text{CO} > \text{MePO} > \text{PhPO}$ . From the literature review, it was known that 4,4'-dichlorobenzophenone would not undergo NAS reactions to give high molecular weight PEK; therefore, perhaps it was not surprising that the first work attempting to prepare PEPO from BCPPO [158] only gave low molecular weight materials. As discussed later in the polymer synthesis section of this chapter, high molecular weight poly(arylene ether)s could not be accomplished in this research with BCPPO, but only with the fluorinated derivatives.

#### 4.1.5 4-Hydroxyphenyl-4'-fluorophenyl Phenyl Phosphine Oxide

As shown in Scheme 29 in the experimental chapter, this monomer could be prepared by the reaction of BFPPPO with excess aqueous KOH in DMSO. Due to the "bridge effect" [29] discussed earlier and the nature of the solvent mixture and temperature, only one fluoro group was displaced. Reactions forming this AB monomer were conveniently followed by thin layer chromatography developed in 50:50 toluene/ethyl acetate where the disappearance of BFPPPO was monitored. It was found that stoichiometry in this route was not very important, as a large



excess of base (1 mole BFPPPO : 4 mole KOH) could be utilized at around 80°C to effect complete reaction in 16 hours. After workup and Kugelrohr distillation at high temperatures, a white solid was afforded with a melting point of 218-220°C.

Spectroscopic studies of this monomer confirmed the structure. The FTIR spectrum (Figure 13) contained all of the peaks discussed earlier for BFPPPO with the addition of a very broad phenol stretch centered about 3500  $\text{cm}^{-1}$  (broad due to hydrogen bonding with P=O). A C-O band was identified at 1237  $\text{cm}^{-1}$  in close proximity to both C-F and P=O stretches at 1159 and 1173  $\text{cm}^{-1}$ , respectively. Proton NMR (Figure 14) gave essentially a mixture of the spectra of BFPPPO and the dihydroxy compound (discussed later), with the additional phenolic proton at 10.3 ppm in deuterated DMSO. A single peak in the  $^{31}\text{P}$ NMR spectrum at 35.3 ppm (in methanol) compared to 35.8 ppm for BFPPPO also confirmed the purity of the AB monomer.

#### 4.1.6 Bis(4-carboxyphenyl)phenyl Phosphine Oxide

This diacid was prepared from the oxidation of bis(4-methylphenyl)phenyl phosphine oxide as described in the experimental

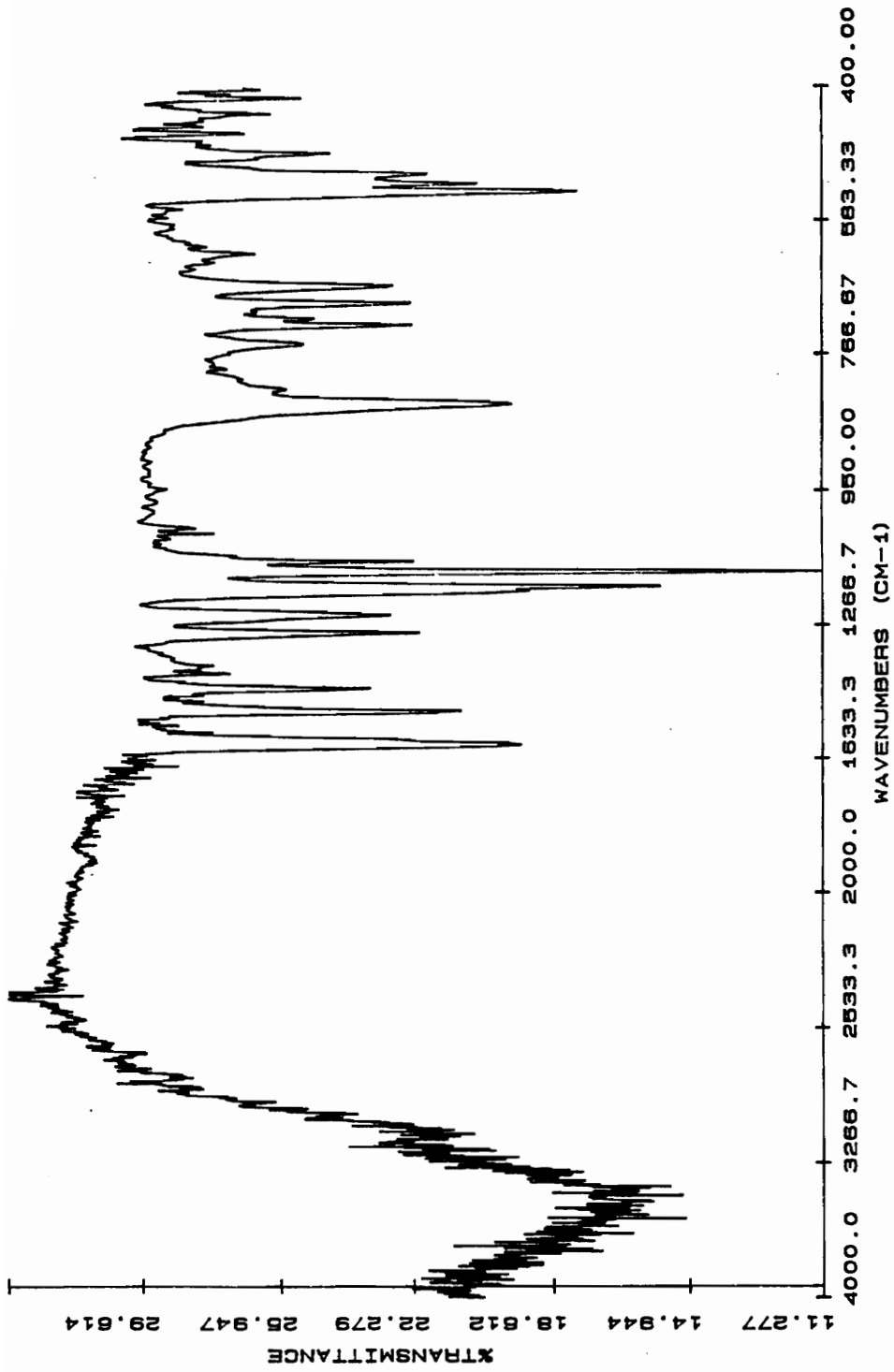
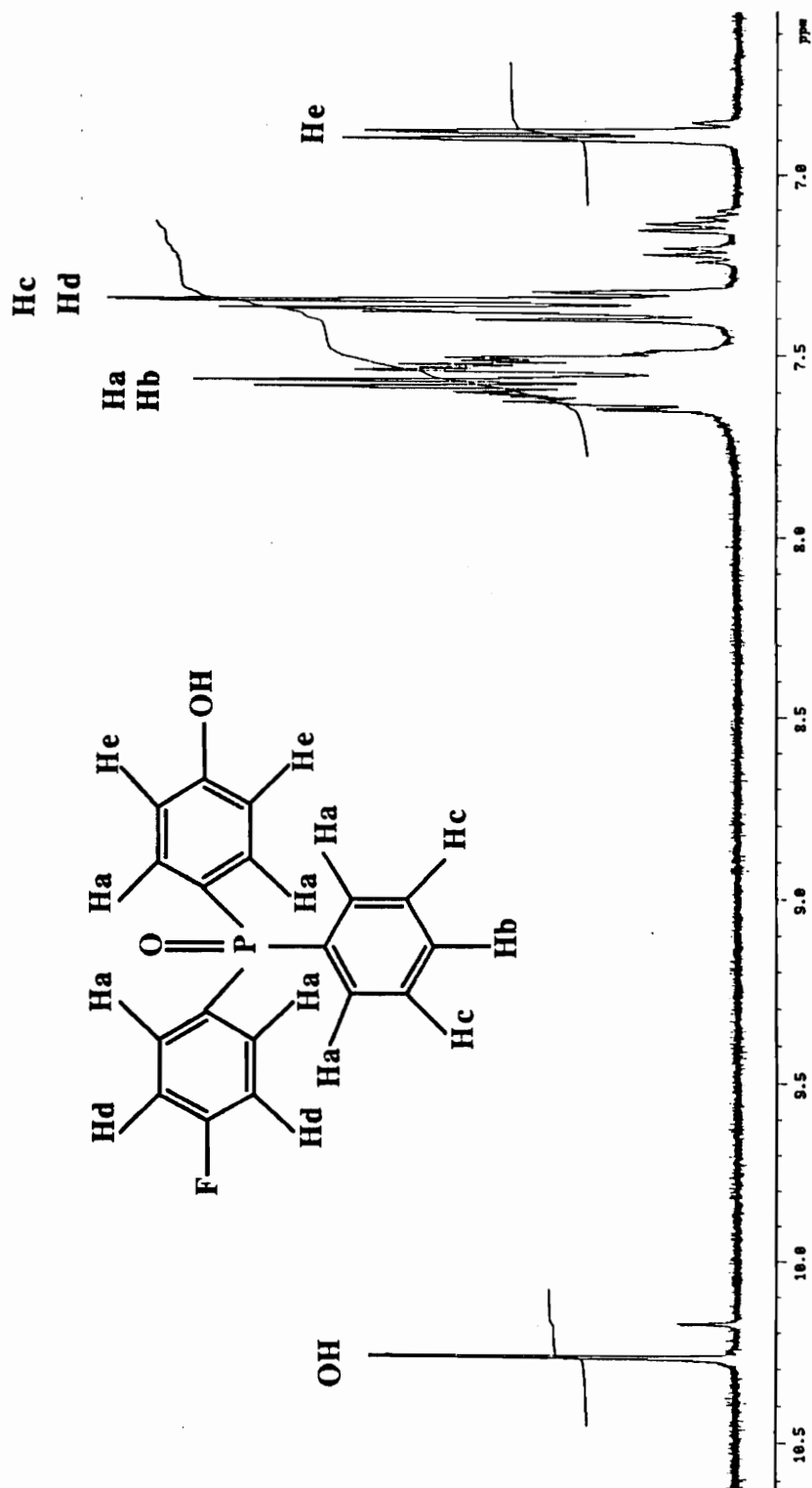


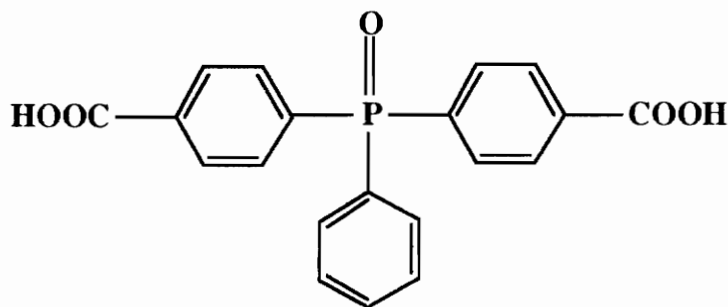
Figure 13. FTIR of 4-hydroxyphenyl-4'-fluorophenyl-phosphine oxide.

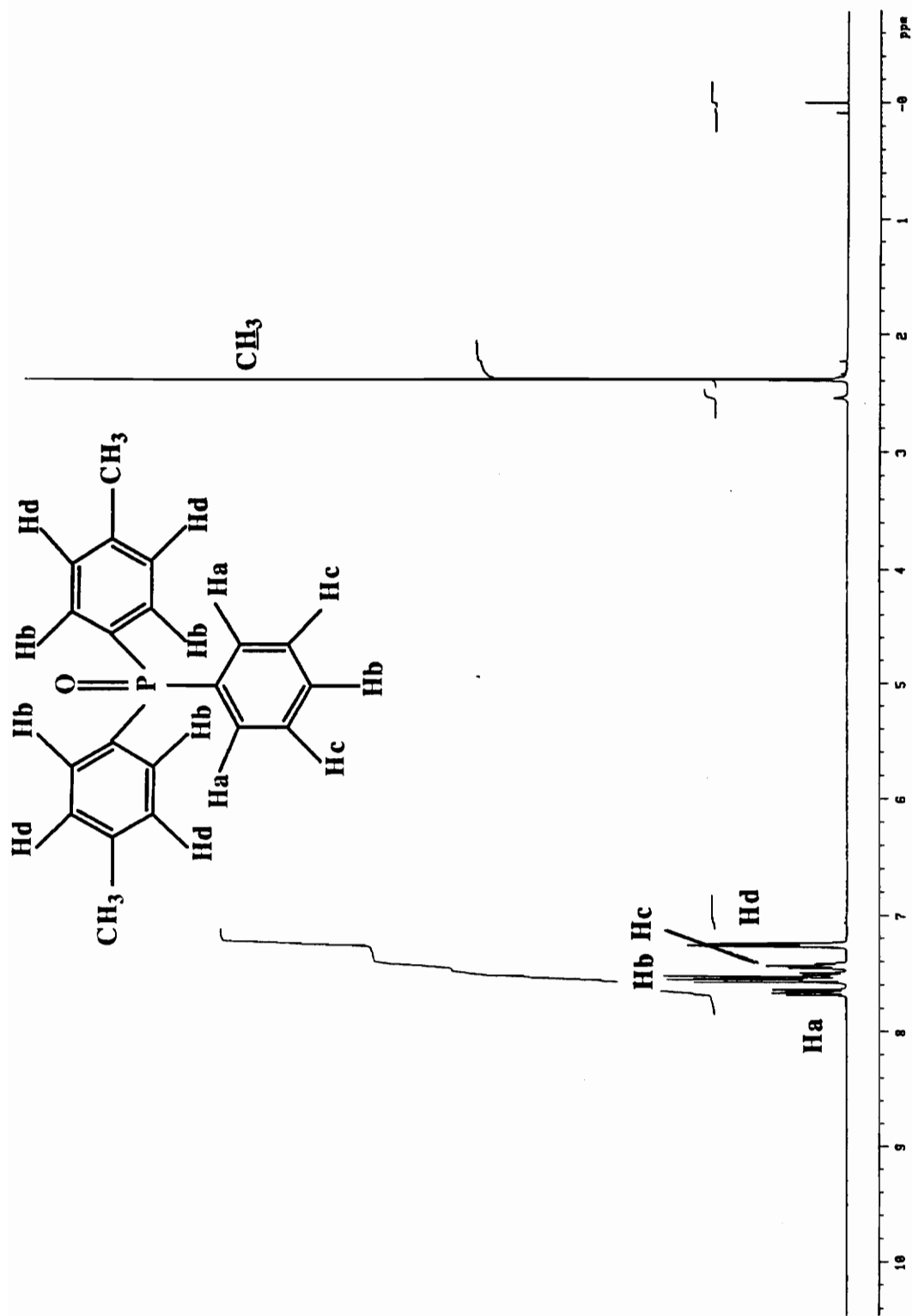
Figure 14.  $^1\text{H}$ NMR of 4-hydroxyphenyl-4'-fluorophenyl phosphine oxide.

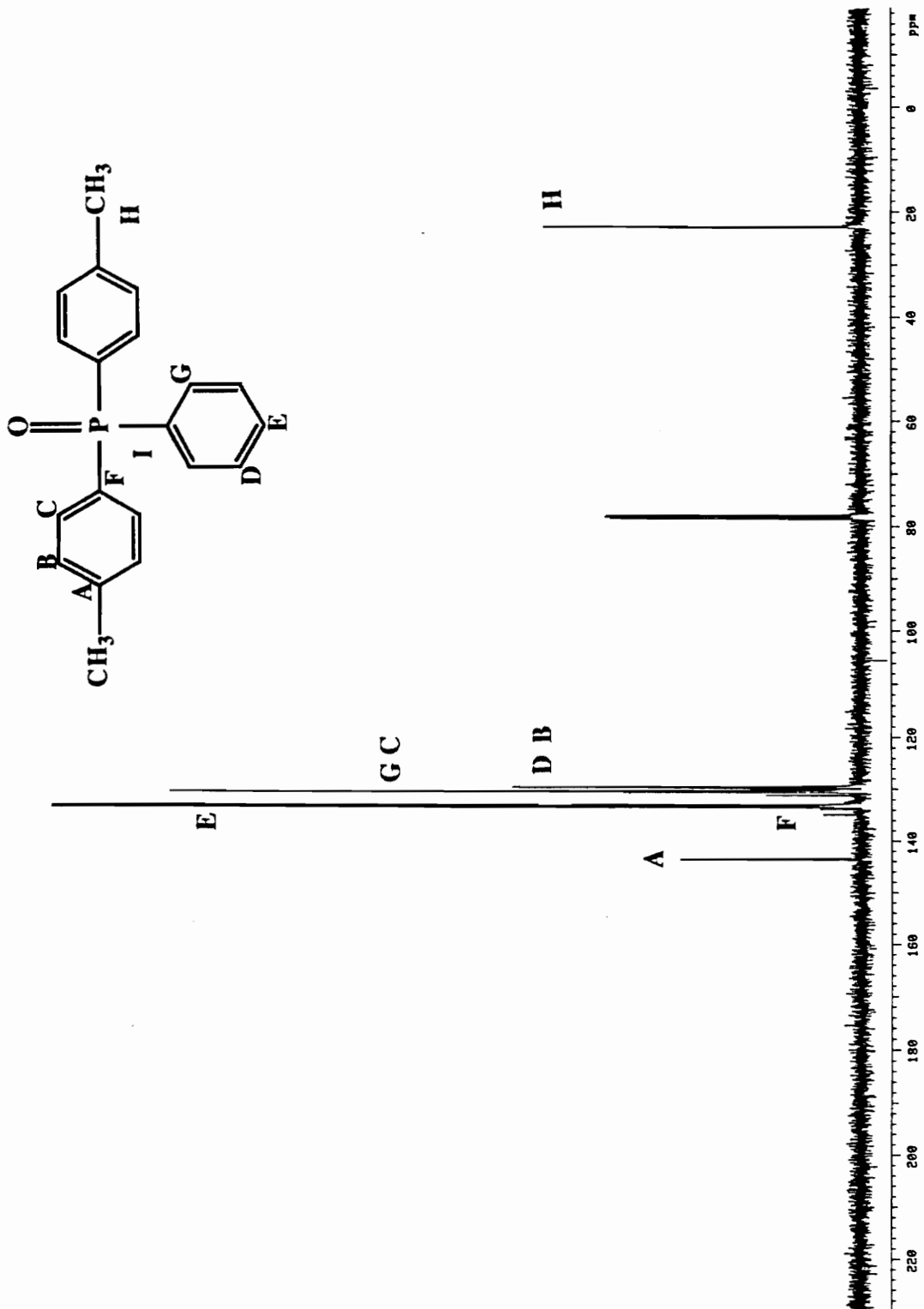


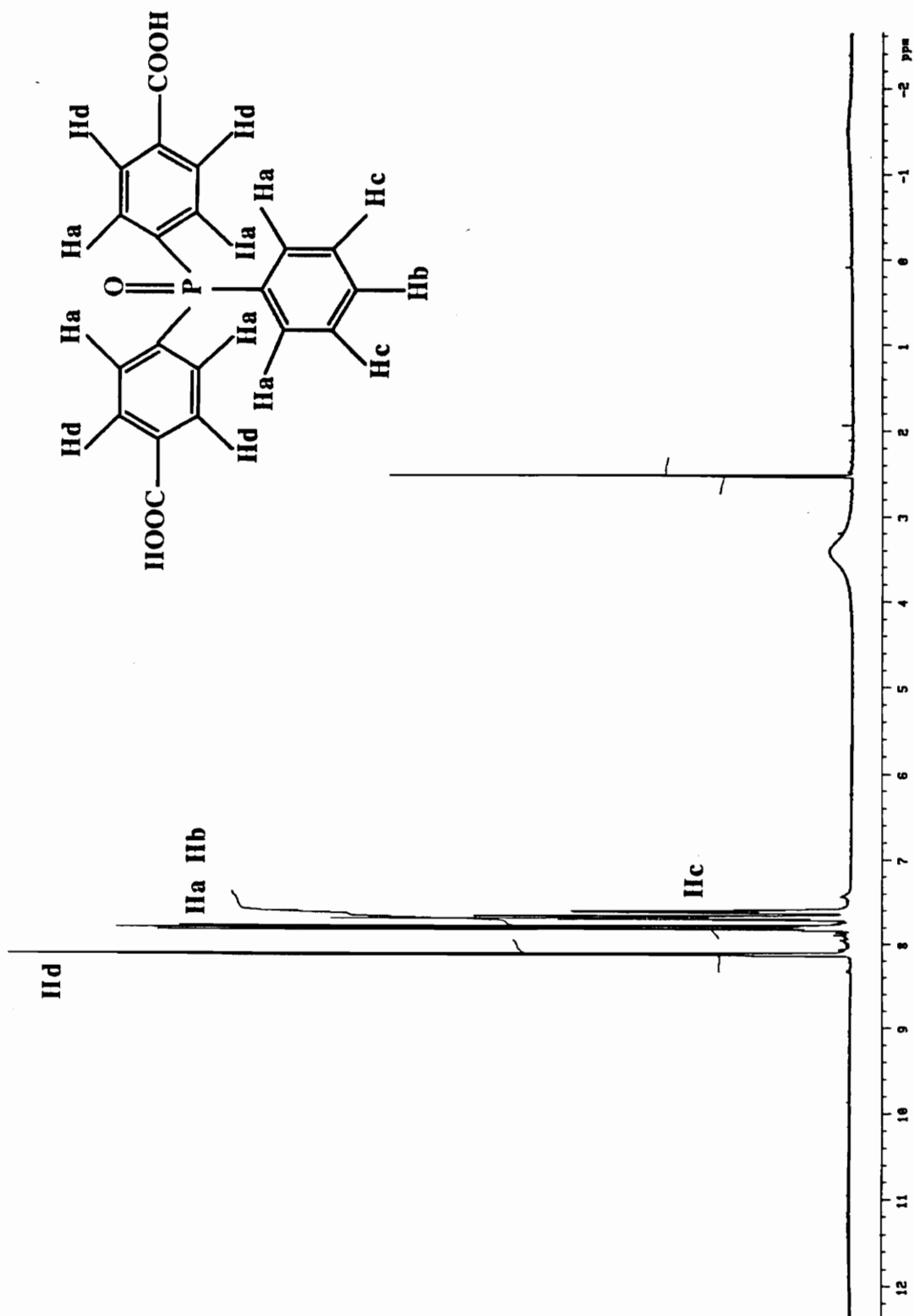
chapter (Scheme 30). Grignard procedures satisfactorily yielded the bismethyl compound, which was at best a waxy solid. If the oil which distilled over in the Kugelrohr unit was allowed to stand for several days, solidification would begin. Also, if treated with hexanes, solidification would begin to occur. Nevertheless, the compound was judged to be acceptable for oxidation by classical routes [194]. Bis(4-methylphenyl)phenyl phosphine oxide was characterized by  $^1\text{H}$ NMR, which again gave similar results to BFPPPO, i.e. aromatic protons chemical shifts 7.2-7.7 ppm and methyl protons chemical shift at 2.4 ppm in  $\text{CDCl}_3$ , assigned according to Figure 15. Carbon NMR of the bismethyl compound afforded the spectra shown in Figure 16, along with the assignments which were similar to BFPPPO. Note the methyl carbon chemical shift at 22.8 ppm.

Oxidation of the dimethyl compound in aqueous potassium permanganate gave about 70% of the desired diacid which was purified by redissolving as the disodium salt in water and reprecipitating by acidifying the solution. When dry, the diacid had a high melting point of 324-26°C.



Figure 15.  $^1\text{H}$ NMR of Bis(4-methylphenyl)phenyl phosphine oxide.

Figure 16.  $^{13}\text{C}$  NMR of Bis(4-methylphenyl)phenyl phosphine oxide.

Figure 17.  $^1\text{H NMR}$  of Bis(4-carboxyphenyl)phenyl phosphine oxide.

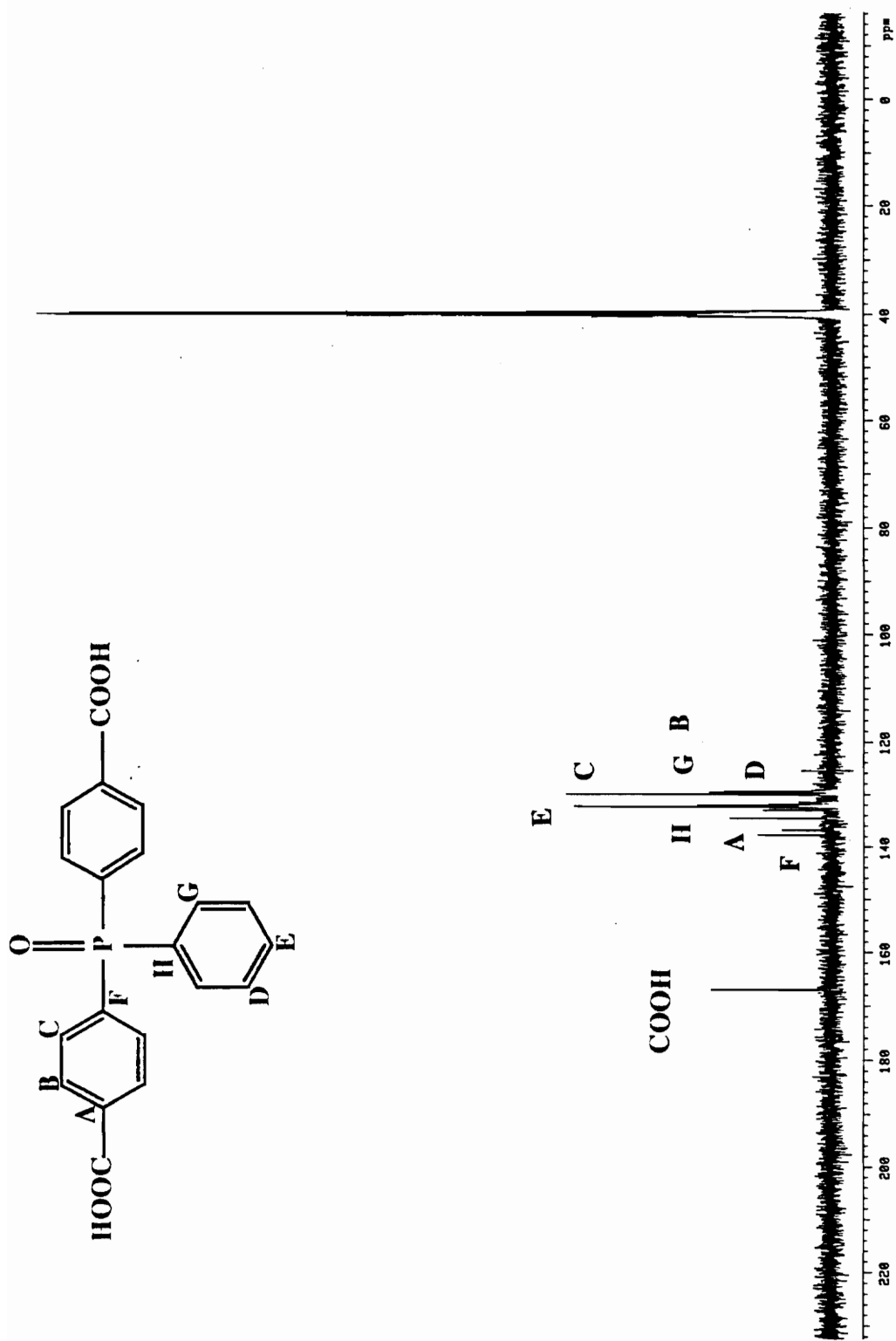


Figure 18.  $^{13}\text{C}$  NMR of Bis(4-carboxyphenyl)phenyl phosphine oxide.

The material was judged to be free of any methyl impurities by  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR (Figures 17 and 18). No methyl proton peak was observed in the  $^1\text{H}$ NMR spectrum (peak at 2.5 ppm is DMSO) and the methyl carbon resonance in the dimethyl compound's  $^{13}\text{C}$ NMR (Figure 16) at 22.8 ppm had disappeared. Again, the assignments for the  $^{13}\text{C}$ NMR were similar to BFPPO and agreed well with calculated values. Only one peak appeared in the  $^{31}\text{P}$ NMR of this diacid, at 25.1 ppm in DMSO.

#### 4.1.7 Bis(4-hydroxyphenyl)phenyl Phosphine Oxide (BHPPO)

As described in the experimental section (Scheme 31), this monomer was prepared by a two step reaction [207]. First, the Grignard preparation of the dimethoxy compound was carried out, followed by strong acid hydrolysis to the bisphenol. Isolation and purification of the bisphenol product proved to be the most difficult part of this procedure. Once isolated and recrystallized several times from methanol, the product melted at 233-36°C. Kugelrohr distillation of the bis(4-methoxyphenyl)phenyl phosphine oxide was unsuccessful due to foaming, but the crude product was a slightly yellow very viscous oil which did not solidify, and gave the  $^1\text{H}$ NMR spectrum ( $\text{CDCl}_3$ ) shown in Figure 19. The methoxy protons at 3.85 ppm (6 protons) stand out against the aromatic region between 7.0-7.8 ppm (integrates to 13 protons). Further evidence of the presence of dimethoxy substitution lies in the  $^{13}\text{C}$ NMR spectrum (Figure 20). The carbon chemical shift of the methoxy carbon falls around 53 ppm. All other shifts were calculated and assigned as shown in the spectrum.

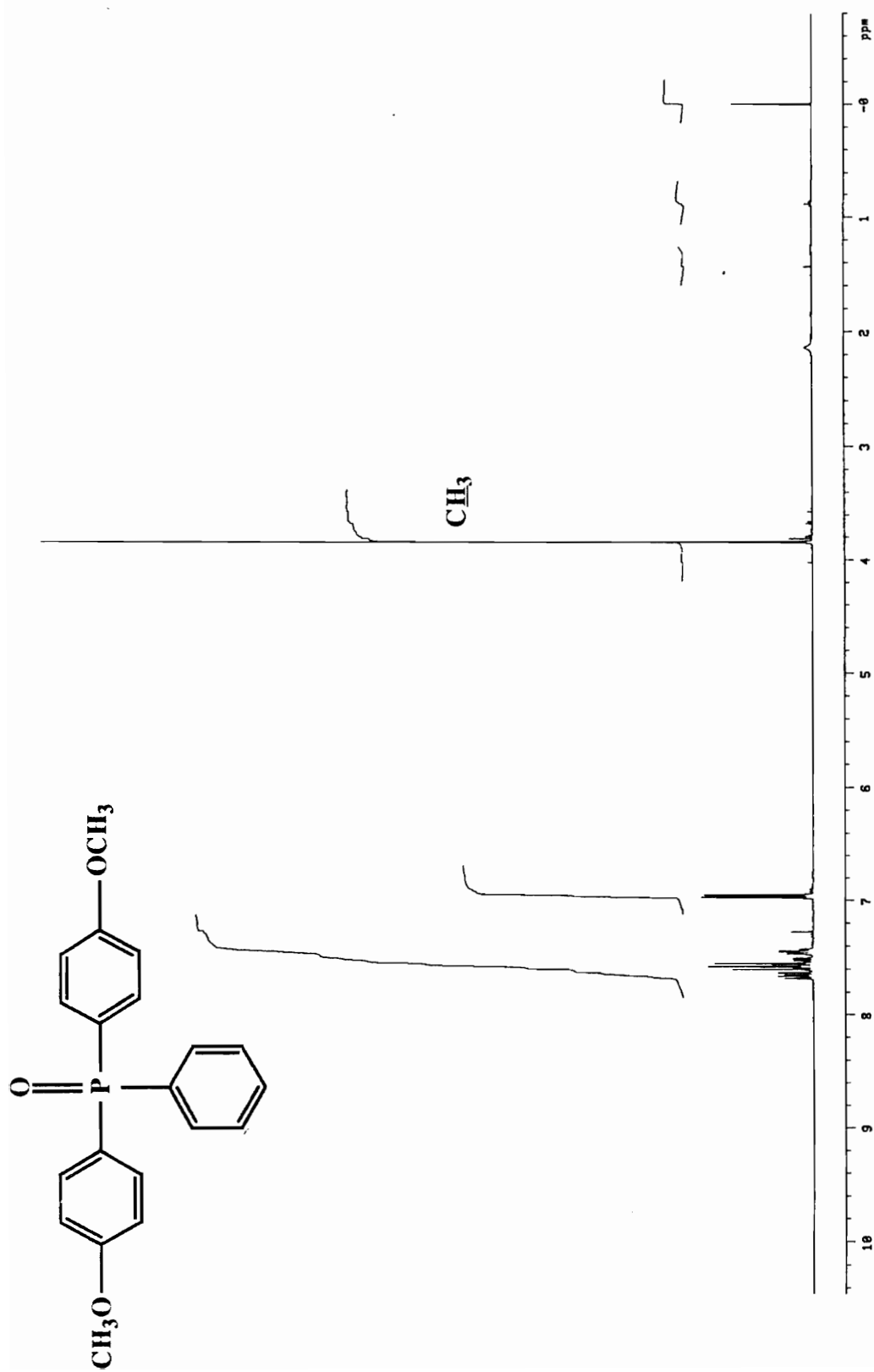


Figure 19.  $^1\text{H}$ NMR of Bis(4-methoxyphenyl)phenyl phosphine oxide.

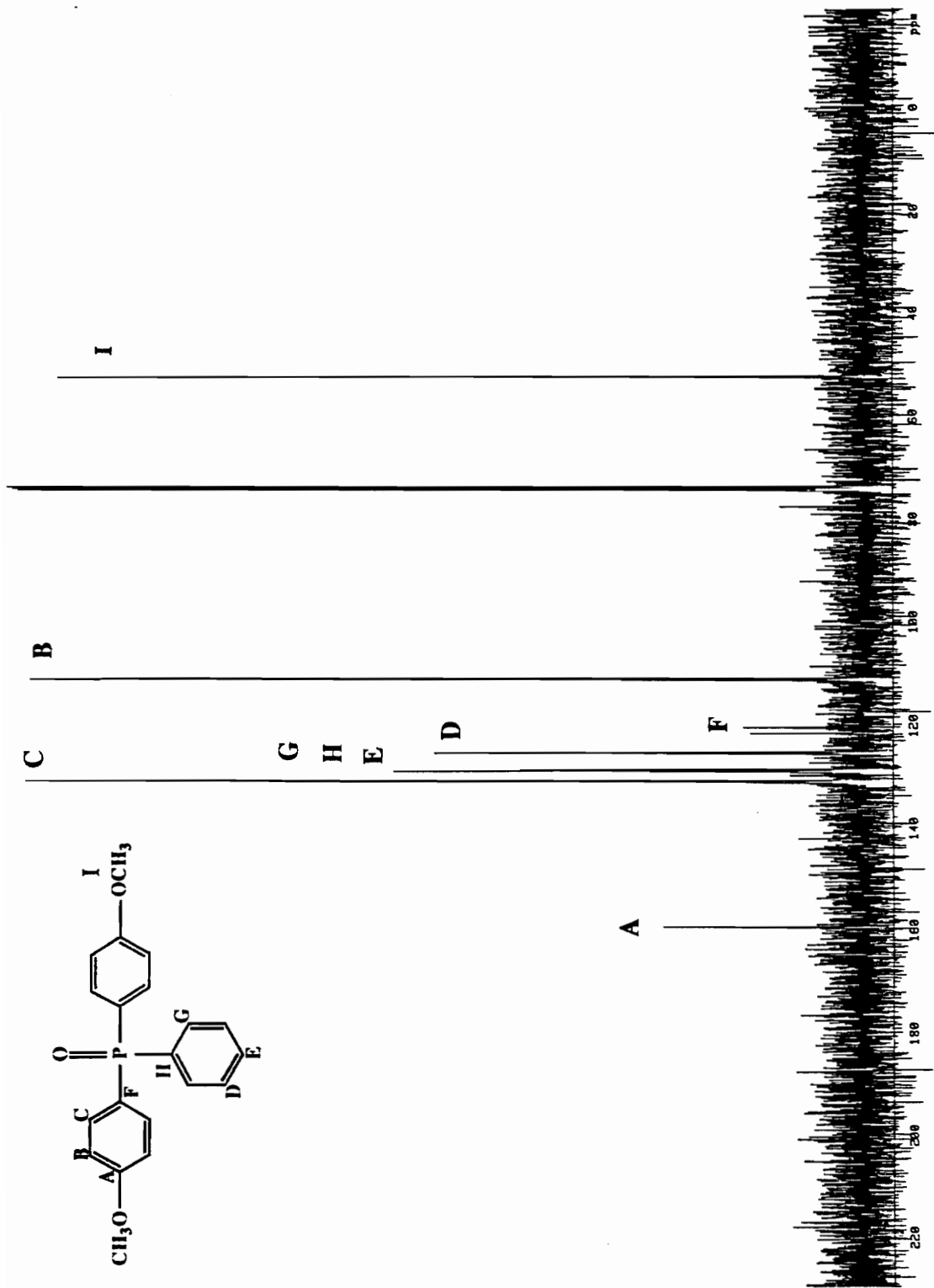
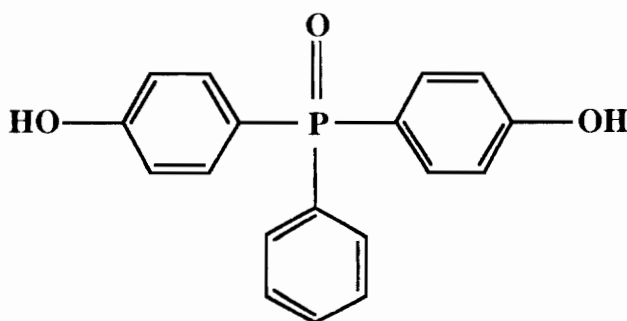


Figure 20.  $^{13}\text{C}$  NMR of Bis(4-methoxyphenyl)phenyl phosphine oxide.



In order to obtain the bisphenol of interest, vigorous hydrolysis conditions (refluxing aqueous HBr) were employed as described in the experimental chapter. After work-up, a white powder was obtained which had to be recrystallized (with considerable losses of material) multiple times from methanol.



The final polymer grade bisphenol was also characterized spectroscopically. Proton NMR (Figure 21) was the primary tool used for the analysis of this monomer. From Figure 21, the hydroxyl protons were observed around 10ppm, while the aromatic protons were assigned as illustrated. Also, FTIR analysis indicated the presence of the broad phenol stretch (ca.  $3500\text{ cm}^{-1}$ ), C-O stretching ( $1248\text{ cm}^{-1}$ ), P=O ( $1177\text{ cm}^{-1}$ ), P-Ph ( $1438\text{ cm}^{-1}$ ) and aromatic C=C ( $1604, 1582, 1505\text{ cm}^{-1}$ )

#### 4.1.8 Bis(4-aminophenyl)phenyl Phosphine Oxide (BAPPO)

This highly desirable monomer was discovered only in extremely rare cases in the literature and most citations in which it appeared involved very laborious routes and procedures; however, one method was found in the Russian literature which seemed fairly simple and was attempted from

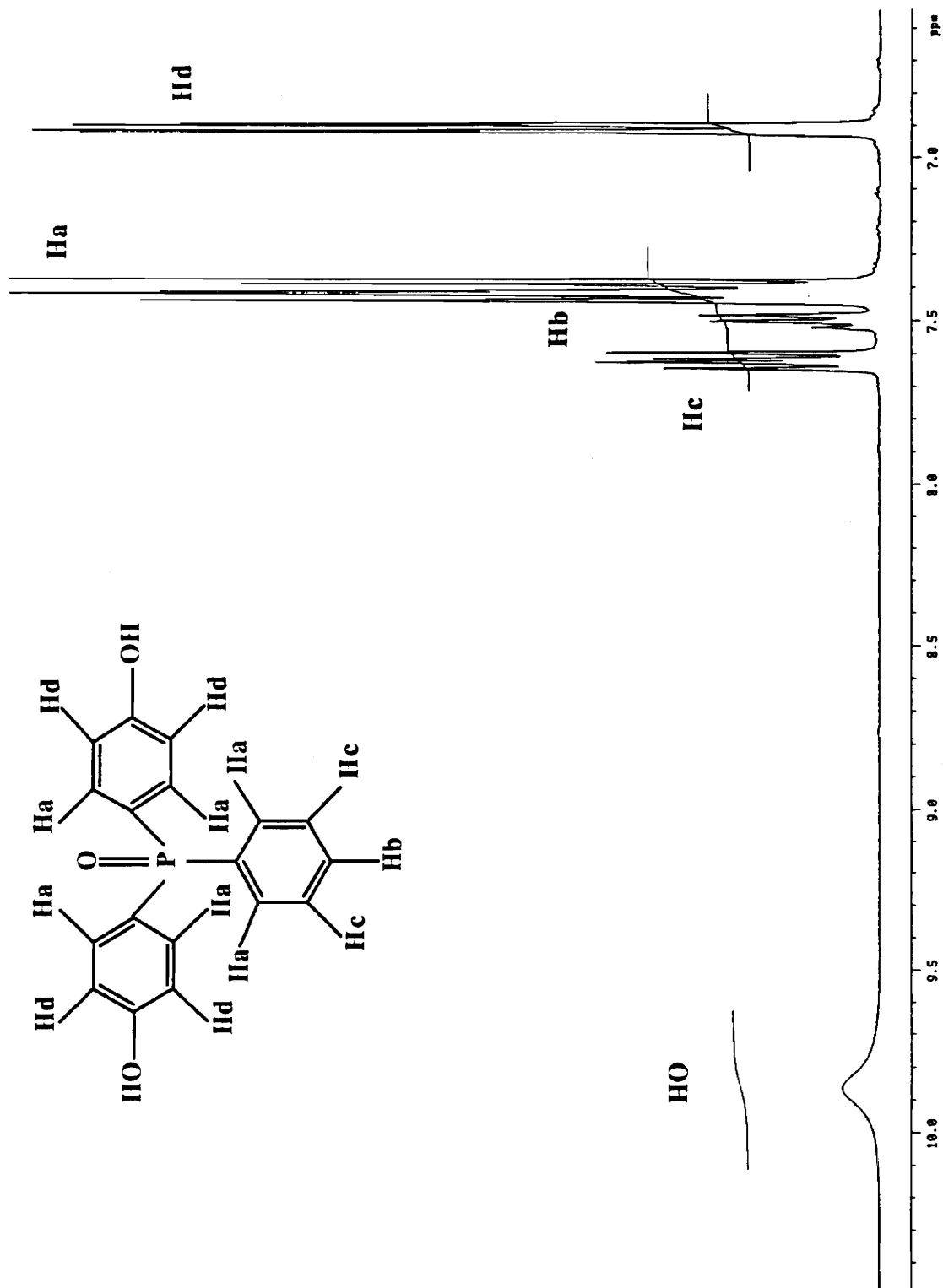
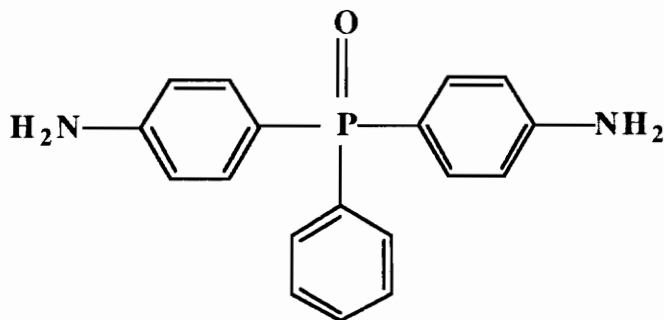


Figure 21.  $^1\text{H}$  NMR of Bis(4-hydroxyphenyl)phenyl phosphine oxide.

a direct English translation [214]. As described in the experimental section (see Scheme 32), this procedure involved heating phenylphosphonic dichloride with aniline hydrochloride for an extended period of time under nitrogen flow. After workup and recrystallization from ethanol, very nice crystals were collected in a 30% overall yield with a melting point of 212-14°C (lit. 220-21°C).

Initially, from  $^1\text{H}$ NMR studies (aromatic region shown in Figure 22), it appeared the desired monomer had indeed been prepared. If the monomer was of the structure shown below, one would expect results very similar to the previous  $^1\text{H}$ NMR spectra shown for the other bis(4-x-phenyl)phenyl phosphine oxides. Therefore, excluding the amine protons,



four sets of peaks should occur: one with the six protons ortho to the phosphine oxide practically equivalent, another those four protons ortho to the amine groups, and two more sets corresponding to the meta and para protons to the phosphoryl on the pendant phenyl ring. In addition, one would expect P-H splitting as observed for all other aromatic regions in these types of monomers. In fact, upon first glance, the  $^1\text{H}$ NMR spectrum (deuterated DMSO) agreed with these speculations; that

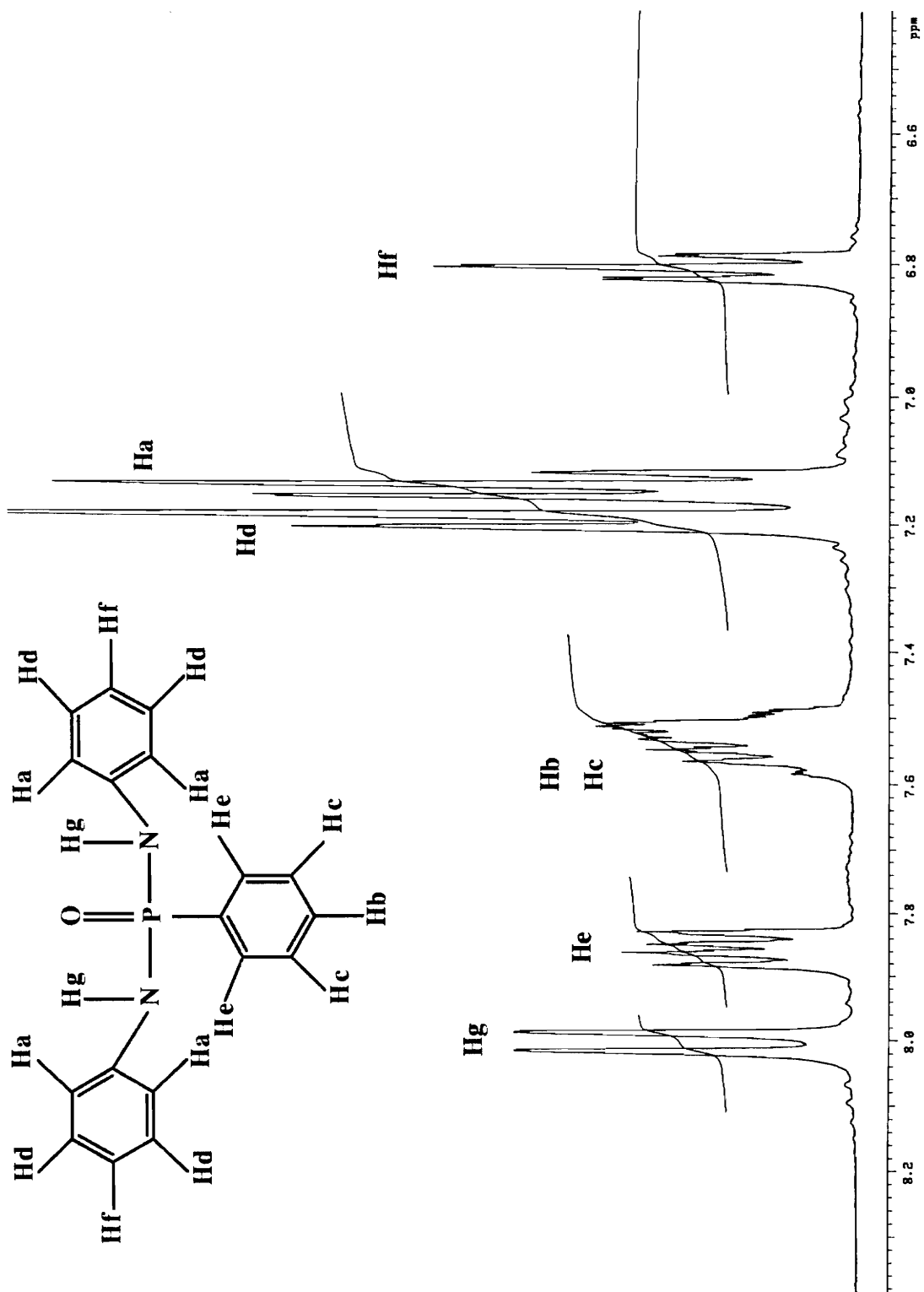
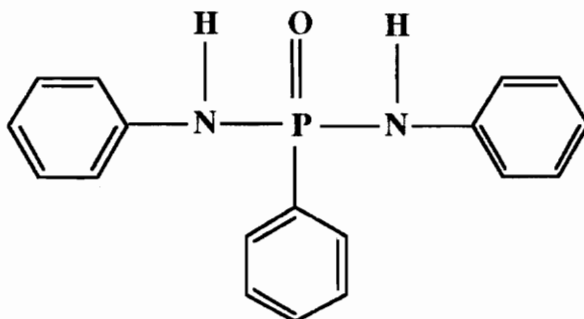


Figure 22.  $^1\text{H}$ NMR of aromatic region of allegedly Bis(4-aminophenyl)phenyl phosphine oxide.

is, four sets of aromatic protons appear along with what was initially assigned to be aromatic amine hydrogens at about 8.0 ppm. Upon closer inspection, however, several discrepancies begin to appear. The integration was (including amine protons, downfield to upfield) 2:2:3:8:2, or upon further expansion, 2:2:3:4:4:2. When compared to the structure above, the ratio should be as for the other similarly substituted monomers, 2:5:2:4. In fact, even the amine protons did not integrate to four as expected, but two. The shift at 8.0 ppm was assigned to protons on nitrogen due to exchange when D<sub>2</sub>O was added to the NMR tube.

Phosphorus NMR of this compound gave a single peak at 8.0 ppm, which cannot be described in terms of the triaryl substituted phosphine oxide structure. A new structure was proposed, phenylphosphoroxo(bisanilide) which corresponded to both the <sup>31</sup>P [293] and <sup>1</sup>H NMR spectra, as well as the observed melting points.



As shown in Figure 22, all protons were easily assigned, and P-H splitting at only one set of peaks was described. Note that elemental analysis performed by the Russian workers would be useless in this case

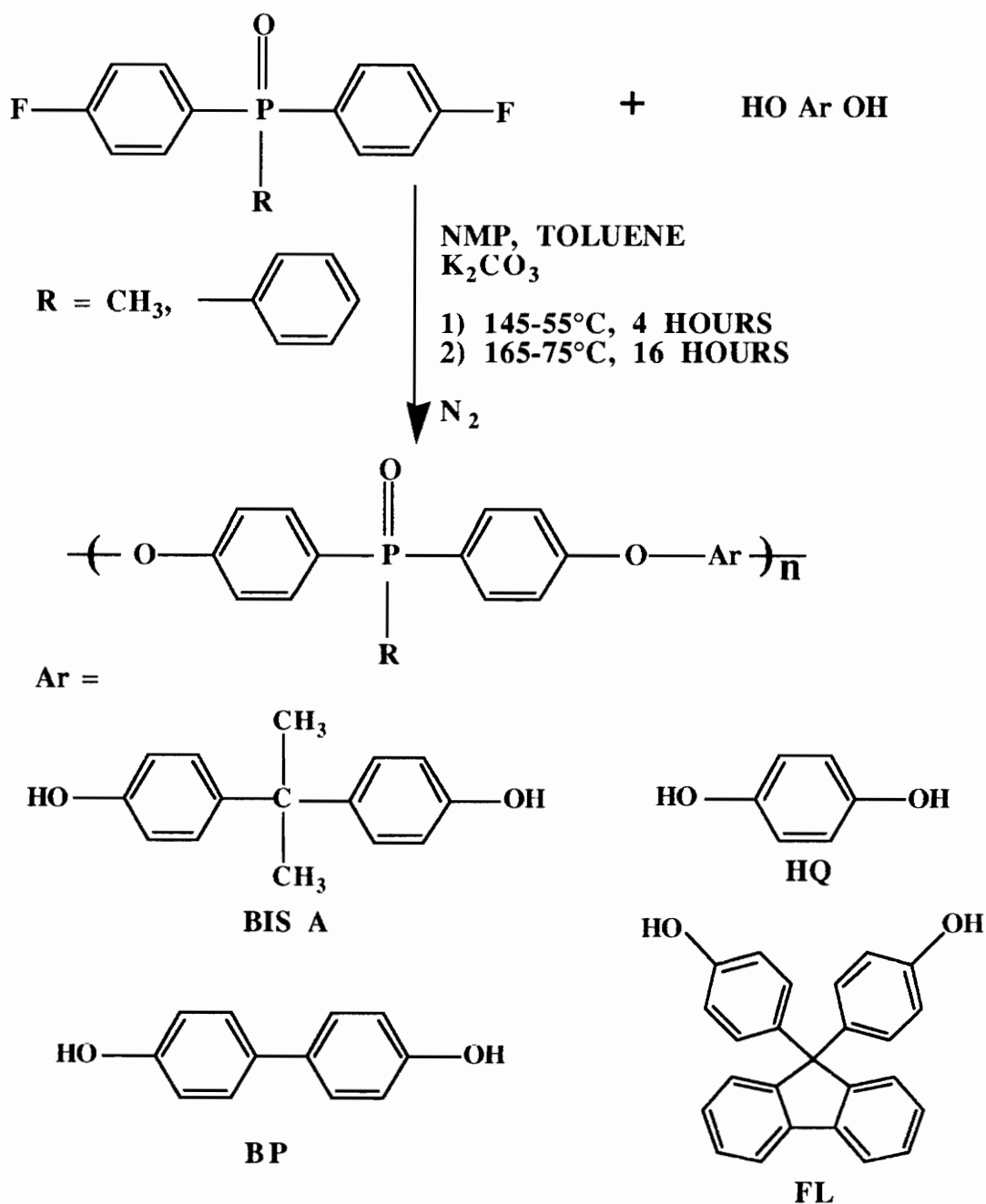
as the structures are isomeric.  $^{13}\text{C}$ NMR also confirmed this structure due to the lack of P-C splitting on many of the peaks. Synthetic aspects help explain the formation of this compound. By heating aniline hydrochloride above its decomposition temperature, aniline was formed, which then reacted with phenylphosphonic dichloride yielding the dianilide by simple splitting off of more HCl gas.

Attempts at polymerization of such a monomer in typical polyimide fashion would certainly yield low molecular weight materials having little value as high temperature polymers. In fact, polyimides claiming to contain this structure were always quoted as having the least thermal stability when compared to other non-phosphorus containing polyimides [218], with total mass loss occurring at 550°C in air! All phosphorus containing polymers prepared in this thesis and related work had at least as good as or better thermal stability than their nonphosphorus analogues. Thus, it is probable that this highly desirable diamine has never been prepared for the synthesis of high polymers.

## 4.2 POLYMER SYNTHESIS AND CHARACTERIZATION

### 4.2.1 High Molecular Weight Poly(arylene ether phosphine oxide)s

As shown in Scheme 37, several high molecular weight poly(arylene ether phosphine oxide)s were prepared from BFPPPO or BFMPPO and aromatic bisphenols in the presence of a weak base, potassium carbonate, and a dipolar aprotic solvent, NMP. Step one in the reaction at approximately



Scheme 37. Synthesis of high molecular weight PEPO.

145-55°C azeotroped off the byproduct water while the second higher temperature step was utilized to drive the polymerization to completion. From the <sup>1</sup>HNMR studies of activated dihalides discussed previously, it

should have been obvious that fluoro leaving groups would be necessary for the synthesis of high molecular weight polymers; since the phosphine oxide activating group was even less electron withdrawing than the ketone moiety, and since high molecular weight PEK cannot be achieved with 4,4'-dichlorobenzophenone, the fluoro group must definitely be the leaving group for the preparation of high molecular weight linear PEPO. Nevertheless, the initial thrust of this project was the investigation of BCPPO as an activated dihalide.

#### 4.2.1.1 Polymerizations Involving BCPPO

Only a few sentences of this section will be dedicated to the attempts at producing high molecular weight PEPO from BCPPO and aromatic bisphenols; however in practice many months were spent laboring over these experiments. From the literature, several workers had attempted to synthesize PEPO from BCPPO, but prepared only low molecular weight materials [158, 239]. Only by incorporating polyfunctional bisphenols, and therefore making a branched system, were polymers of higher solution viscosity prepared with this monomer [239]. This thesis research also supported these findings, with not even a single experiment producing acceptable polymer molecular weights. Many aprotic dipolar solvents were tried as the polymerization media, with little or no success. Under typical conditions in NMP, polymers with intrinsic viscosity of 0.1 dL/g or less were always produced. The "best" polymer prepared from BCPPO was that from biphenol utilizing diphenylsulfone as the solvent at 320°C for sixteen hours; still, this polymer only gave an intrinsic viscosity of



0.3 dL/g, which is still below the widely accepted minimum value of 0.40 dL/g for any desirable properties in poly(arylene ether)s.

#### 4.2.1.2 Polymerizations Involving Activated Difluorides Containing the Phosphine Oxide Unit

Thus, the chosen route to PEPO was from BFPPPO or BFMPPO as shown above in Scheme 37. Using the procedures outlined in the experimental section, very high molecular weight materials could repeatedly be prepared in NMP or DMAc. Visually, the PEPO materials were tan (from NMP) or almost white (from DMAc) and highly fibrous. An interesting observation was made while attempting to precipitate these polymers from either the reaction solvent or other solvents. Most of the homopolymers prepared were very fibrous in nature, but tended to accumulate together, normally around the blender stir blades. The polysulfone counterparts tended to form fibers which separated from one another and floated freely in the precipitation mixture. This phenomena is certainly related to the hydrogen bonding capabilities of PEPO, since separate fibers of PEPO could be formed by precipitating in a non-hydrogen bonding solvent such as hexanes. Coagulation into hexanes is not advised, since this solvent will not draw out trapped NMP or inorganic salt byproducts. Careful control of methanol or isopropanol to water ratios resulted in acceptable precipitation results.

Once reprecipitated and dried, PEPO showed predicted solubility patterns. As illustrated below, BIS A PEPO was soluble in a variety of common solvents such as THF, chlorinated solvents and aprotic dipolar

Table 9. Solubility characteristics of PEPO.

BISPHENOL	THF	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	ØCl	NMP	DMAc
BIS A	S	S	S	S	S	S
HQ	PS	S	S	S	S	S
BP	IS	S	S	PS	S	S

solvents. On the other hand, biphenol based PEPO were not soluble in ether solvents, but freely soluble in chlorinated solvents and aprotic dipolar solvents. These solubility patterns were no doubt related to chain stiffness, with solubility decreasing as chain rigidity increased.

#### 4.2.1.2.1 Spectroscopic Analysis of BFPPPO Based Polymers

Structural confirmation was carried out via spectroscopic methods. Figure 23 illustrates a FTIR spectrum of a BIS A PEPO thin film cast on a KBr window. Both full and expanded regions are shown, along with the FTIR spectrum of a UDEL sample in Figure 24 for more helpful peak identification. Peak identities along with their assignments are given in Table 10 for both of these samples.

Proton NMR of PEPO materials were complex as were their monomeric counterparts, because of splitting with phosphorus. A typical <sup>1</sup>H NMR spectrum of a high molecular weight BP PEPO is shown in Figure 25. Referenced to TMS at 0 ppm, note again the downfield shift of the water peak in CDCl<sub>3</sub> due to hydrogen bonding with the phosphine oxide group.

Table 10. FTIR peak assignments for BIS A PEPO and UDEL PSF.

POLYMER (CM <sup>-1</sup> )		ASSIGNMENTS	
BIS A PEPO	UDEL	BIS A PEPO	UDEL
3063	3061	AROM. C-H	AROM. C-H
1590, 1494	1586, 1505	AROM. C=C	AROM. C=C
1436	---	AROM. C-P	---
---	1324	---	O=S=O ASYM.
1245	1242	AROM. C-O-C	AROM. C-O-C
1193	---	P=O	---
---	1150	---	O=S=O SYM.
750	---	C-P	---

All aromatic protons appear between 7.0 and 7.8 ppm, with basically two sets of resonances corresponding to 1) those protons ortho to an ether linkage and 2) all other protons. The eight protons ortho to an ether linkage fall about 7.12 ppm, while the four ortho protons to the biphenyl linkage along with the six protons ortho to the phosphoryl group and the other three protons on the pendant phenyl ring lie between 7.45-7.75 ppm. The absence of any small side bands around this aromatic region indicated high molecular weight, as it will be shown later that controlled molecular weight polymers always had small peaks around the main aromatic regions corresponding to end group aromatic protons.

As another method for the confirmation of polymer structure, <sup>13</sup>CNMR was utilized. A sample spectrum is shown in Figure 26 for high molecular

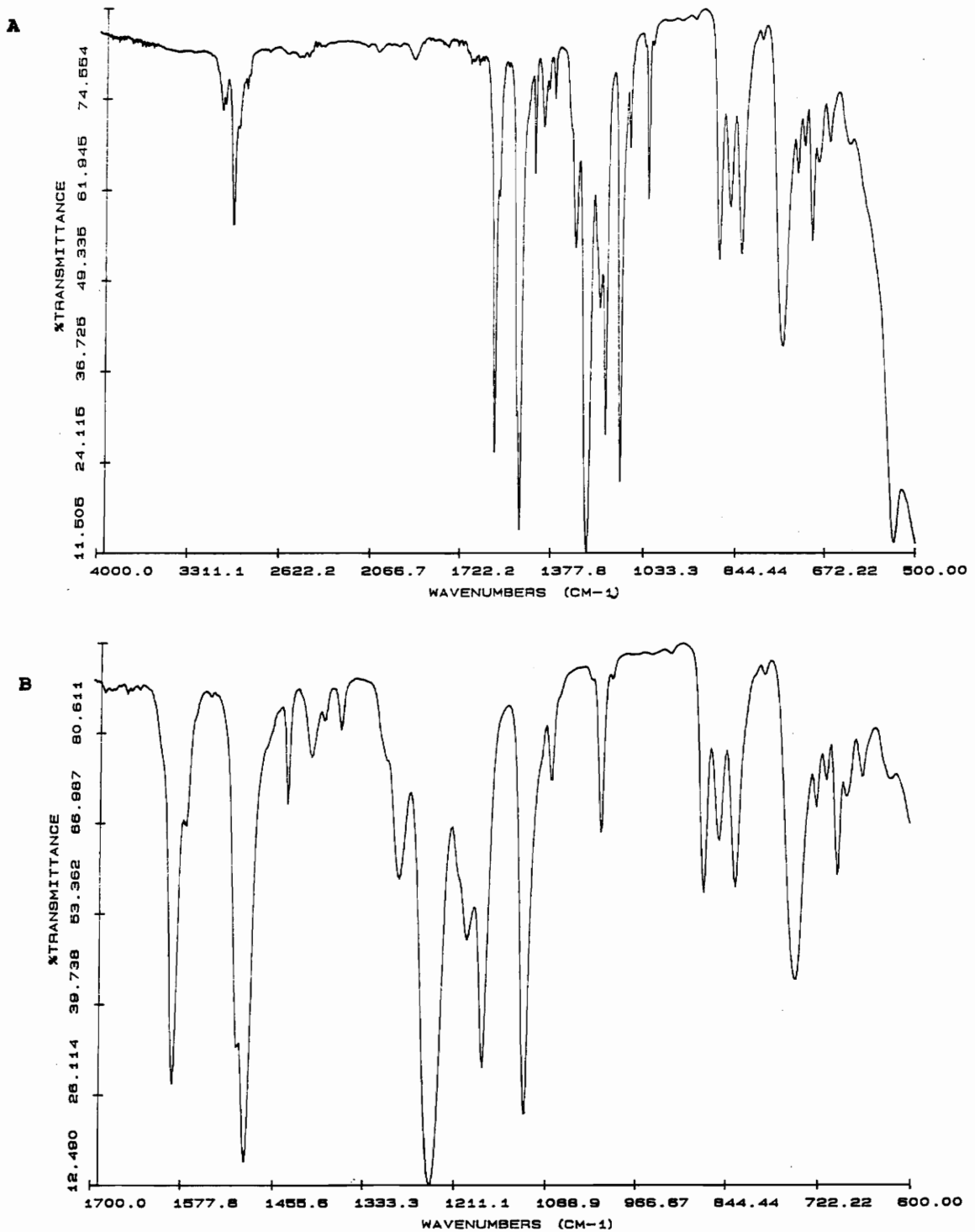


Figure 23. FTIR spectrum of high molecular weight BIS A PEPO : A) entire spectrum and B) expanded region.

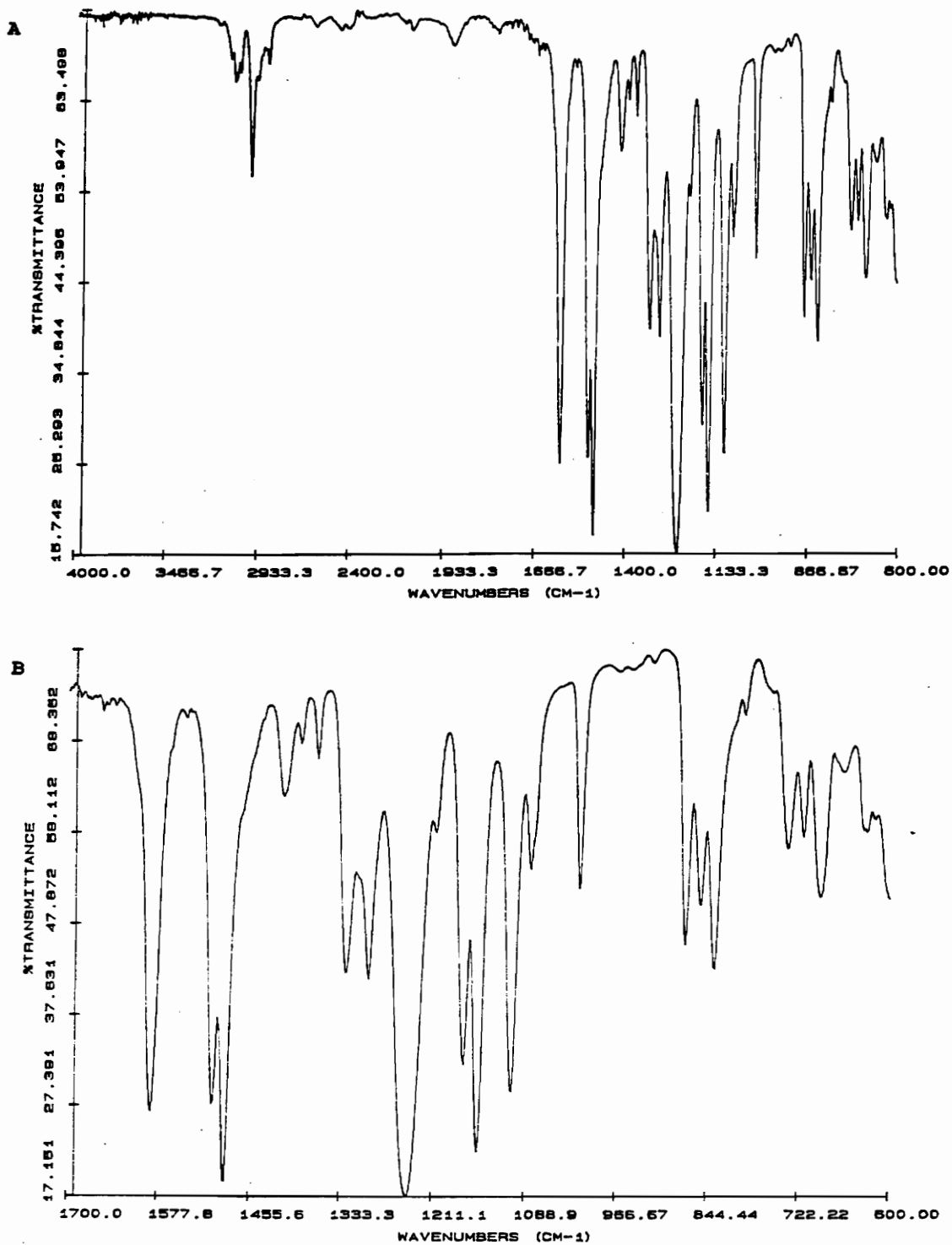
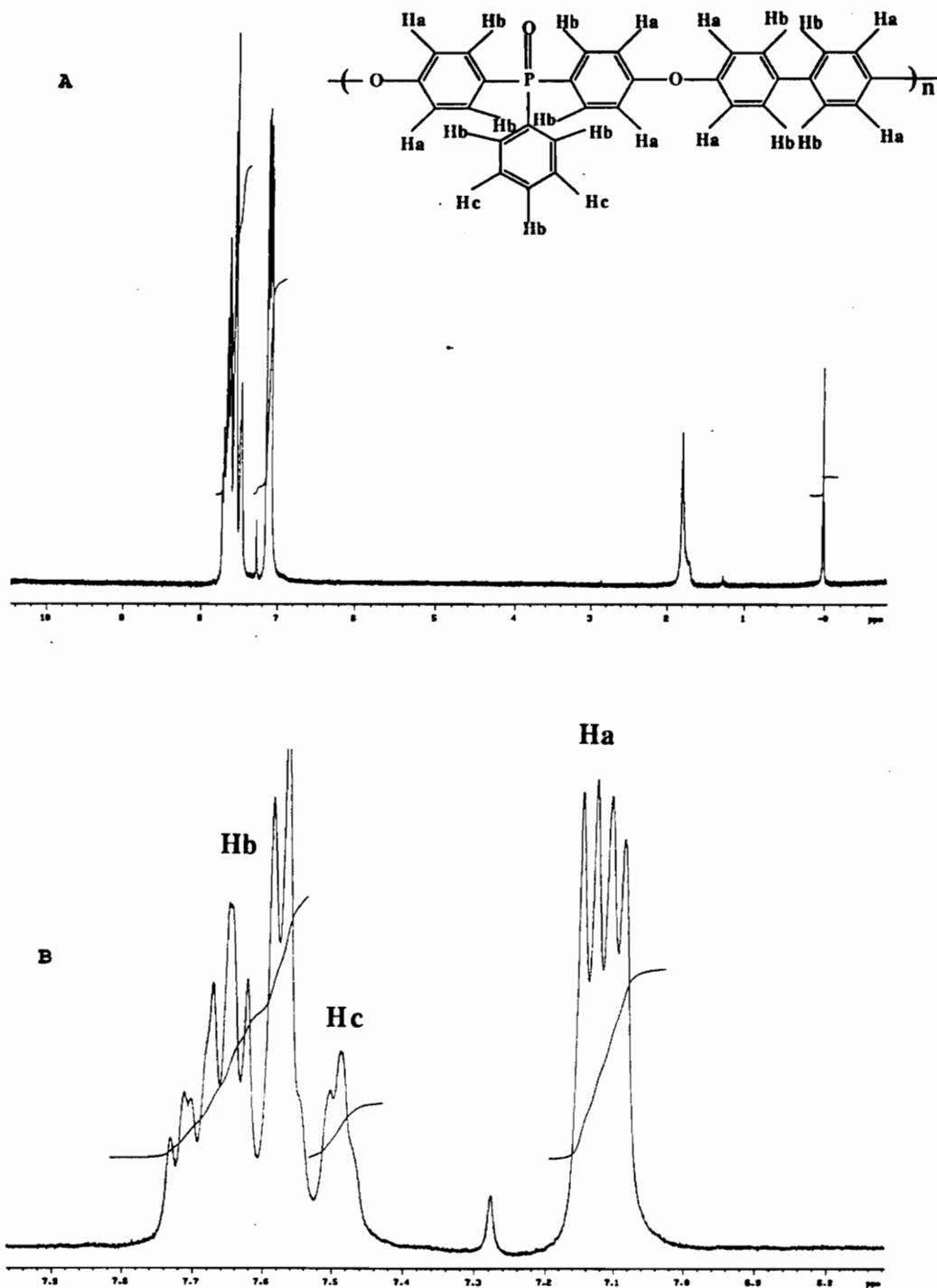
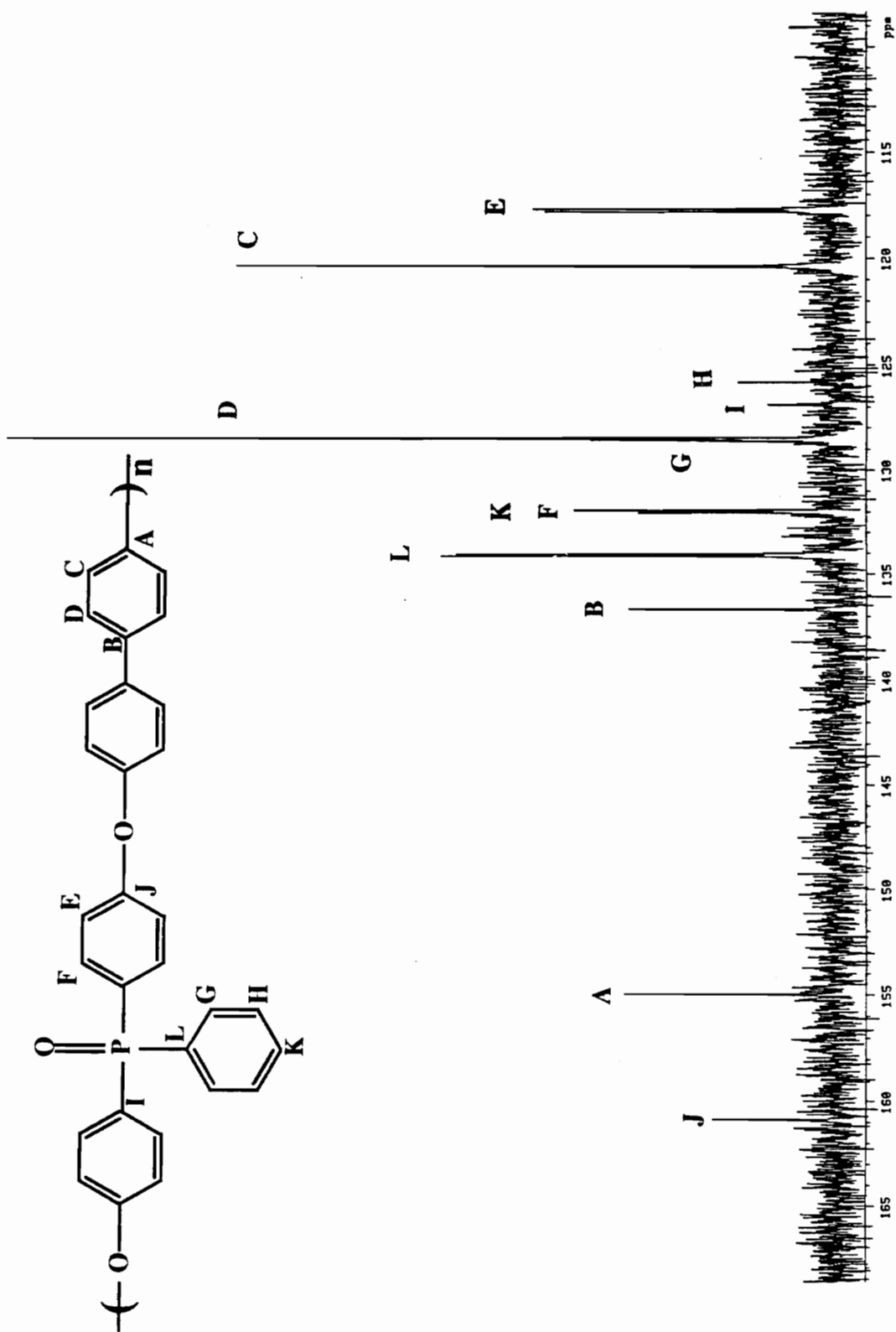


Figure 24. FTIR spectrum of high molecular weight UDEL PSF : A) entire spectrum and B) expanded region.



Figure 26.  $^{13}\text{C}$  NMR spectrum of high molecular weight BP PEPO.

weight BP PEPO. Again used were the estimated values for phosphine oxide substitution shown for BFPPPO previously. Calculated values for carbon chemical shifts were close to actual values as shown below.

<u>Carbon atom</u>	<u><math>\delta</math> (experimental, ppm)</u>	<u><math>\delta</math> (calculated, ppm)</u>
A	155.2	156.7
B	136.7	136.7
C	120.5	119.7
D	128.7	129.2
E	118.0	118.8
F	132.0	131.3
G	132	129.7
H	127	128.2
I	128.7	129.6
J	161	161
K	132	131.7
L	134.5	134.7

Phosphorus NMR on all PEPO were simple one peak spectra (24.6 ppm downfield from 85%  $H_3PO_4$ ) in DMAc solution.

#### 4.2.1.2.2 Spectroscopic Analysis of BFMPPO Based Polymers

Similar to those procedures above for BFPPPO based PEPO, the BFMPPO polymers were spectroscopically characterized in much the same way. Many



equivalent results were obtained since the only structural difference was the substitution of a methyl group for the pendant phenyl ring. Polymers based on BFMPPO will be referred to as (Me) PEPO to avoid confusion with the more commonly used PEPO for the BFPPPO based materials. FTIR spectra (see Figure 27) were comparable between the two types of PEPO, with the major differences being the disappearance of P-phenyl stretches and the appearance of P-methyl stretching at 1403, 1306 and 885  $\text{cm}^{-1}$ .

Nuclear magnetic resonance studies of these macromolecules (Figures 28 and 29) also confirmed polymer structure. While the methyl protons chemical shift was 2.0 ppm, the aromatic region was somewhat more simplified relative to BFPPPO based PEPO. Three sets of aromatic protons were assigned according to Figure 28. Likewise,  $^{13}\text{C}$ NMR chemical shifts were calculated as previously discussed and the assignments are shown in Figure 29.

#### 4.2.1.2.3 Viscosity and Thermal Data for PEPO Thermoplastics

Intrinsic viscosities were desired for these PEPO homopolymers to obtain a qualitative understanding of their molecular weights. Visual inspection of the polymerization mixtures as being very viscous upon completion of reaction, as well as the fibrous nature of the final products led one to believe very high molecular weights were being formed. Indeed, intrinsic viscosities of both the BFPPPO and BFMPPO series of PEPO displayed quite high values in methylene chloride at room temperature, as illustrated in Table 11. Also included in Table 11 is

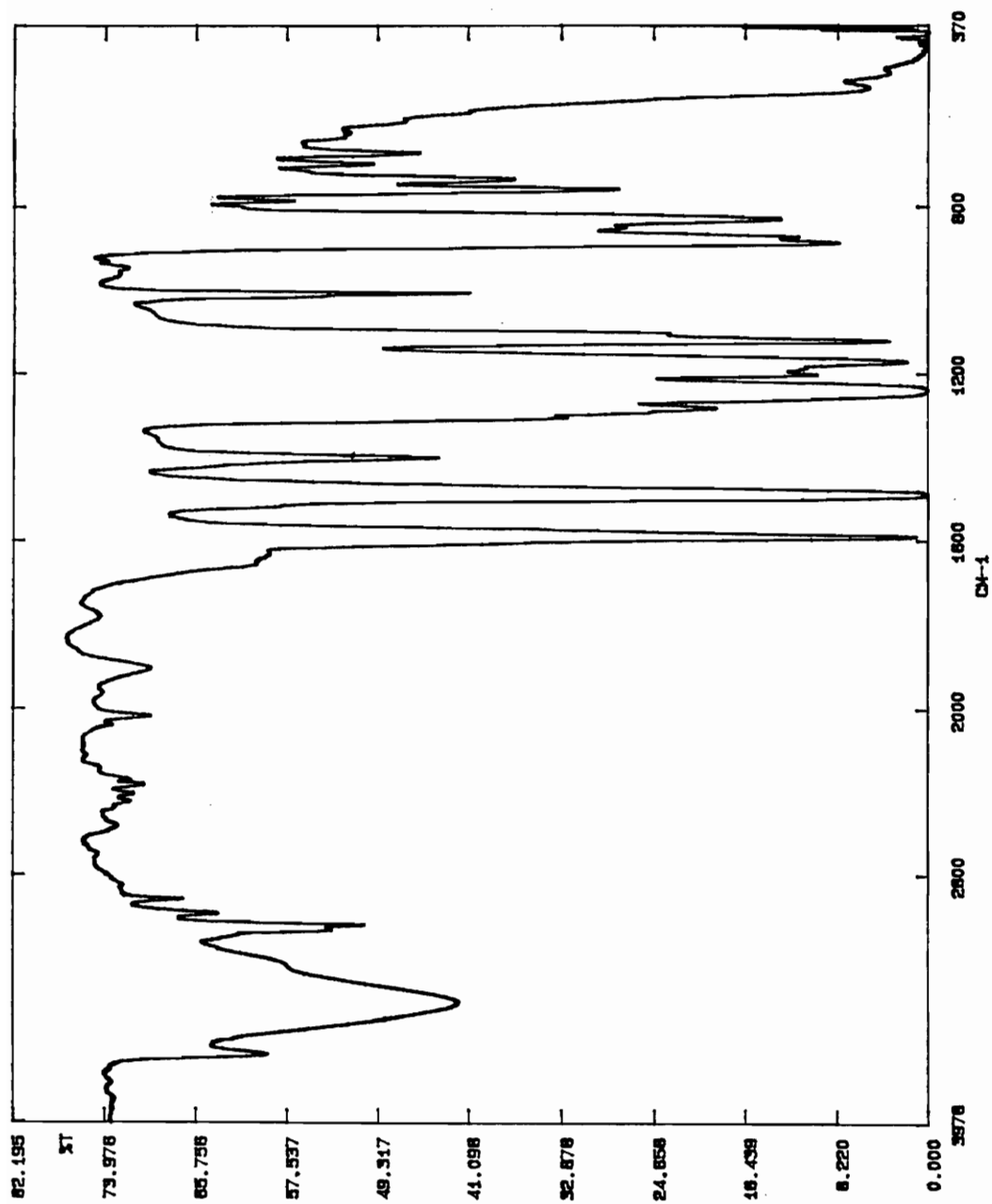


Figure 27. FTIR spectrum of high molecular weight BP (Me) PEPO.

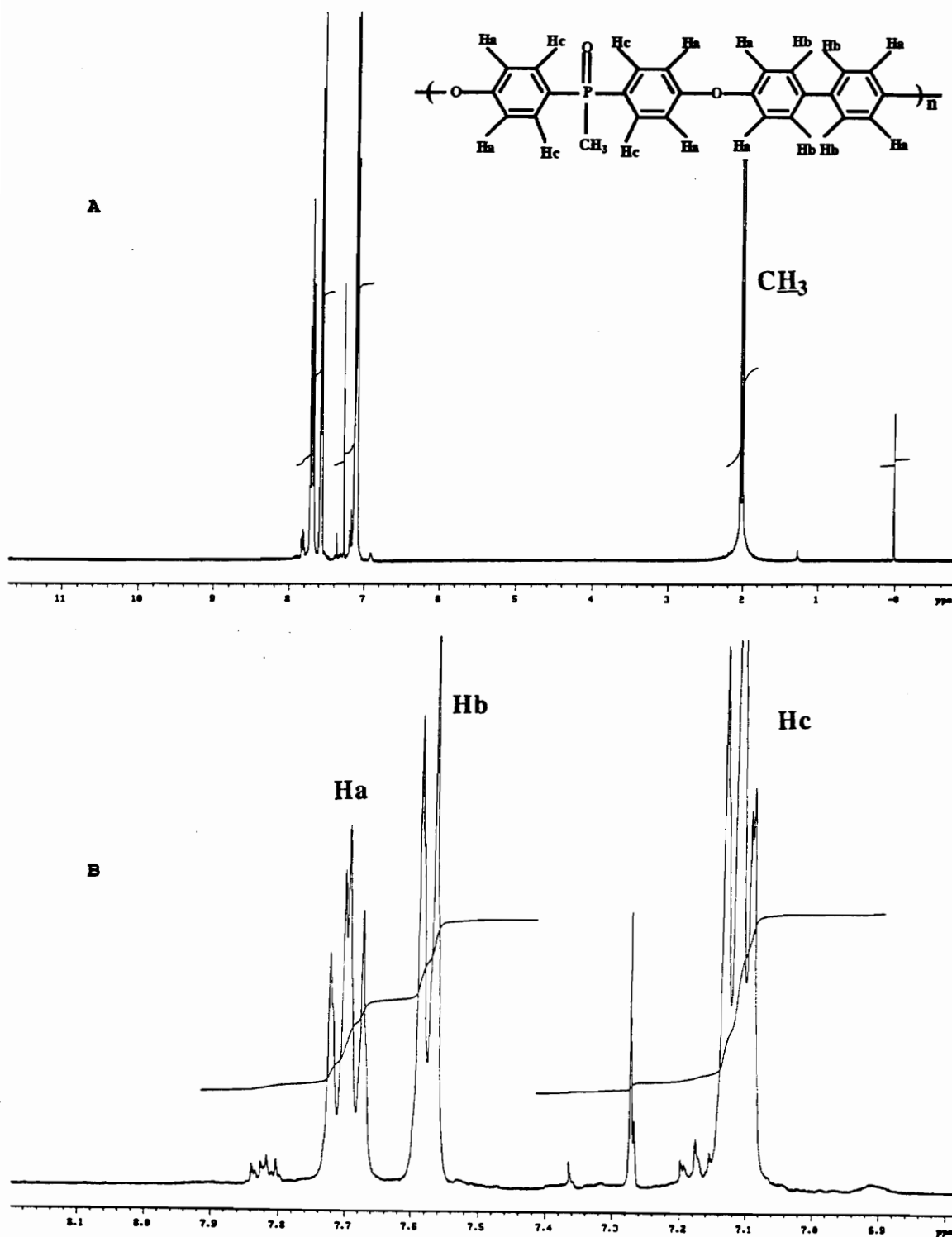


Figure 28. <sup>1</sup>H NMR spectrum of high molecular weight BP (Me) PEPO : A) entire spectrum and B) expanded aromatic region.

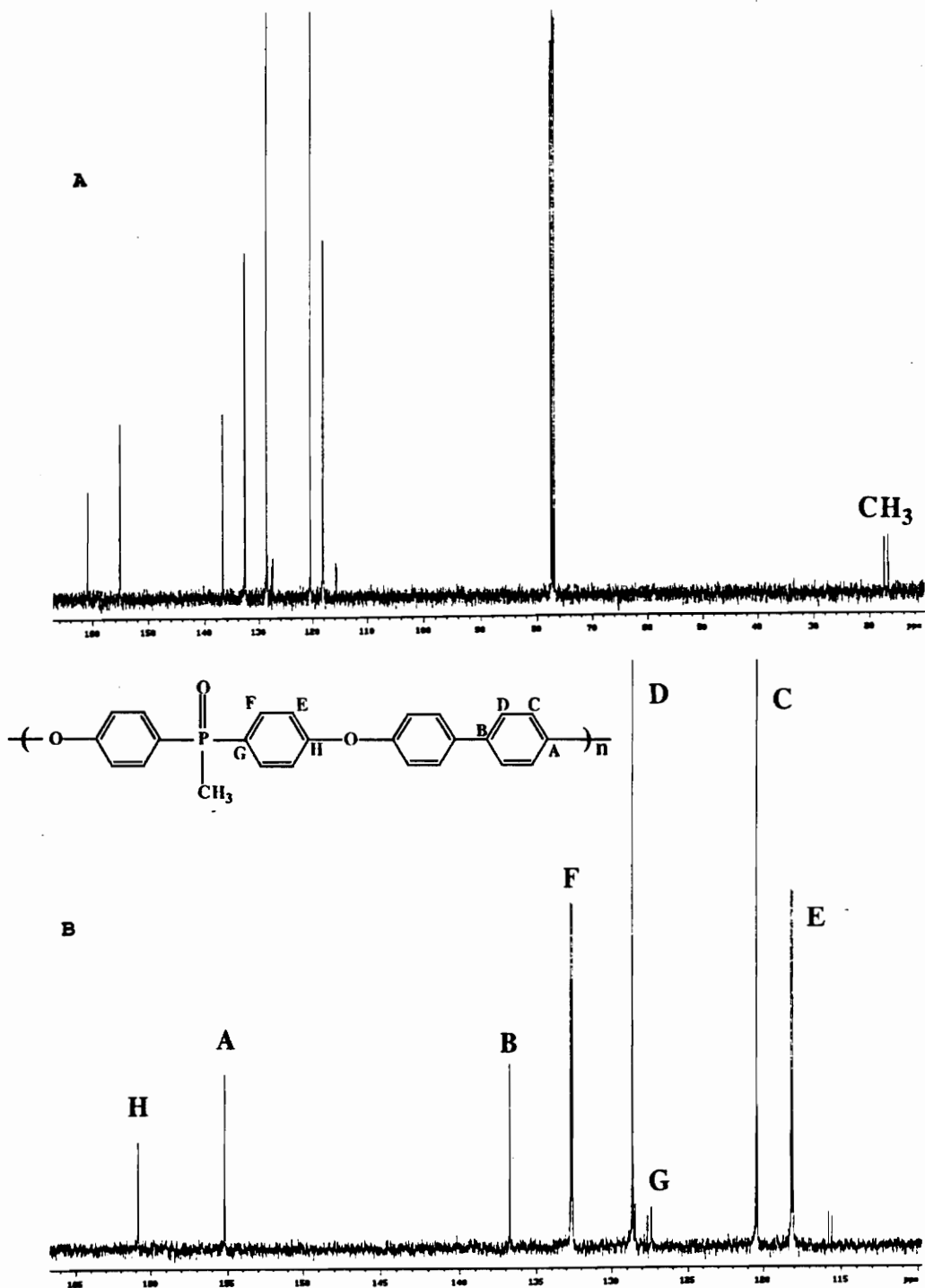
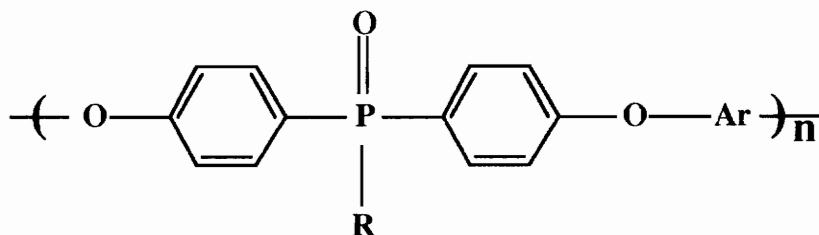


Figure 29.  $^{13}\text{C}$  NMR spectrum of high molecular weight BP (Me) PEPO : A) entire spectrum and B) expanded aromatic region.

Table 11. Intrinsic viscosity and thermal data for PEPO.



BISPHENOL	$[\eta]$ 25°C CH <sub>2</sub> Cl <sub>2</sub>	(dL/g)	T <sub>g</sub> (°C) *	TGA (°C) **
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R = PHENYL

BIS A	1.38		205	490
HQ	1.03		215	520
BP	2.25		245	520
FL	0.60		282	530
UDEL	0.40		190	495

R = METHYL

BIS A	1.04		195	470
HQ	0.72		207	500
BP	0.75		234	495
FL	0.30		272	500

\* Values are from second run after quench cool from first run

\*\* Values are temperature at 5% weight loss in air

the intrinsic viscosity of Udel polysulfone for comparison purposes. From these values, it can easily be observed that high molecular weight was definitely accomplished in every case, except for perhaps FL (Me) PEPO. In all other cases, where intrinsic viscosities were above 0.60 dL/g, clear, flexible and creasable, slightly yellow colored films could be cast from solution. All of these samples gave higher viscosities than the commercial sample of polysulfone, so high molecular weight was qualitatively assigned.

Hydrolytic stability of these materials was at least qualitatively guaranteed by the fact that boiling water had apparently no effect on the molecular weight properties of these polymers. At times, PEPO were stirred in hot to boiling water for periods of several hours to wash out any excess bases or salts, and resulting viscosities after drying were unchanged from those above.

Studies on the glass transition temperatures ( $T_g$ ) of the PEPO was performed primarily by DSC, and this data is also summarized for the PEPO homopolymers in Table 11. Immediately obvious was the fact that all PEPO, regardless of chain rigidity, were amorphous. This is also the case with some polysulfones of otherwise identical structures, but not the case for the class of PEK, as discussed in the background. Ranging from 205°C-282°C, the  $T_g$ 's of BFPPPO based PEPO were some 10-15°C higher than their known polysulfone counterparts [52], probably owing to the bulky nature of the phenyl phosphine oxide group. On the other hand, the (Me) PEPO had almost identical  $T_g$ 's as their polysulfone analogues, indicating similar molar volumes for these two systems. As another

indication of high molecular weight formation, compression molding of PEPO materials at temperatures some 50°C greater than their  $T_g$  gave clear tough plaques of these materials which were useful later in mechanical and fire testing of PEPO.

Also shown in Table 11 are the 5% weight loss values of the PEPO series in air at 10°C/min by dynamic TGA. All BFPPO PEPO displayed 5% weight loss around 500°C, while their methyl pendant derivatives performed quite well, only decreasing the weight loss values by 20-30°C. An observation made for all PEPO homopolymers, which was found to be true also for all copolymers and blends as well, was the significant amounts of char formation at temperatures in excess of 600°C in air. Shown in Figure 30 are the TGA traces for BP PEPO in air at various heating rates (1,2,5 and 10°C/min). For reference purposes, thermograms at 10°C/min for samples of commercial Udel polysulfone and PEEK are also illustrated in Figure 31. By comparing these two figures, it is obvious that phosphorus was contributing to char formation in these new materials. While both Udel and PEEK had completely volatilized in air around 700°C, some char was observed for PEPO in excess of 800°C. Percents of char formation varied with which PEPO was investigated, with typical amounts ranging from 10-40% at 800°C in air at this 10°C/min heating rate. Amounts of char were observed to decrease with decreasing heating rate, due to the longer residence time for the polymeric materials; however this fact also applies to the non-phosphorus analogues, as they were completely volatilized at lower temperatures for

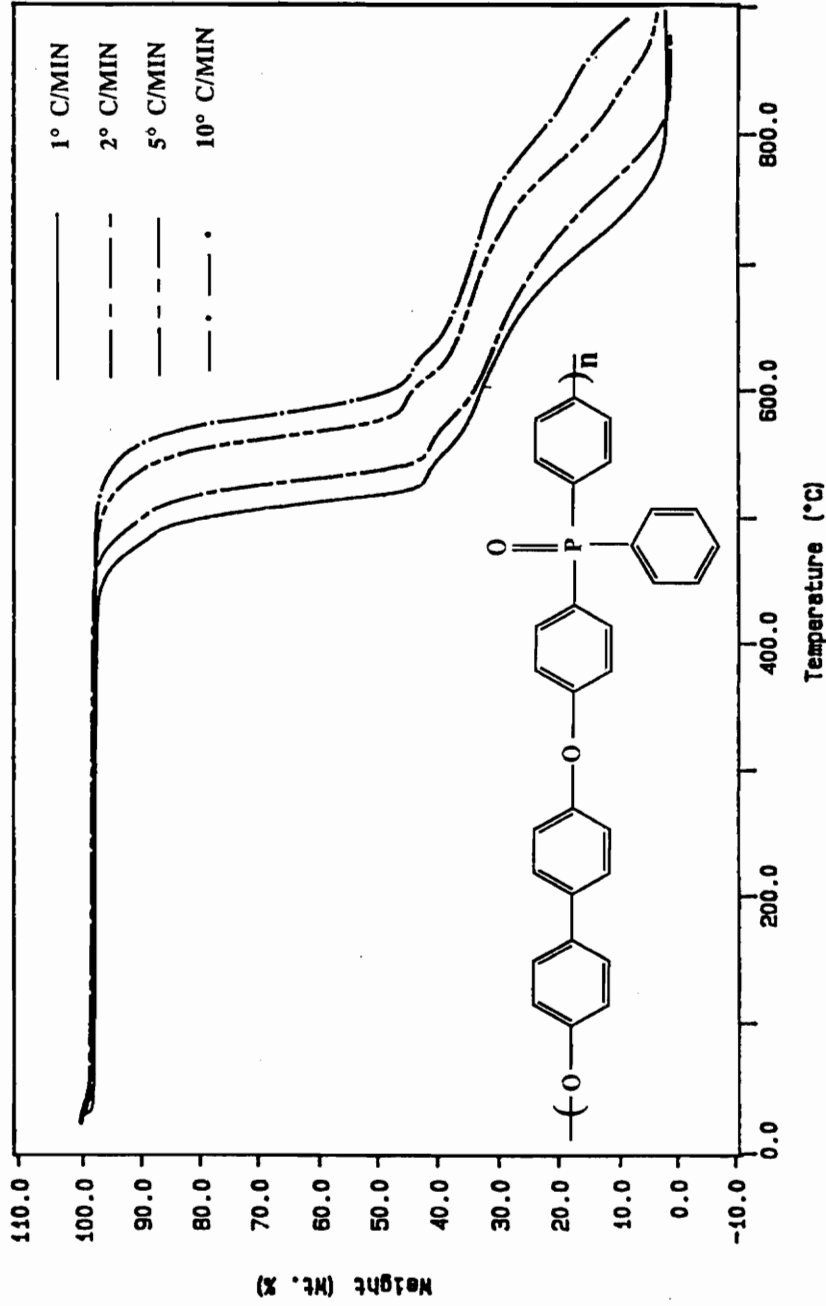


Figure 30. TGA thermograms in air of high molecular weight BP PEPO at various heating rates.



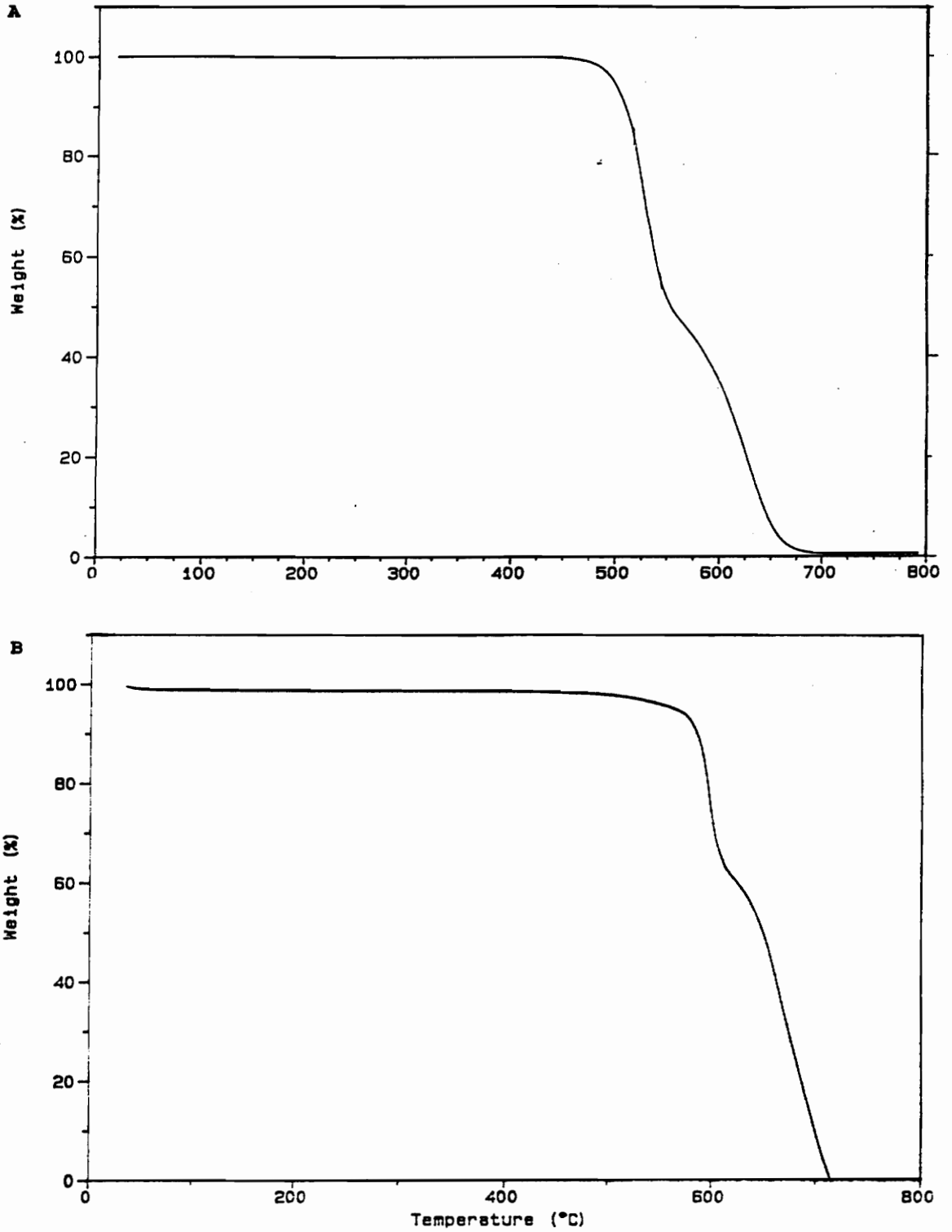


Figure 31. TGA thermograms for : A) Udel and B) PEEK at 10°C/min in air.

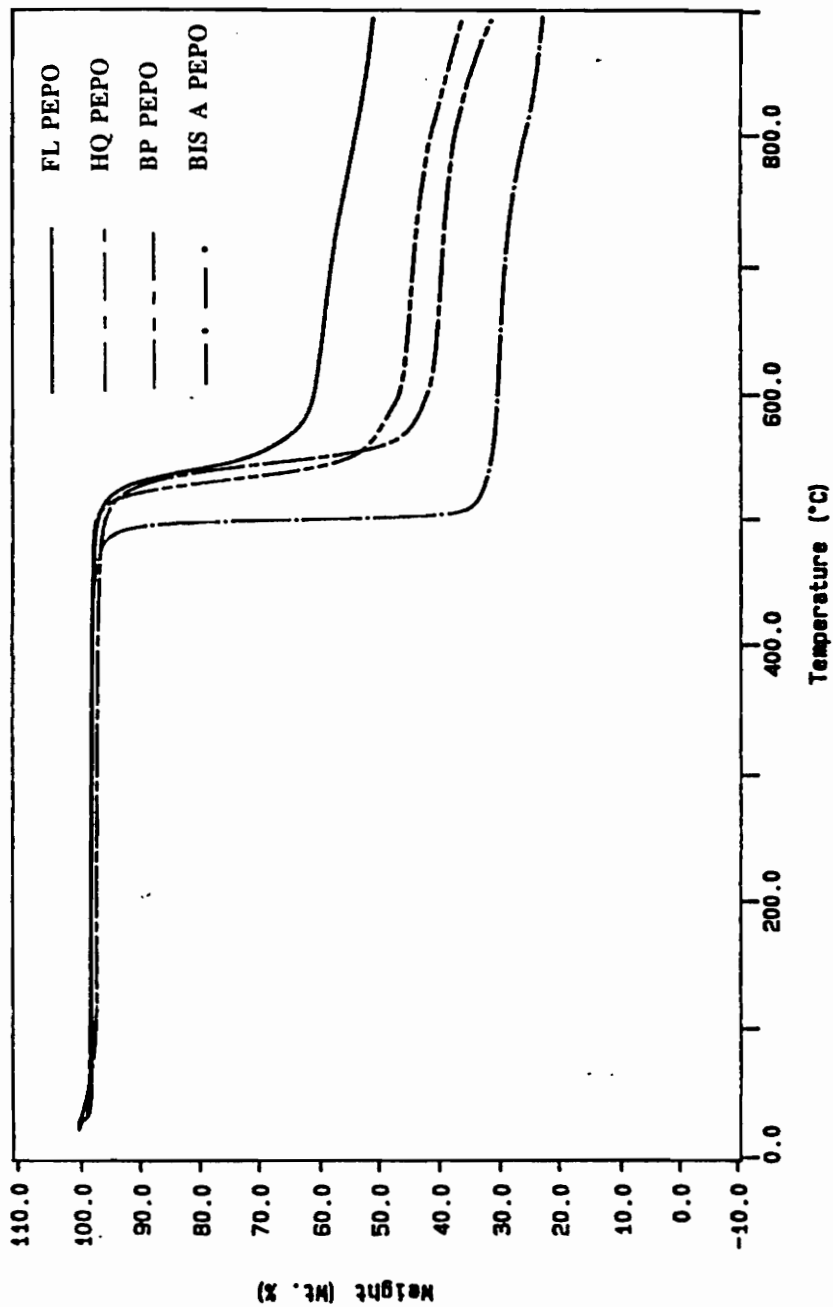


Figure 32. TGA thermograms in nitrogen of high molecular weight PEPO's at 5°C/min.

lower heating rates.

The degradation was a two step process in air; however investigations as to thermal degradation of PEPO in nitrogen (Figure 32) indicated only a single stage of rapid degradation. Occurring at 500°C for BIS A PEPO and about 50°C higher for the other PEPO, this step gave 25-50% char residues at 800°C. Therefore, it was speculated that the second stage of degradation observed in air is probably due to some oxidative type reactions followed by volatilization.

As a final test adding to the case for thermal stability, isothermal TGA were performed in air at various temperatures to give a more realistic view of high temperature performance. As shown in Figure 33, isothermal holds at 300, 350 and 400°C in air gave intriguing results. Practically no weight loss occurred at 300°C over the eight hour period; the sample held at 350°C for eight hours displayed a 7% mass loss. For the sample held at 400°C for eight hours, a 60% weight loss occurred over this period, but the remaining 40% seemed to be stable at this temperature as the curve continued to flatten out after the eight hour period. Therefore, one could expect these materials to be stable for long times at 300°C, and perhaps even higher.

#### 4.2.1.2.4 Pyrolysis Investigations of PEPO Materials

Formation of char appears to play an important role in the self-extinguishing properties of engineering thermoplastics and char yields have previously been correlated with the limiting oxygen index (LOI) of

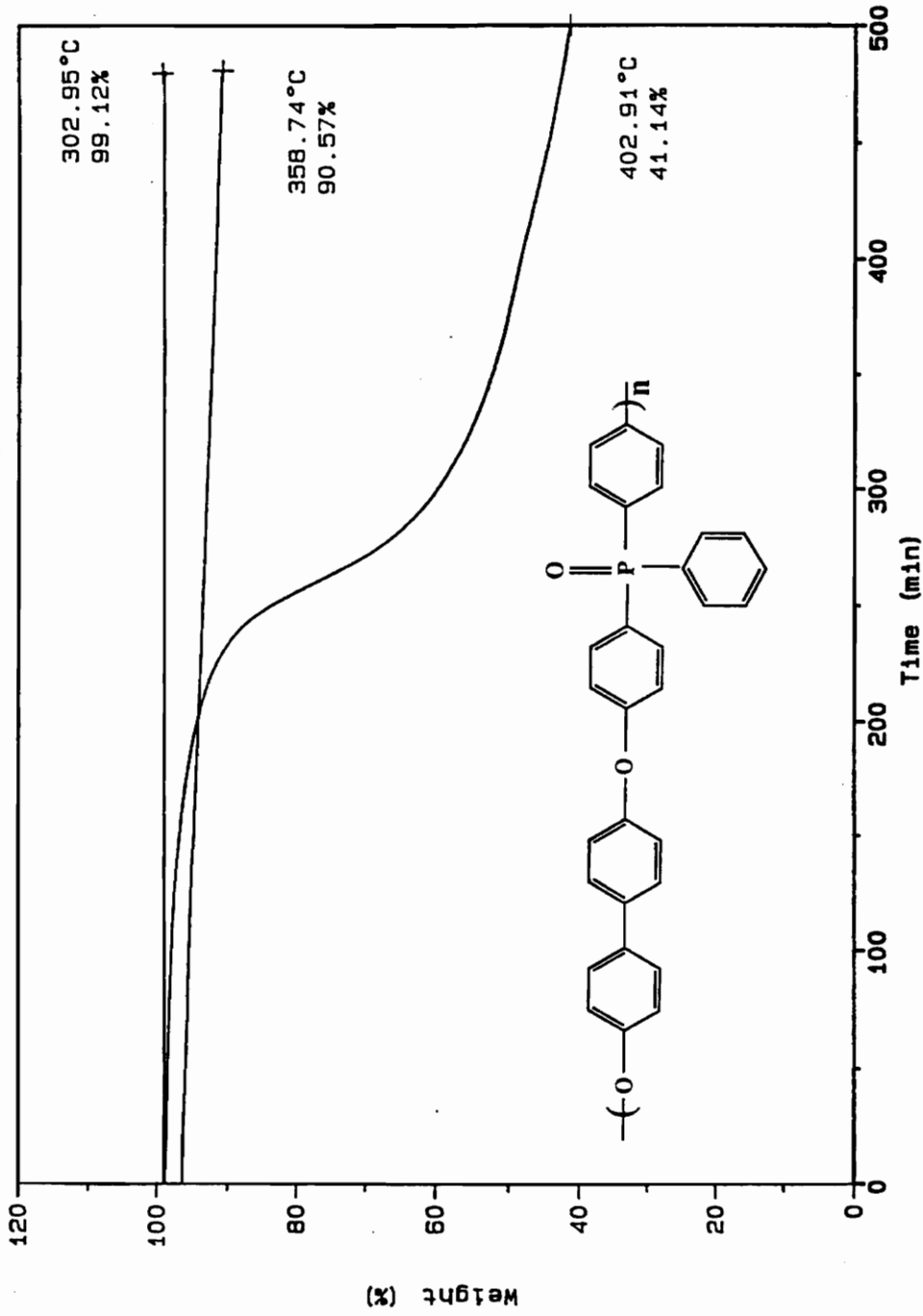


Figure 33. Isothermal (eight hour) TGA thermograms in air of high molecular weight BP PEPO.

many polymers [260, 267, 268, 277-279]. The LOI has been the most quoted measure of polymers' resistance to flame environments, but it seems to be dependent on such a long list of variables that it appears a single number cannot possibly describe the behavior of a polymer when burned. In a qualitative test developed here, films on the order on 0.5-1mm thick were exposed to a bunsen burner flame in air for constant amounts of time, then removed after a predetermined period in the flame. In all cases, non-phosphorus containing engineering thermoplastics (PEEK, UDEL, Ultem polyimide, etc.) with very high literature LOI values appeared to completely volatilize; on the other hand, all phosphorus containing PEPO systems immediately extinguished upon removal from the flame. This test could be repeated several times for any single PEPO sample. Candle-like burning was sustained for PEEK, UDEL and Ultem films after removal from the flame. As a consequence of these qualitative results, an effort was put forth to examine both the volatile and non-volatile portions of several engineering thermoplastics compared with the same for PEPO.

As discussed in the background, the study of polymeric materials containing the triphenyl phosphine oxide moiety chemically bound within the polymer chain as flame retardant polymers has been limited. On the other hand, poly(arylene ether sulfone)s and poly(arylene ether ketone)s have been explored in terms of thermogravimetry or pyrolysis in order to obtain a more detailed analysis of the degradation process [33, 267, 269, 274, 280, 281]. Typically, these materials begin to degrade by chain scission at the sulfone or ketone group to give sulfur dioxide or

carbon monoxide, respectively, along with several phenyl radicals. The radicals formed from this first chain breaking reaction go on to initiate further chemistry, finally totally volatilizing the polymer at sufficiently high temperatures. Using pyrolysis/gas chromatography/mass spectrometry techniques, along with neutron activation analysis, the ability to determine the fate of phosphorus in the burning process, as well as observing the degradation products of PEPO compared to other engineering thermoplastics was demonstrated.

Typical pyrograms (600°C) of two PEPO and their PAE analogs (i.e. BIS A PEPO vs. UDEL and HQ PEPO vs. PEEK) are illustrated in Figures 34 and 35 along with peak identifications from extensive model compound studies. One note should accompany discussions regarding decomposition, this being that any volatile formed which boiled lower than -100°C would not be trapped and therefore not identified. The first striking difference between the pyrograms of PEPO and the other PAE was the lack of initial gas formation in the vapor. For Udel polysulfone, sulfur dioxide was clearly formed during the decomposition process, and presumably carbon monoxide was a primary product for PEEK degradation. Typically, other than the lack of SO<sub>2</sub> or CO formation, degradation products were similar for PEPO's and their PAE counterparts (i.e. Udel vs. Bis A PEPO and PEEK vs. HQ PEPO). In the case of the Bisphenol A based polymers, the pyrograms were more complicated than the hydroquinone based polymer pyrograms due to the presence of isopropylidene linkages along the backbones, giving various degradation products characteristic of this type of moiety [269].

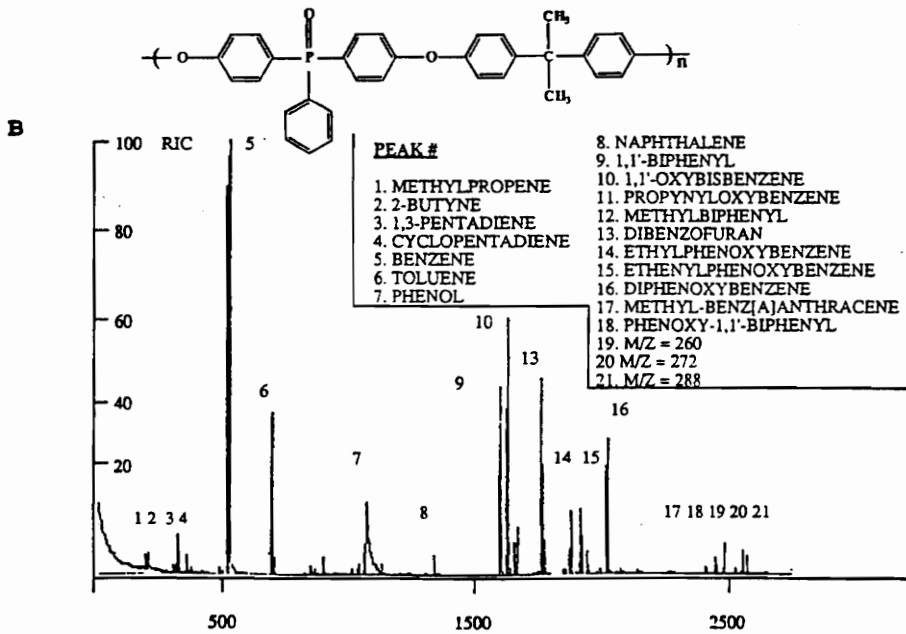
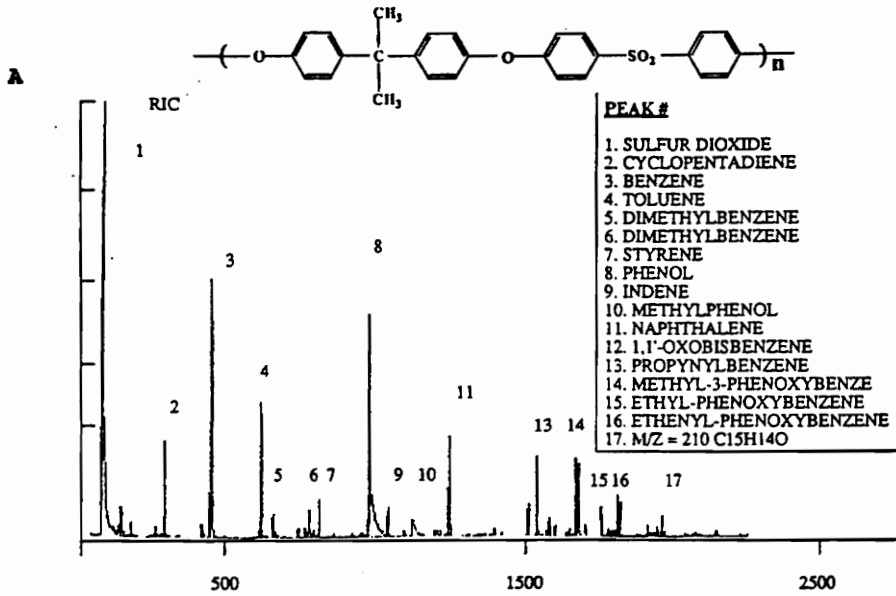


Figure 34. Pyrograms of A) UDEL vs. B) BIS A PEPO.

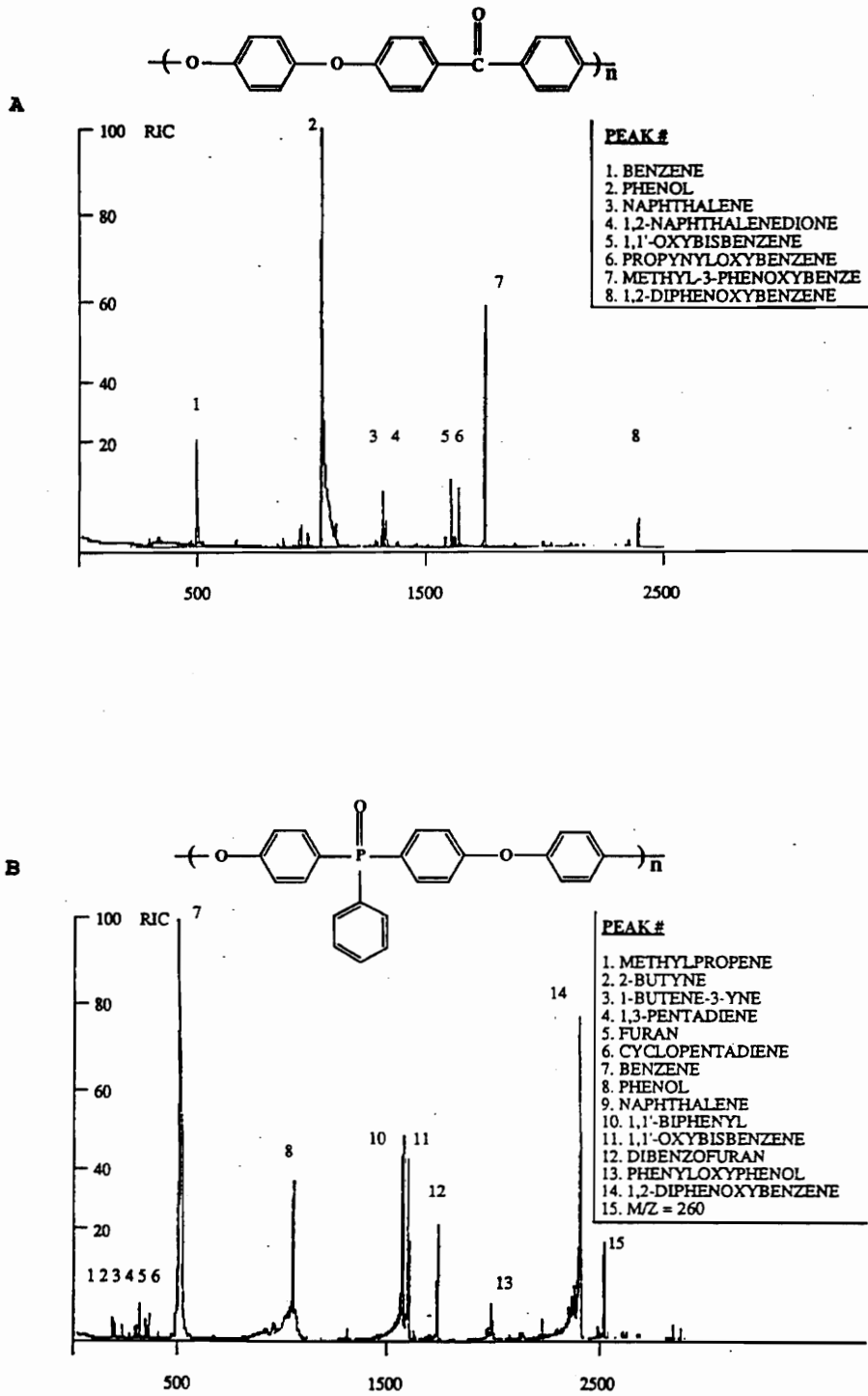


Figure 35. Pyrograms of A) PEEK vs. B) HQ PEPO.



Pyrolysis of a TPPO standard at 600°C gave a single peak in the pyrogram corresponding to the starting model compound, indicating the surprisingly high thermal stability of this molecule. The large amounts of char formed in all cases with PEPO (Table 12), along with the fact that very few if any phosphorus containing volatiles were identified, also pointed to the presence of phosphorus in the char. On the other hand, other poly(arylene ether)s gave essentially no char to analyze upon pyrolysis at 600°C.

Table 12. Char yields of PEPO systems upon pyrolysis at 600°C.

PEPO POLYMER	% YIELD DATA	
	RESIDUE (CHAR)	PYROLYSATE
BIS A	31.0	65.8
HQ	49.7	53.4
BP	43.4	31.6

In order to confirm the presence of phosphorus in either the char or volatile fractions of the decomposition products, neutron activation analysis (NAA) was employed. This technique allows one to analytically determine atomic percents of constituents either in the volatile or the solid phases. Experimental details of this technique will be outlined in a future publication [294].

From NAA, we indeed confirmed that phosphorus containing degradation products were for the most part nonvolatile. Again, it should be noted that other poly(arylene ether)s gave essentially no char to analyze at 600°C in air, while the PEPO materials all gave substantial amounts of char at 600°C in air (see Table 12). Table 13 summarizes the data from NAA experiments on both pyrolysis volatiles and char.

Table 13. Neutron activation analysis of PEPO.

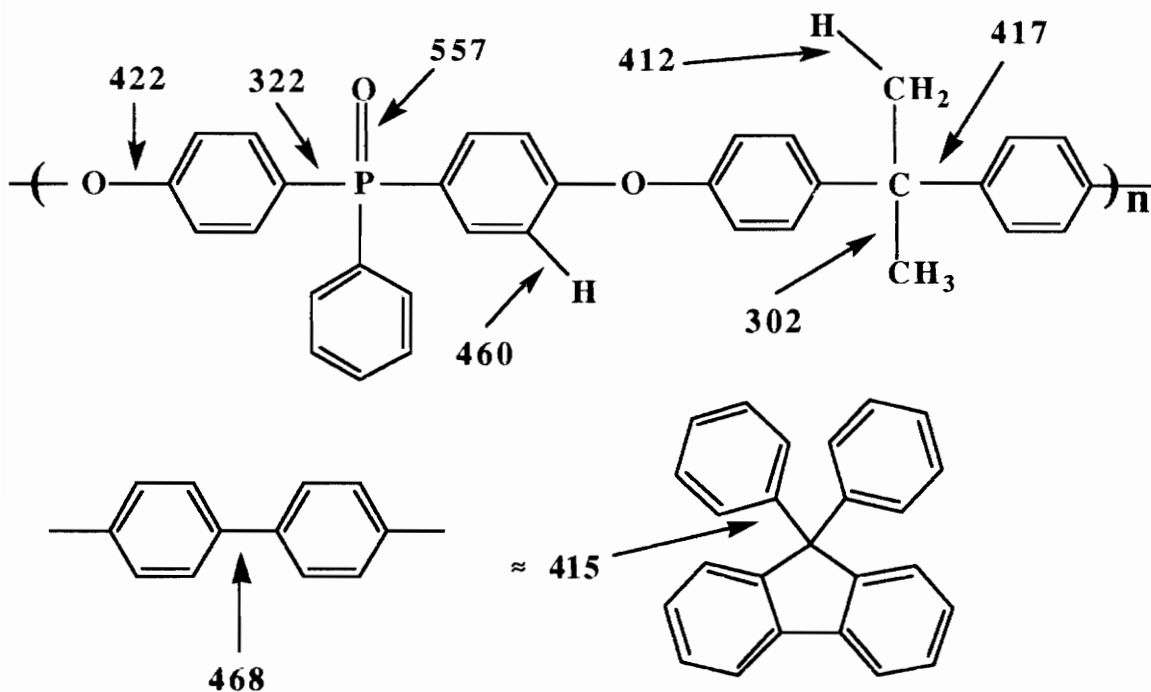
PEPO POLYMER	PHOSPHORUS CONTENT (WEIGHT %)	
	CALCULATED	EXPERIMENTAL (NAA)
BIS A : INITIAL	6.2	6.4
CHAR	---	12.0
VAPOR	---	2.2
HQ : INITIAL	8.1	9.0
CHAR	---	15.6
VAPOR	---	0.9
BP : INITIAL	6.6	6.8
CHAR	---	12.6
VAPOR	---	1.7

Obviously, the char is much richer in phosphorus than the initial polymer, normally by (nearly) a factor of how much volatile was formed. In all cases, the char is approximately double the content of phosphorus compared to the undegraded PEPO sample, while the volatile fraction contains typically 1-2% phosphorus. These findings indicate a dual mechanism for reduced flammability, both gas and solid phase modes of

fire-retardance, but the primary route must be the condensed phase reactions due to the much larger content of phosphorus in the solid after pyrolysis. Therefore, it can be concluded that phosphorus plays a very important role in char formation promotion, and a minor role in diluting those flammable volatiles formed. In other words, from Figure 3 in the background section dealing with mechanisms of polymer burning, the phosphoryl moiety is primarily promoting formation of carbonaceous char, thus limiting combustible volatile formation.

#### 4.2.1.2.5 Mechanistic Suggestions for PEPO Degradation

Further analysis of these results along with some additional TGA/mass spectrometry results helped clarify the mechanism of PEPO degradation. Hirose, *et al.*, have reported in the literature [241] the bond dissociation energies for PEPO and theoretically suggested routes to polymer degradation. According to the structures below, one can make certain predictions about the most probable pathways for macromolecular degradation if they follows random chain scission giving highly reactive free radical species. Since the carbon-phosphorus bond is the weakest bond in the all aromatic PEPO and the second weakest in BIS A PEPO, it must be assumed that it is one of the initial sites of bond breakage. Additionally, the pendant phenyl-phosphorus bond will probably break first as it is the least constrained and most exposed of the three C-P bonds. A major occurrence here is the lack of ability for the splitting off of a simple "P=O" gas, as would be the case for UDEL or PEEK, with SO<sub>2</sub> or CO, respectively. The major resulting gaseous products containing



phosphorus have been only briefly speculated [282, 284] to be perhaps phosphorus acids, but these same acids have also been theorized to remain in the condensed phase. Add to this the fact that these results were for phosphate type additives in vinyl polymers or polyesters, and one can conclude that almost nothing is known about the role of phosphorus on polymer burning when it is chemically linked into a high temperature high performance system.

The TGA/MS data is summarized here as it will be detailed in an upcoming publication [295]. The results of this work are a composite of TGA/MS work performed in nitrogen on a series of PEPO and show the relative intensities of four degradation products of these polymers as a function of the progress of decomposition. Benzene, phenol, biphenyl and diphenylether were observed as the major degradation products for this

series of polymers. Benzene was the major degradation product for all of the PEPO materials. Major trends to note include the following : 1) large amounts of phenol relative to benzene were given off for BIS A PEPO and FL PEPO; 2) a large amount of biphenyl was given off for BP PEPO and FL PEPO; 3) a large amount diphenyl ether was given off for FL PEPO.

These data suggests several trends in the decomposition of PEPO. First, it appears that other than the initial C-P bond breakage, BIS A PEPO also loses mass through breakage of the aromatic carbon-isopropyl moiety carbon bond, giving some diphenyl ether; breakage of the C-O bonds would result in the formation of phenol. For the BP PEPO, biphenyl is a major product due to the high bond strength of the biphenyl C-C link, and again, scission of the C-O bond results in phenol. Finally, for FL PEPO, breakage of the fluorene tetrasubstituted carbon bonds with the aromatic rings would result in large amounts of biphenyl, while diphenyl ether would form as it did for BP PEPO.

From the pyrolysis studies mentioned previously, it was known that most of the phosphorus species remained in the char; normally, 10% or less of phosphorus species was contained in the vapor. Thus, some char forming reaction must be attributed to phosphorus since sulfones did not form this char. More work is needed to specify the chemical species present in the char. Specifically, mass spectral analysis combined with XPS results should help identify any phosphorus species present in the char.

#### 4.2.1.2.6 Mechanical Characterization of PEPO

Mechanical properties of these materials were of interest, as most engineering polymers are known to be dimensionally stable below  $T_g$  and impact resistant due to secondary low temperature relaxations [179]. One method for the study of the mechanical properties of PAE is by dynamic mechanical thermal analysis (DMTA) [180, 296]. Figure 36 illustrates the results from DMTA runs on the HQ and BP based PEPO's as both the loss tangent ( $\tan \delta$ ) and storage modulus ( $E'$ ) versus temperature curves. A prominent  $\gamma$  relaxation was observed centered around  $-85^\circ\text{C}$  for both polymers, which is indicative of a material with high impact strength, and has been attributed to  $180^\circ$  ring flips in other PAE's [181]. Additionally, quite broad but noticeable  $\beta$  transitions occurred around  $60-70^\circ\text{C}$  for both materials. This transition was of interest, as several papers have surfaced trying to explain the existence of multiple relaxations in other PAE [297, 298]. Thermal history may play a large role in determining the origin of this transition. Finally, the  $\alpha$  transition at the respective  $T_g$ 's of the polymers is observed as the most prominent peak in the spectra. Excellent dimensional stability below the  $T_g$  was observed as indicated by the flat response of  $E'$  below the  $T_g$ .

Thermomechanical analysis (TMA) was utilized for glass transition temperature confirmation in the penetration mode and coefficient of thermal expansion determination in the expansion mode. Indeed, glass transition temperatures measured via TMA (penetration) were very close

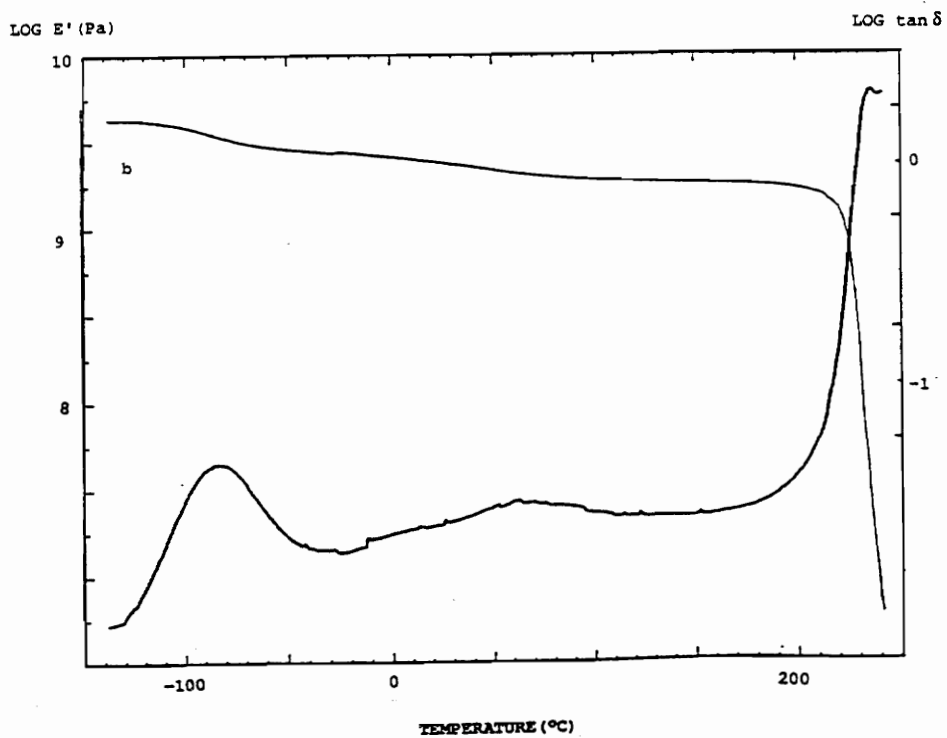
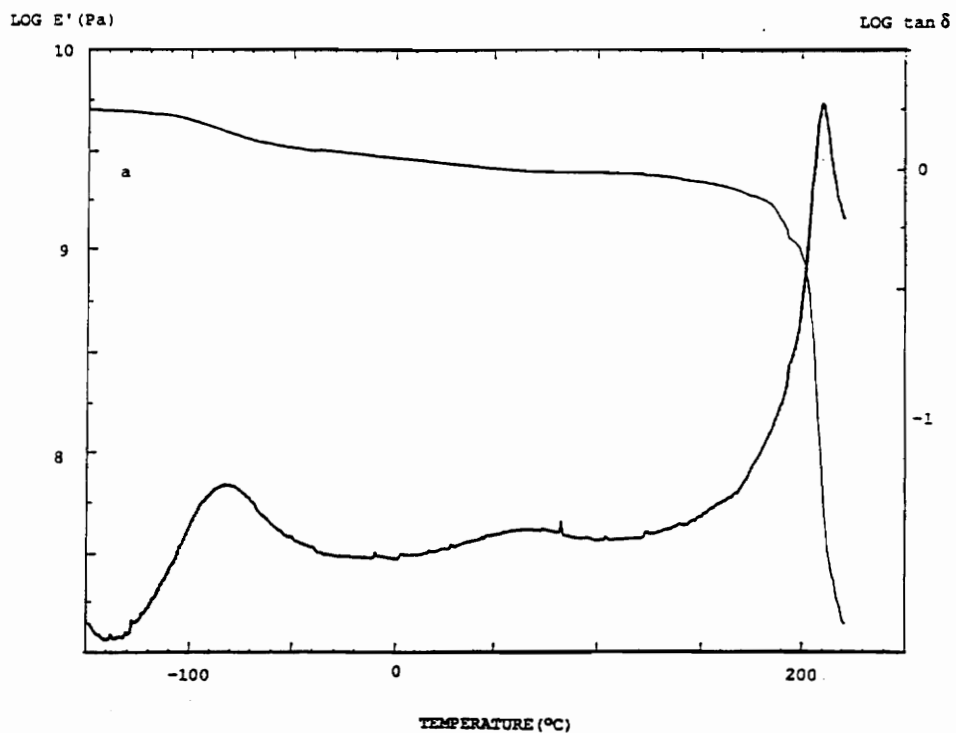


Figure 36. DMTA traces for : A) HQ PEPO and B) BP PEPO.

(within 2°C) to those acquired from DSC. Coefficients of thermal expansion were calculated in the range of 60-100°C for each sample at a heating rate of 5°C/min and 1 mN force. A sample TMA run is illustrated in Figure 37. Summarized CTE values are given below for the series of PEPO thermoplastics, along with that of UDEL for comparison.

<u>POLYMER</u>	<u>CTE</u> (X10 <sup>5</sup> )
BIS A PEPO	5.99
HQ PEPO	5.23
BP PEPO	5.12
UDEL	5.16

Mechanical properties of PEPO compressed films as measured via stress-strain analysis are summarized in Table 14. An extensometer was not in use for these measurements, which resulted in modulus values roughly one half their actual values. For comparison purposes, a commercial sample of UDEL was also run. One trend which appeared was the decreasing % strain at break as chain rigidity and T<sub>g</sub> increased. Stress at break was fairly constant for all the poly(arylene ether)s. Finally, Young's modulus values in the general trend of FL PEPO > HQ PEPO > BP PEPO > BIS A PEPO were also observed, which were in the same area as that of UDEL. The large difference in % strain at break between UDEL and the series of PEPO could be a result of film quality, with PEPO containing some particulate matter, perhaps dust.



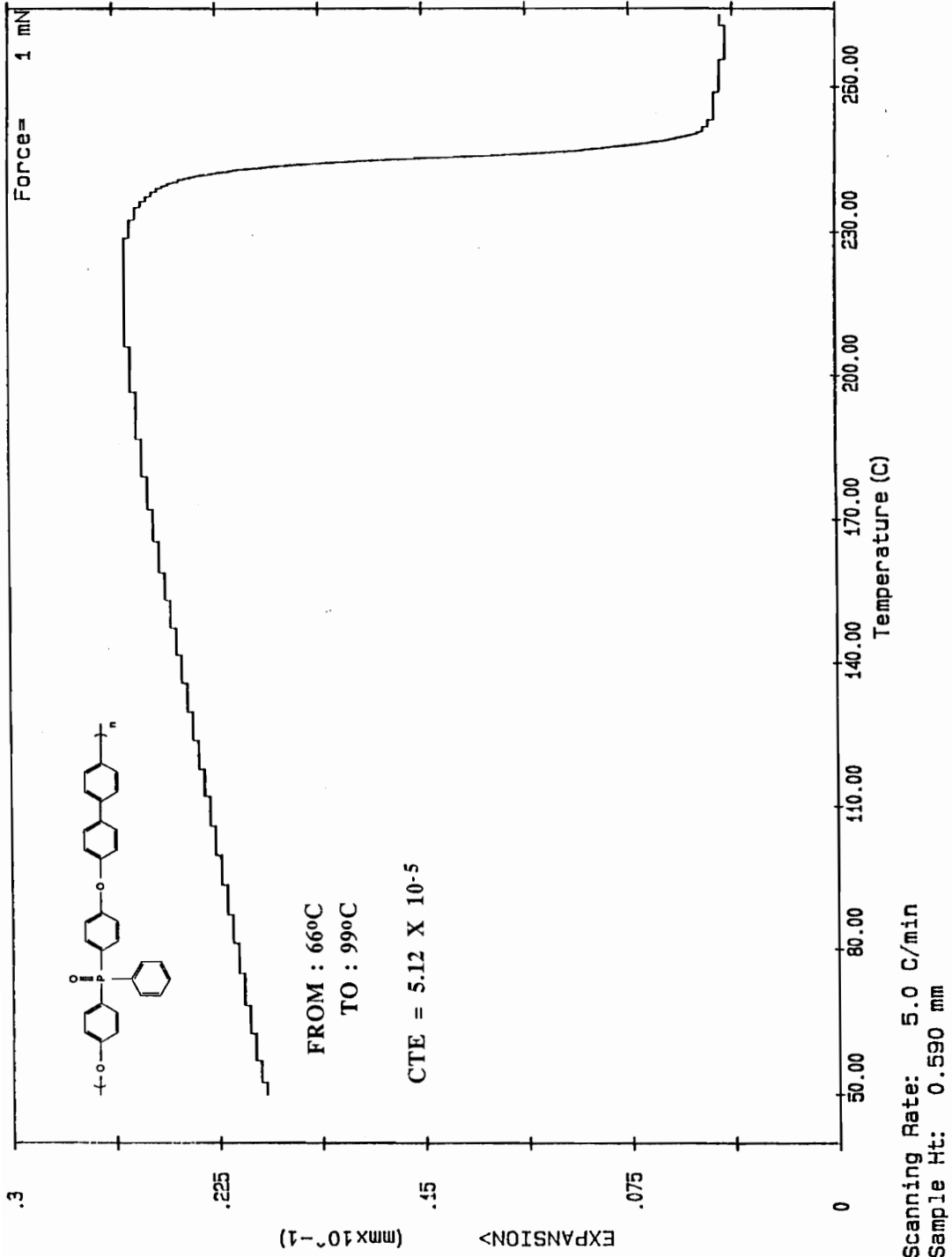


Figure 37. TMA thermogram of BP PEPO.

Table 14. Stress strain results for PEPO and UDEL.

POLYMER	% STRAIN AT BREAK	STRESS AT BREAK (KSI)	YOUNG'S MODULUS (KSI)
BIS A PEPO	58	8.0	158
HQ PEPO	48	10.2	171
BP PEPO	30	10.2	142
FL PEPO	9.4	13.5	224
UDEL PSF	153	10.0	198

#### 4.2.1.2.7 Electrical Properties of PEPO

Dielectric thermal analysis (DETA) of polymeric materials can be utilized for the determination of the dielectric constant of the material. Shown in Figure 38 are the DETA thermograms of both BP PEPO and UDEL at 3°C/min and frequencies of 1, 10 and 100KHz. As expected, as the frequency increased, the observed  $T_g$  of the samples also increased. The major difference encountered between the two materials was the observation that as the loss tangent curves for the PEPO material begin to maximize, the curve starts to increase to infinity, while the same curves maximize fully before going toward infinity for the Udel® sample. The onset of the increase in  $\tan \delta$  is indicative of the approach to the  $T_g$  of the sample. Also, the increase of  $\tan \delta$  to infinity may be indicative of residual solvent or other impurities, as it denotes approximate ionic conductivity. Nevertheless, the dielectric constant and dielectric loss of the BP based PEPO as compared to the Udel® sample were 3.21 and 0.009 and 3.10 and 0.006, respectively.

#### 4.2.2 Controlled Molecular Weight Poly(arylene ether phosphine oxide)s

As described in the both the background and the Appendix to this thesis, controlled molecular weight oligomers can be interesting for several reasons. For example, amine terminal poly(arylene ether)s have been incorporated into epoxy resins as chemically reacted tougheners [71]; moreover, these amine terminated resins can be post-reacted with maleic anhydride to produce maleimide terminated poly(arylene ether)s which have been useful in the toughening of traditionally brittle

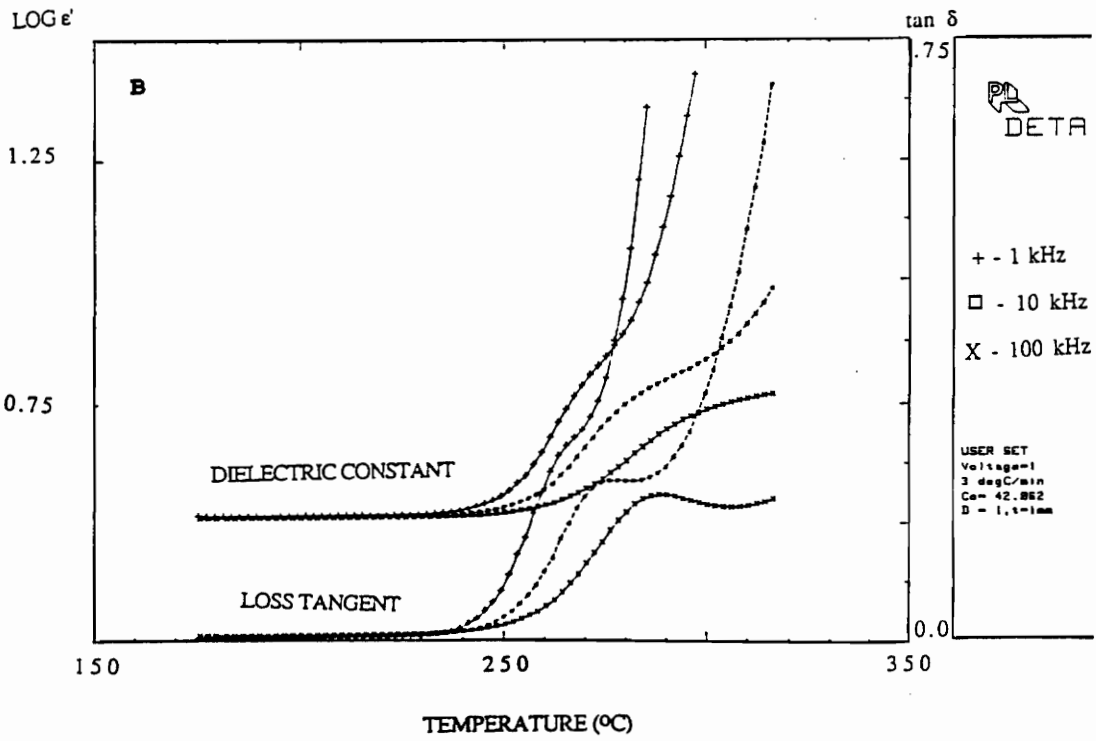
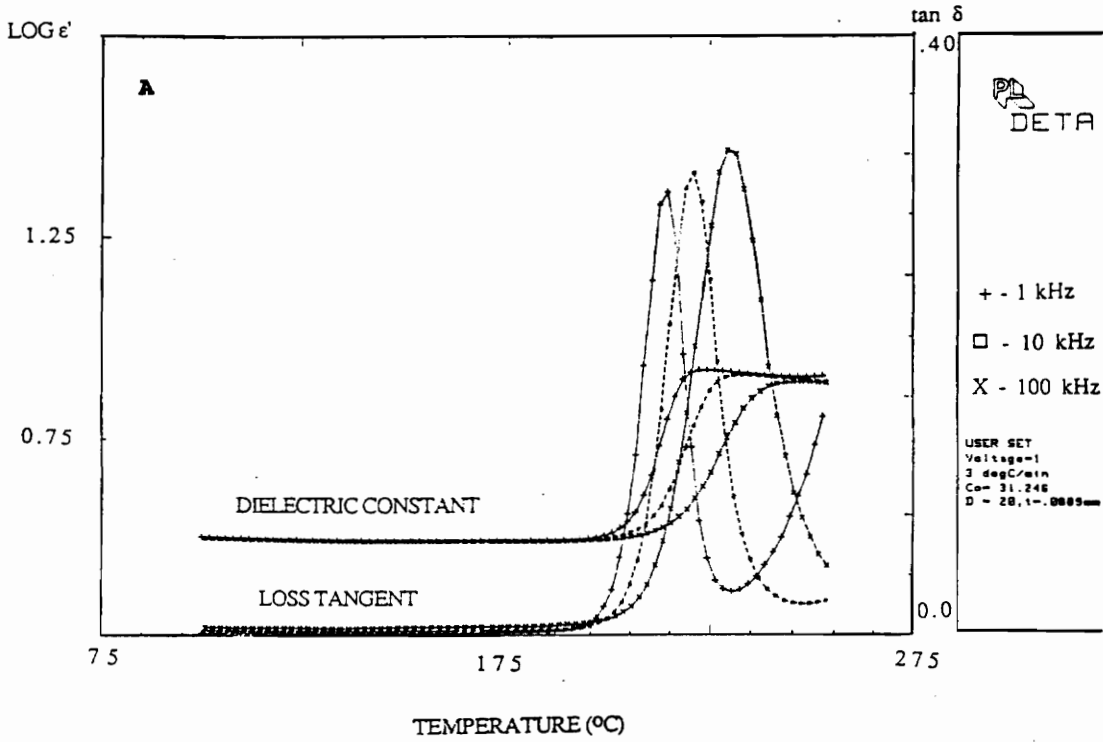
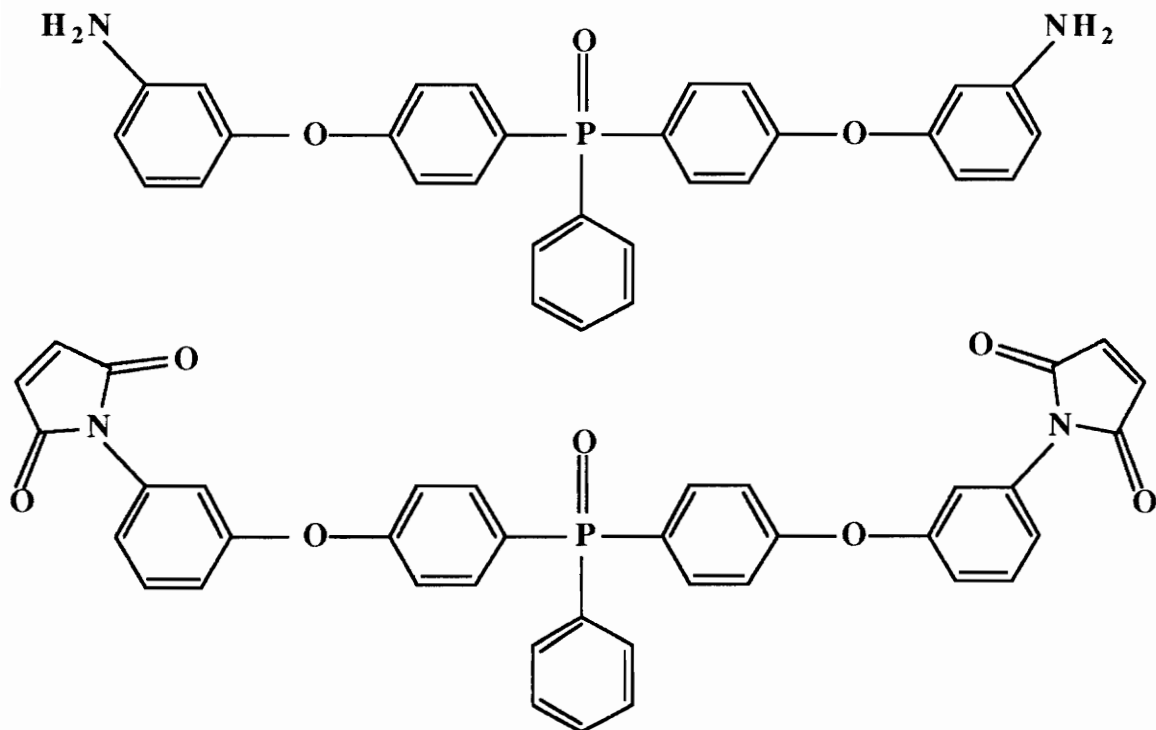


Figure 38. DETA thermograms for A) UDEL and B) BP PEPO.

bismaleimide networks [75, 108]. Additional utility for functionalized poly(arylene ether)s has been in the field of block or segmented copolymers, as described in the background section. Two types of copolymers were prepared in this study : amine and t-butyl terminated PEPO. The amine terminated PEPO were later utilized for introduction into "ceramer" systems [299], for toughening bismaleimides by post-reacting amine terminated PEPO with maleic anhydride [300], and for use in perfectly alternating polysiloxane copolymers. Nonfunctional t-butyl termination was desired for a series of BP PEPO oligomers for confirmation of polymer molecular weights via  $^1\text{H}$ NMR and for the investigation of DMAc as solvent for these systems to improve polymer color.

#### 4.2.2.1 Amine Terminated PEPO

One note should be made before proceeding to discuss controlled molecular weight oligomers. Two other workers in the field [301, 302] have published their results regarding the "ultimately" controlled molecular weight PEPO, as illustrated below. These materials, referred to as bis(4-(3-aminophenoxy)phenyl)phenyl phosphine oxide and the corresponding bismaleimide, were prepared from the NAS reaction of BFPPPO with m-aminophenol under identical conditions as for polymerizations, followed by post-reaction with maleic anhydride to produce the desired bismaleimide. The all para isomer of the diamine has also been prepared [303]. These diamines have been utilized for the preparation of amorphous high  $T_g$  soluble polyimides with excellent



adhesive and thermal properties. The bismaleimide also had high thermal transitions, was tough and flame retardant.

To synthesize amine terminated PEPO oligomers, the same procedure was followed as for high molecular weight materials with the exception of addition of *m*-aminophenol as prescribed in the appendix of this thesis. Biphenol based PEPO were prepared due to ease of precipitation of the low molecular weight species in isopropanol/water mixtures. Oligomeric BIS A PEPO and HQ PEPO were more difficult to precipitate. Titration of the amine end groups of these oligomers with HBr/acetic acid titrants was utilized for determination of number average molecular weight. Results of the titrations are given in Table 15. Spectroscopically, the amine N-H stretch was observed at  $3500\text{ cm}^{-1}$  in the FTIR.

Table 15. Amine terminated BP PEPO molecular weight determination.

<Mn> THEORY (g/mol)	<Mn> TITRATED (g/mol)	$[\eta]_{25^{\circ}\text{C}}$ (dL/g) CH <sub>2</sub> Cl <sub>2</sub>	T <sub>g</sub> (°C)
3000	3380	---	197
5000	6500	0.214	207
10000	11400	0.313	217

The results show the expected increase in viscosity and T<sub>g</sub> with increasing molecular weight. Both intrinsic viscosity and glass transition temperature data agreed well with the t-butyl end-capped polymers described next.

#### 4.2.2.2 t-Butyl Terminated PEPO

Procedural details for the synthesis of these polymers has been outlined in the experimental section and in the appendix. Termination of BP PEPO with t-butyl groups allowed the confirmation of number average molecular weight control via <sup>1</sup>HNMR. Since the methyl protons on the t-butyl groups were the only aliphatic character along the BP PEPO chains, integration of these protons (18/chain) versus the aromatic protons allowed fairly simple determination (see experimental) of M<sub>n</sub>. An additional aspect of this particular project was the utilization of DMAc as solvent at lower reaction temperatures, producing a much cleaner

appearing polymer. The color of the PEPO samples prepared in DMAc was much lighter, almost white, while the polymers synthesized in NMP were more tan in color. A sample  $^1\text{H}$ NMR spectrum for a theoretical 5000g/mol BP PEPO is shown in Figure 39. Again, the water peak was shifted downfield to 2.0 ppm due to hydrogen bonding. The methyl protons appear as a clean singlet at about 1.3 ppm, with the aromatic protons chemical shifts downfield between 7 and 8 ppm. This region has been expanded in the figure as well. One must be careful when integrating the spectrum not to add in the additional peak from  $\text{CHCl}_3$  at about 7.24 ppm. If compared to the expanded aromatic region of high molecular weight BP PEPO shown previously in Figure 25, it is obvious to spot the endgroup contributions to the aromatic region as small side bands next to the major aromatic peaks. The total integration of all aromatic protons relative to the methyl protons gives the ratio necessary for number average molecular weight calculation. A sample calculation follows.

From the equations set up in the experimental section,

$$\# \text{ Aromatic protons}/18 = (Z*n + Y)/18 = (21*n + 21)/18 = \text{ratio from NMR}$$

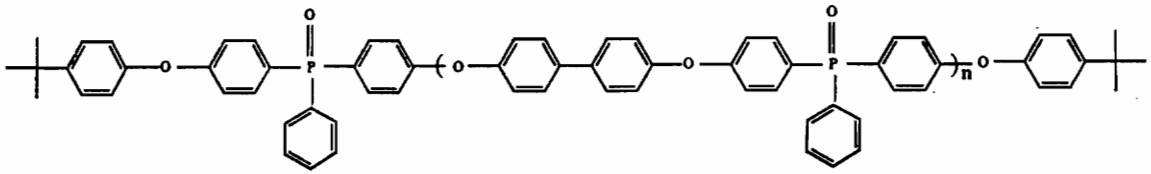
$$\text{where } Z = \# \text{ aromatic protons in repeat unit} = 21$$

$$Y = \# \text{ aromatic protons in end groups} = 21$$

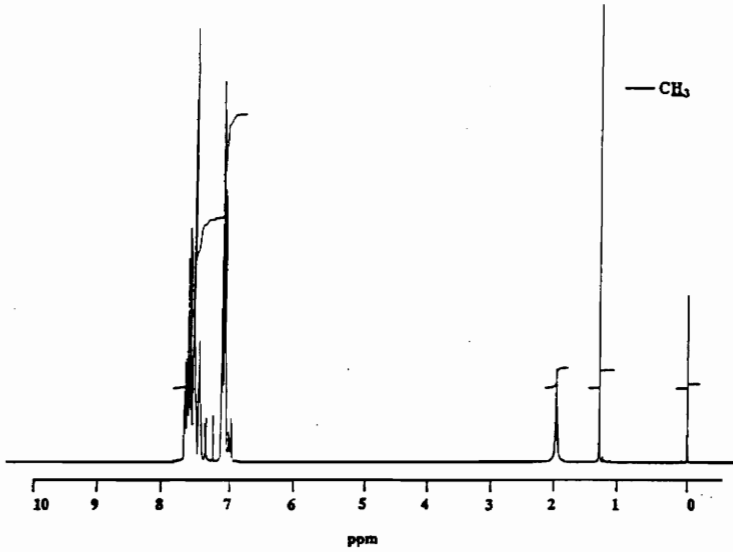
$$n = \text{number of repeat units}$$

Thus, for the theoretical 5000 g/mol oligomer, the ratio of the aromatic protons to aliphatic protons was  $70.69/4.86 = (21*n + 21)/18$ . Solving for n, multiplying this answer by 460.472 (molecular weight of repeat





A



B

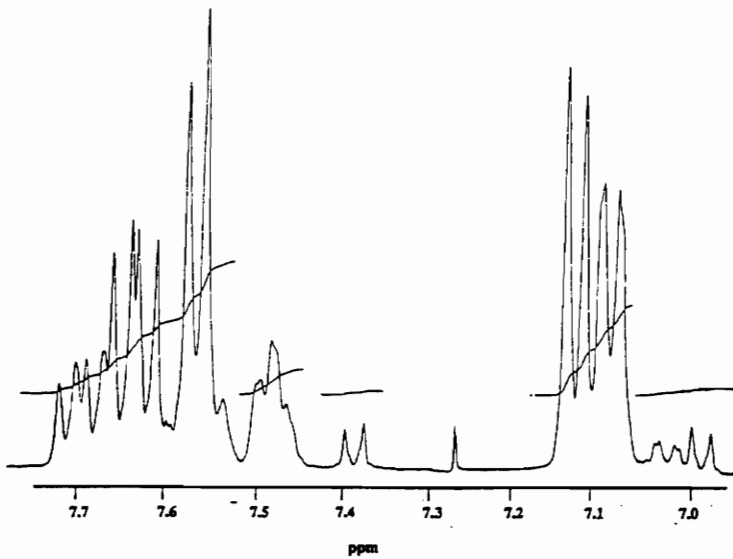


Figure 39.  $^1\text{H}$ NMR spectrum for theoretical 5000 g/mol t-butyl terminated BP PEPO : A) entire spectrum and B) expanded aromatic region.

unit) and adding 574.7 g/mol to this gives oligomer molecular weight. It was found that the average of at least three samples must be taken to get an accurate reading. Different samples can give quite varied results, due to the small value of 18 protons compared to many aromatic protons, especially for the higher molecular weight oligomers. Also, more concentrated NMR samples gave more reliable results.

Characteristics of these oligomers are summarized in Table 16. Obviously, as molecular weight increased, so did both intrinsic viscosity and glass transition temperature. Intrinsic viscosities and  $T_g$ 's agreed well with the amine terminated polymers discussed above. All of these oligomers had 5% weight loss around 500°C in air by TGA. The molecular weights by NMR were in good agreement to the theoretical molecular weights. Discrepancies could be due to filtration problems, the miscalculation of the degree of polymerization as described in the appendix, or other factors.

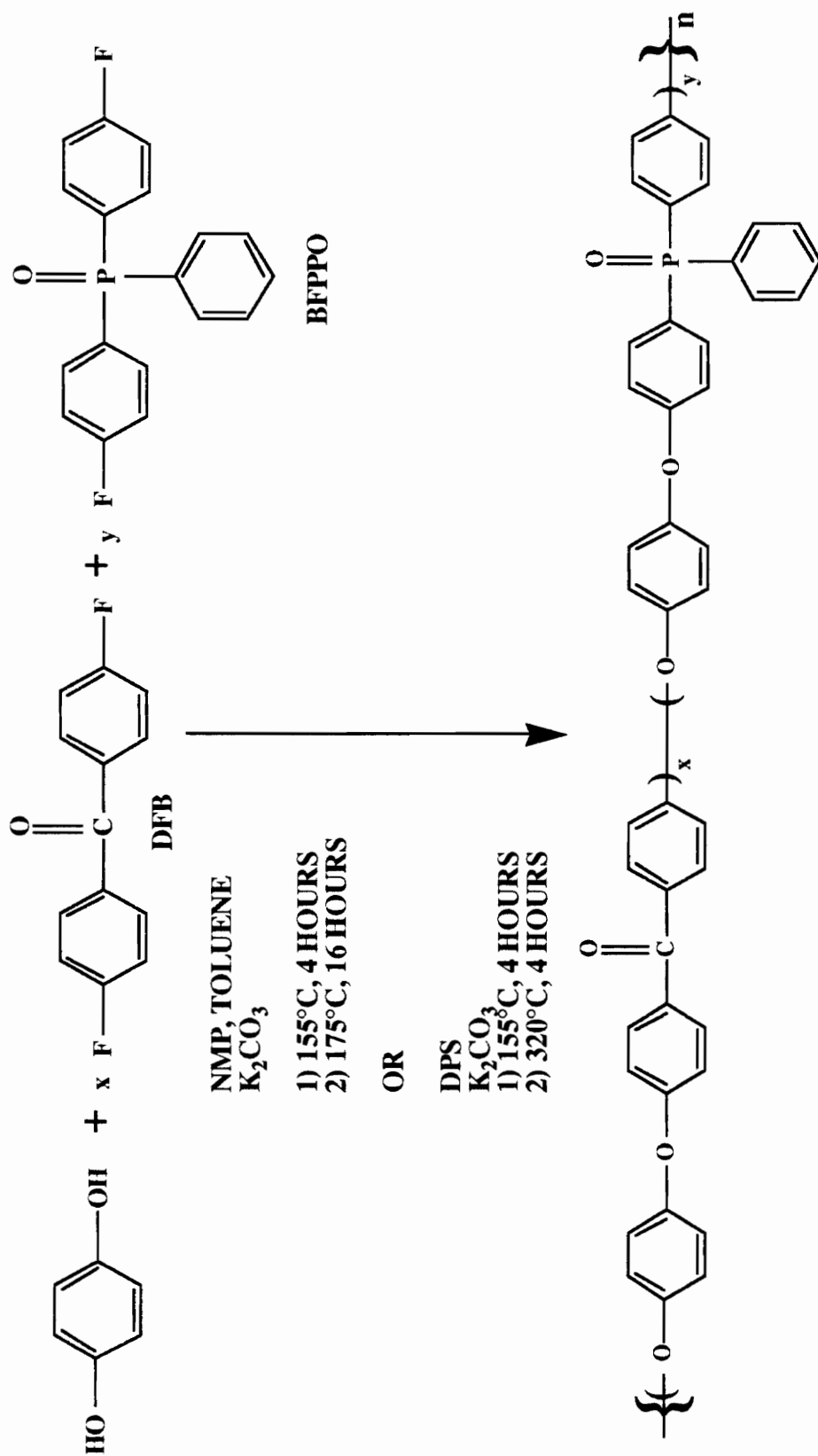
Table 16. Characteristics of t-butyl terminated BP PEPO.

$\langle M_n \rangle$ THEORY (g/mol)	$\langle M_n \rangle$ $^1\text{H}$ NMR (g/mol)	$[\eta]$ $^{25^\circ\text{C}}$ (dL/g) $\text{CH}_2\text{Cl}_2$	$T_g$ ( $^\circ\text{C}$ )
5000	6200	0.215	207
10000	11000	0.319	219
15000	17900	0.372	229
20000	20500	0.445	232

#### 4.2.3 High Molecular Weight Poly(arylene ether ketone)-Poly(arylene ether phosphine oxide) Random Copolymers

The experiences revealed above for the poly(arylene ether phosphine oxide) homopolymer thermoplastic materials led to the belief that copolymers of hydroquinone with combinations of DFB and bis(4-fluorophenyl)phenyl phosphine oxide (Scheme 34 in experimental but repeated below) may proceed at lower temperatures than those reported for the PES-PEEK copolymers discussed in the background, due to the bulkiness of the phenyl phosphine oxide unit. This phosphoryl moiety should play a role in keeping the growing copolymer chains in solution by limiting crystallization.

Random or statistical copolymers of hydroquinone with the DFB:BFPPPO ratio as high as 1:1 (mole basis) could be successfully prepared according to Scheme 34 at relatively low temperatures in NMP compared to those conditions utilized for the synthesis of other PEEK homopolymer or copolymer materials; above 50 mol % DFB incorporation, the high temperature route utilizing DPS as solvent must be used to avoid premature precipitation of the polymer (Table 17). Solubility in organic solvents decreased as the mol % DFB was increased due to the increasing rigidity of the chains. Above 30 mol % DFB, the polymers were no longer soluble in methylene chloride and at 50 mol % DFB, the polymers were only soluble in very hot NMP. High molecular weight polymers were confirmed by viscosity measurements which all gave intrinsic viscosity values of at least 0.55 dL/g. Glass transition temperatures generally



Scheme 34. Preparation of random or statistical PEEK:PEPO copolymers.

decreased with increasing ketone content, although some difference in molecular weights could lead to some of the scatter in the data observed since no molecular weight control was attempted.

Spectroscopic analyses of these copolymers confirmed both the presence of the ketone moiety and the theoretical composition. For example, Figure 40 shows the FTIR spectrum of the 70:30 PEPO:PEEK statistical copolymer. The prominent addition to the spectrum compared to the PEPO homopolymer was the carbonyl stretch due to the benzophenone linkage at  $1651\text{ cm}^{-1}$ . Also, the  $^{13}\text{CMNR}$  spectrum showed a new chemical shift due to the carbonyl carbon at 162 ppm. Compositional analysis was performed by  $^1\text{HNMR}$ , as illustrated in Figure 41. As shown in the figure, the ratio of aromatic protons should be as follows for Ha : Hb : Hc : Hd : He --  $4 * 0.3 = 1.2$  :  $6 * 0.7 = 4.2$  :  $1 * 0.7 = 0.7$  :  $2 * 0.7 = 1.4$  : 8. The experimentally found ratio was 1.26 : 4.19 : 0.74 : 1.41 : 8.0. Therefore, the copolymer was judged to have the desired composition, as it should if high molecular weight was formed.

One of the more interesting aspects of this work was the crystallinity behavior of the 50:50 and the 70:30 mol% DFB:BFPPPO material by DSC (Figures 42 and 43). On the first run in the DSC, the 50:50 material showed a  $T_g$  at about  $187^\circ\text{C}$  and a melting endotherm at around  $313^\circ\text{C}$ . When quenched from the melt, this polymer showed only a  $T_g$  at  $178^\circ\text{C}$  when rerun in the DSC; however, if reheated and annealed at  $250^\circ\text{C}$  for 90 minutes, crystallinity could be regenerated to give another melting endotherm at  $300^\circ\text{C}$  with a somewhat smaller heat of fusion when run again in the DSC. For PES-PEEK copolymers previously synthesized

Table 17. Characteristics of PEEK/PEPO random copolymers.

COMPOSITION (MOL % BFPP0:DFB)	25°C [ $\eta$ ] <sub>CH<sub>2</sub>Cl<sub>2</sub></sub> (dL/g)	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	SOLUBILITY	
				CH <sub>2</sub> Cl <sub>2</sub>	NMP
100 : 0 (HQ PEPO)	1.03	215	NA	YES	YES
70 : 30	0.58	190	NO	YES	YES
60 : 40	0.55*	192	NO	NO	YES (WARM)
50 : 50	-----	181**	303**	NO	YES (BOILING)
30 : 70	-----	158**	302**	NO	NO
0 : 100 (PEEK)***	-----	143	345	NO	NO

\* MEASURED IN NMP

\*\* VALUES FROM DSC FIRST RUN

\*\*\* LITERATURE VALUES

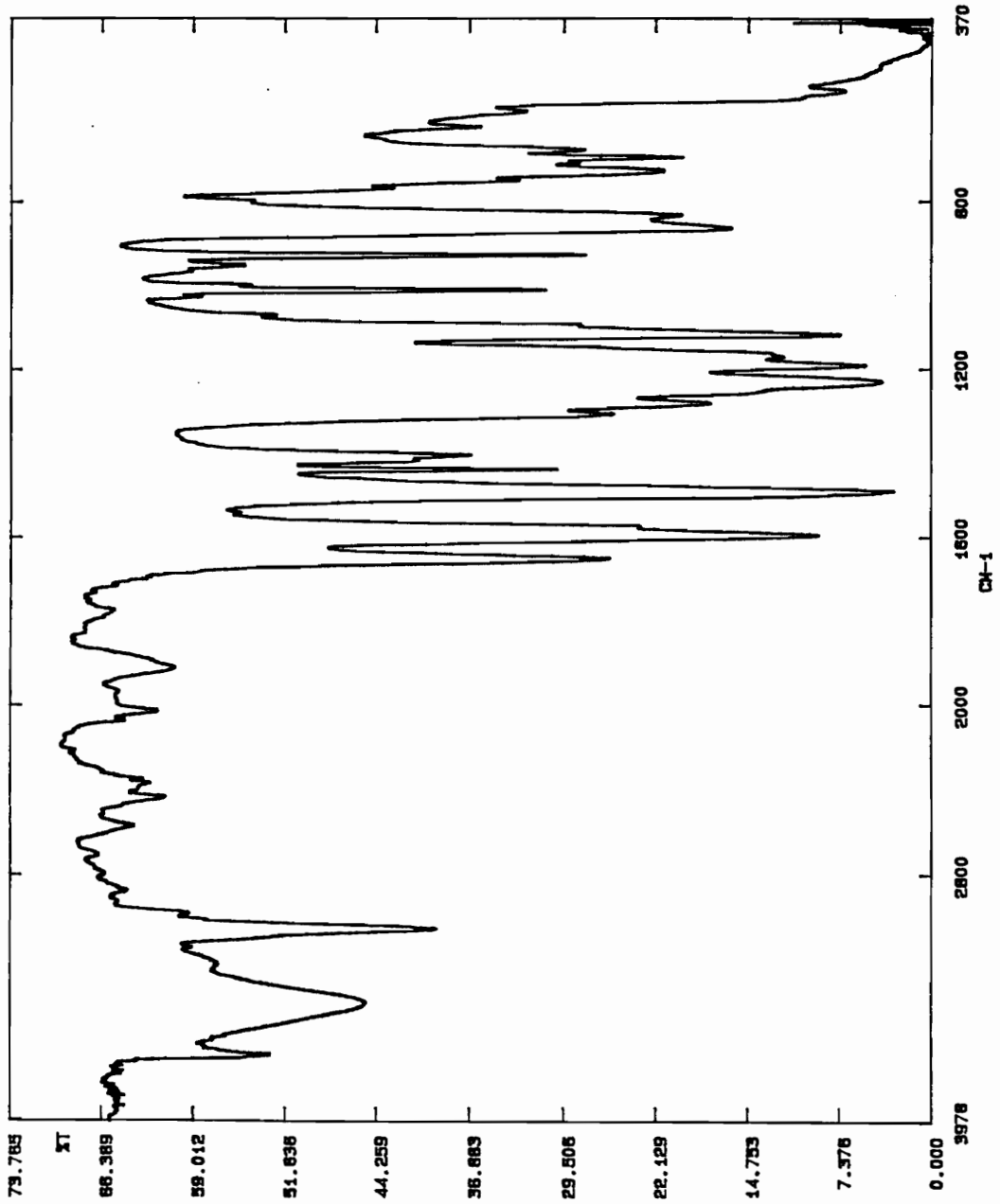


Figure 40. FTIR spectrum of 70 : 30 PEPO : PEEK random copolymer film.

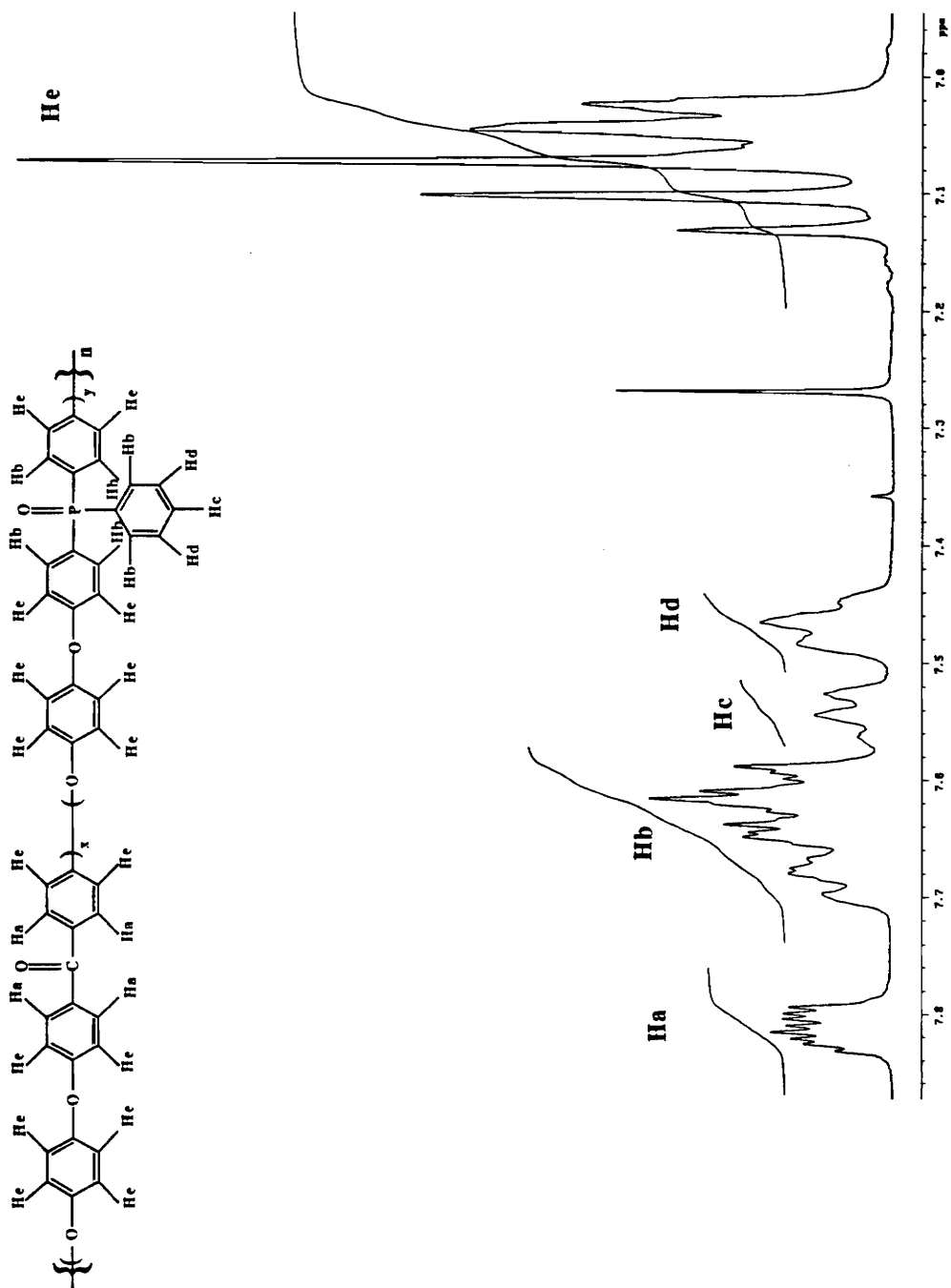


Figure 41. Aromatic region of  $^1\text{H}$ NMR spectrum of 70 : 30 PEPO : PEEK random copolymer.



[129, 130], high reaction temperatures were employed (250-260°C) and melting endotherms were explained as solvent induced crystallization phenomena. Although it is not clear whether this holds true in this particular case, it would seem that the first run to 350°C would rid the material of any small amounts of solvent which may remain.

For the 70 : 30 PEEK/PEPO copolymer prepared in DPS at 320°C, more intriguing DSC results were observed. As illustrated in Figure 43, the first run in the DSC showed several transitions. A glass transition temperature of 158°C followed by a crystallization exotherm (235°C) and two melting endotherms (302 °C, 329°C) all were observed. The sample was then cooled to 235°C and held there for one hour. Quench cooling followed by rerunning the DSC resulted in the trace shown in the bottom half of Figure 43. A  $T_g$  of 170°C was observed, followed by three apparent melting endotherms at 252, 300, and 329°C. Crystallization at 250°C for 150 minutes followed by rerunning the scan resulted again gave three melting transitions, at 265, 302, and 329°C. Finally, crystallization at 270°C for two hours and rescanning gave three melting peaks at 282.5, 310, and 328°C. Two melting transitions had previously been observed and investigated for PEEK homopolymer [304-307]. Normally explained as melting and reforming more perfect crystals, this phenomenon's explanation has been a controversy for several years. No mention of a third transition in PEEK materials has been noted in the literature, and this matter requires further research before any statements can be made regarding the origin of a new melting endotherm.

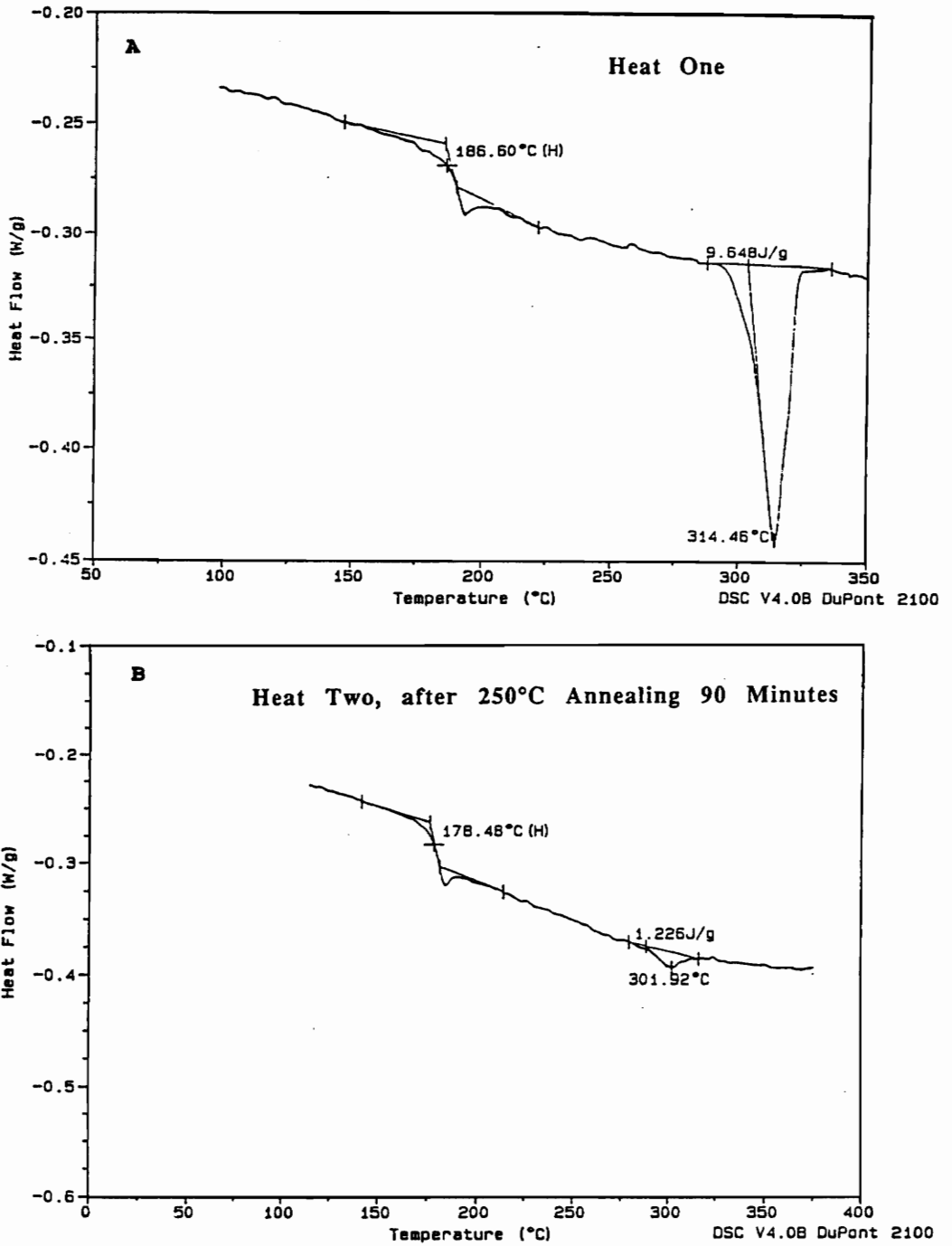


Figure 42. DSC results for 50:50 PEPO:PEEK random copolymer : A) first heat and B) second heat, after crystallizing at 250°C for 90 minutes.

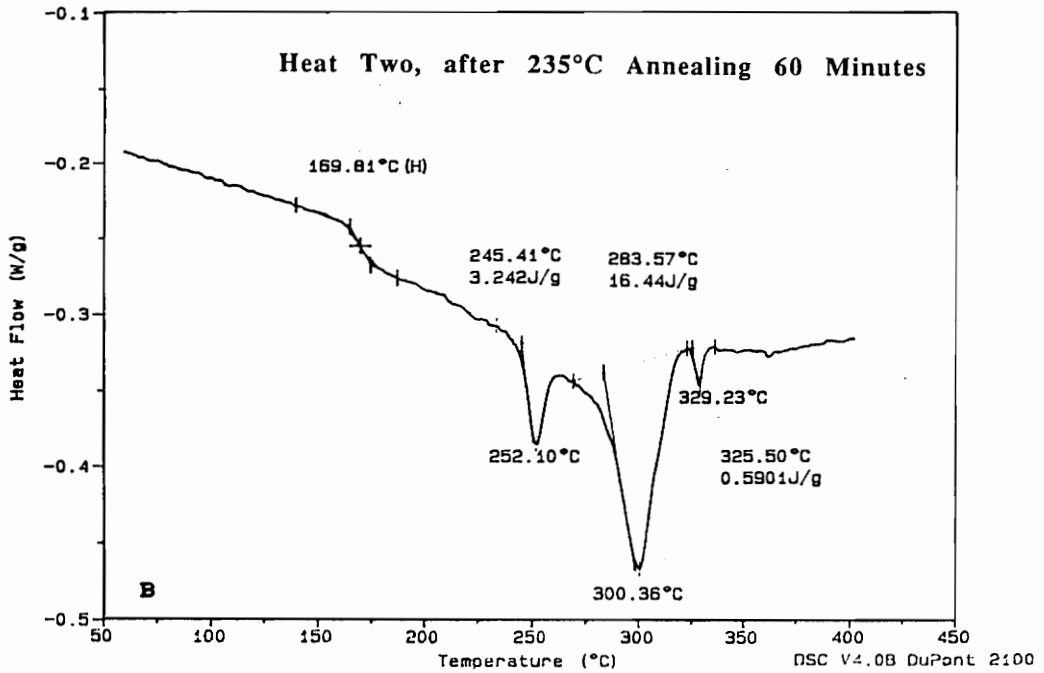
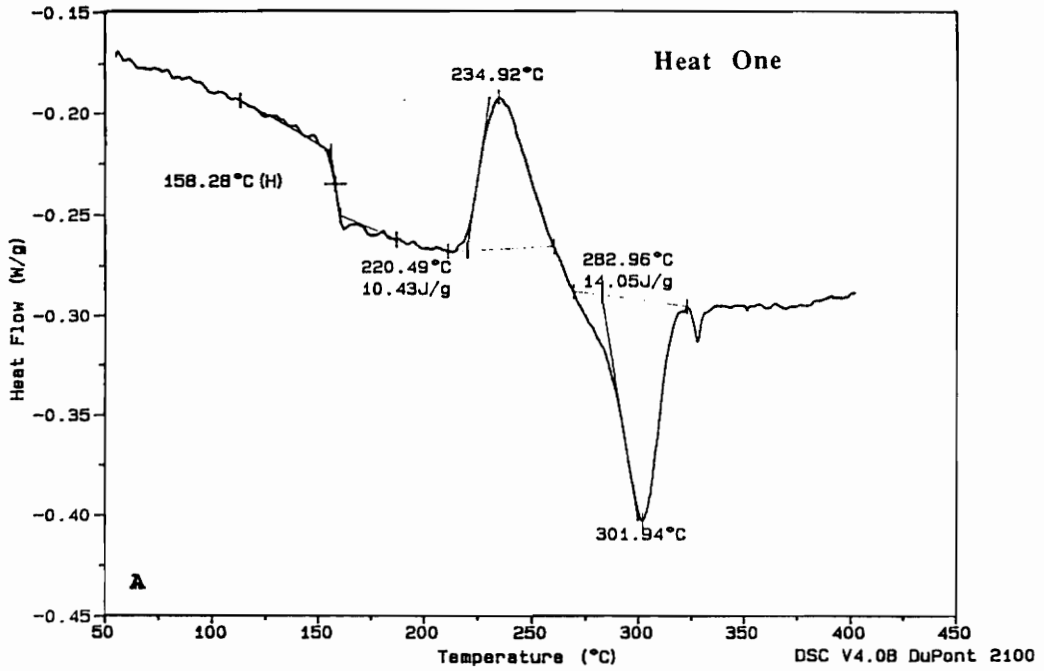


Figure 43. DSC results for 30:70 PEPO:PEEK random copolymer : A) first heat and B) second heat, after crystallizing at 235°C for 60 minutes.

#### 4.2.4 Blends of PEPO with PEEK

Melt blends of PEPO materials based on hydroquinone and biphenol with PEEK were prepared as discussed in the experimental. Both blends gave clear amber films when quenched from the melt, indicative of no gross phase separation and little or no crystallization. These films were subjected to differential scanning calorimetry (DSC) in order to investigate the miscibility of the two components. A typical DSC first run on the mixture of 30 weight % biphenol based PEPO/70 weight % PEEK is shown in Figure 44. From it, two  $T_g$ 's were noted, one near the literature value for PEEK and another near the value previously reported for biphenol based PEPO (245°C). The latter transition is somewhat smeared (see Figure 44) probably due to the presence of PEEK crystallites present at that temperature. The melting and crystallization transitions of the blend occurred at about the same temperatures as those reported in the literature for PEEK. Hydroquinone based PEPO blended with PEEK showed similar results in the 30 weight percent blend.

In order to confirm the presence of two phases, DMTA of the blends were investigated. As shown in Figure 45 for the 30% HQ PEPO/PEEK blend, these results indeed established the existence of two phases by the appearance of their respective  $T_g$ 's as decreases in the log  $E'$  curve. Although not miscible, the presence of a second compatible phase with higher  $T_g$  than PEEK contributed to higher modulus after the  $T_g$  of PEEK by a factor of almost one on a log scale.

Thermogravimetric analysis of all copolymers and blends also showed

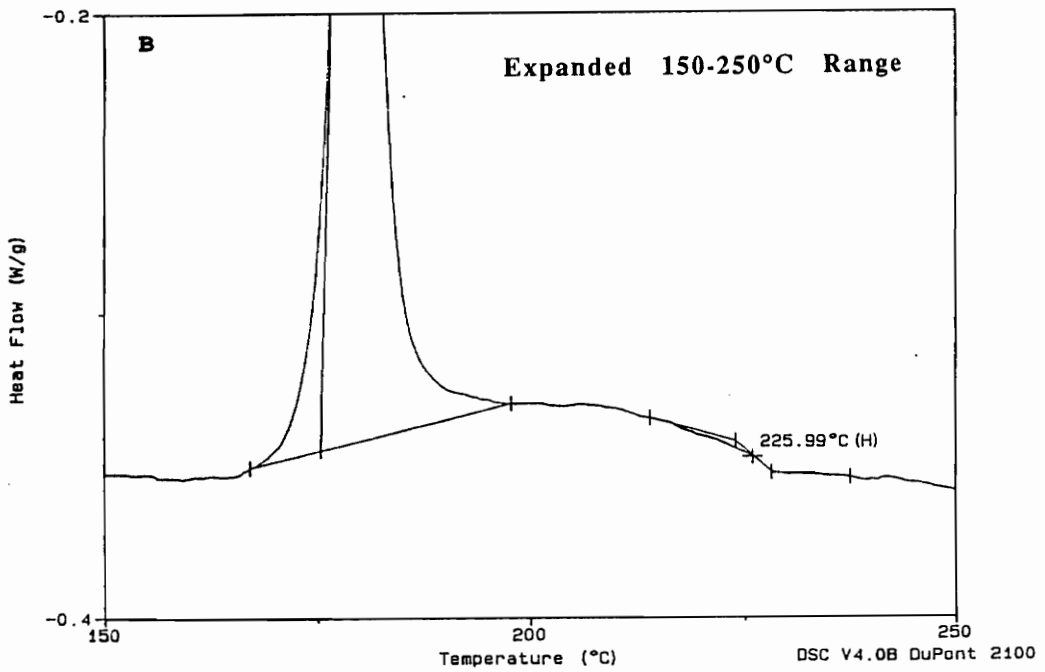
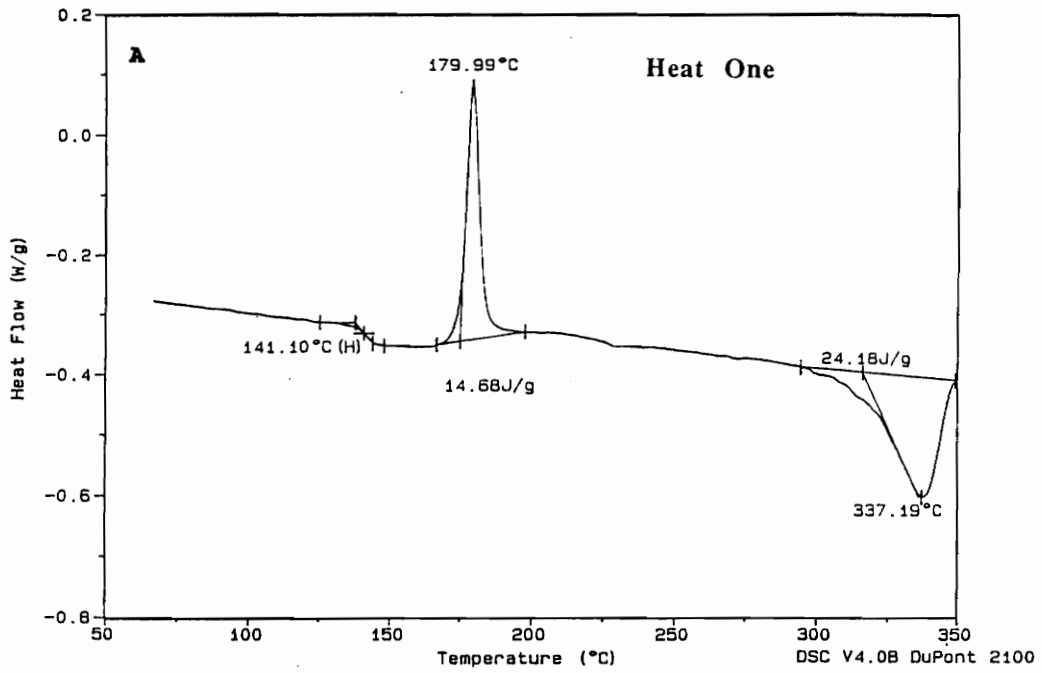


Figure 44. DSC trace of amorphous film for 30 weight % BP PEPO melt blended with PEEK.

significant char yields as tabulated in Table 18. From the table, it is obvious that the inclusion of any amount of PEPO into a chemically linked macromolecule or a physical mixture of polymers resulted in considerable char formation at 800°C in air. The materials with higher contents of phosphorus in general gave higher char yields.

#### 4.2.5 Polymerization of AB Type Monomer

4-hydroxyphenyl-4'-fluorophenyl-phenyl phosphine oxide was prepared and purified as previously discussed. This monomer was polymerized under the same conditions as the high molecular weight PEPO, utilizing NMP as the solvent and potassium carbonate as the weak base at temperatures of 165°C. An amber solution resulted which when worked up could not be precipitated into methanol water mixtures, but gave nice results when precipitated into water alone. When dried, the polymer ("poly(ether triphenyl phosphine oxide)") gave an FTIR spectrum (film on KBr disk) as shown in Figure 46. Primary stretches were as follows : 3058  $\text{cm}^{-1}$  (aromatic C-H), 1584 and 1490  $\text{cm}^{-1}$  (aromatic C=C), 1438 and 999  $\text{cm}^{-1}$  (P-aromatic C), 1245  $\text{cm}^{-1}$  (aromatic C-O-C) and 1174  $\text{cm}^{-1}$  (P=O). The  $^1\text{H}$ NMR spectrum also confirmed the theoretical structure, as assigned in Figure 47. Only four aromatic resonances appeared, which integrated to 5:1:2:4, corresponding to the structure shown in the figure.  $^{13}\text{C}$ NMR analysis (Figure 48) of this polymer also confirmed the structure, as calculated and experimental chemical shifts were quite close, as shown below and assigned in the figure. Phosphorus NMR in  $\text{CDCl}_3$  resulted in only a single peak at 28.7 ppm in  $\text{CDCl}_3$ .

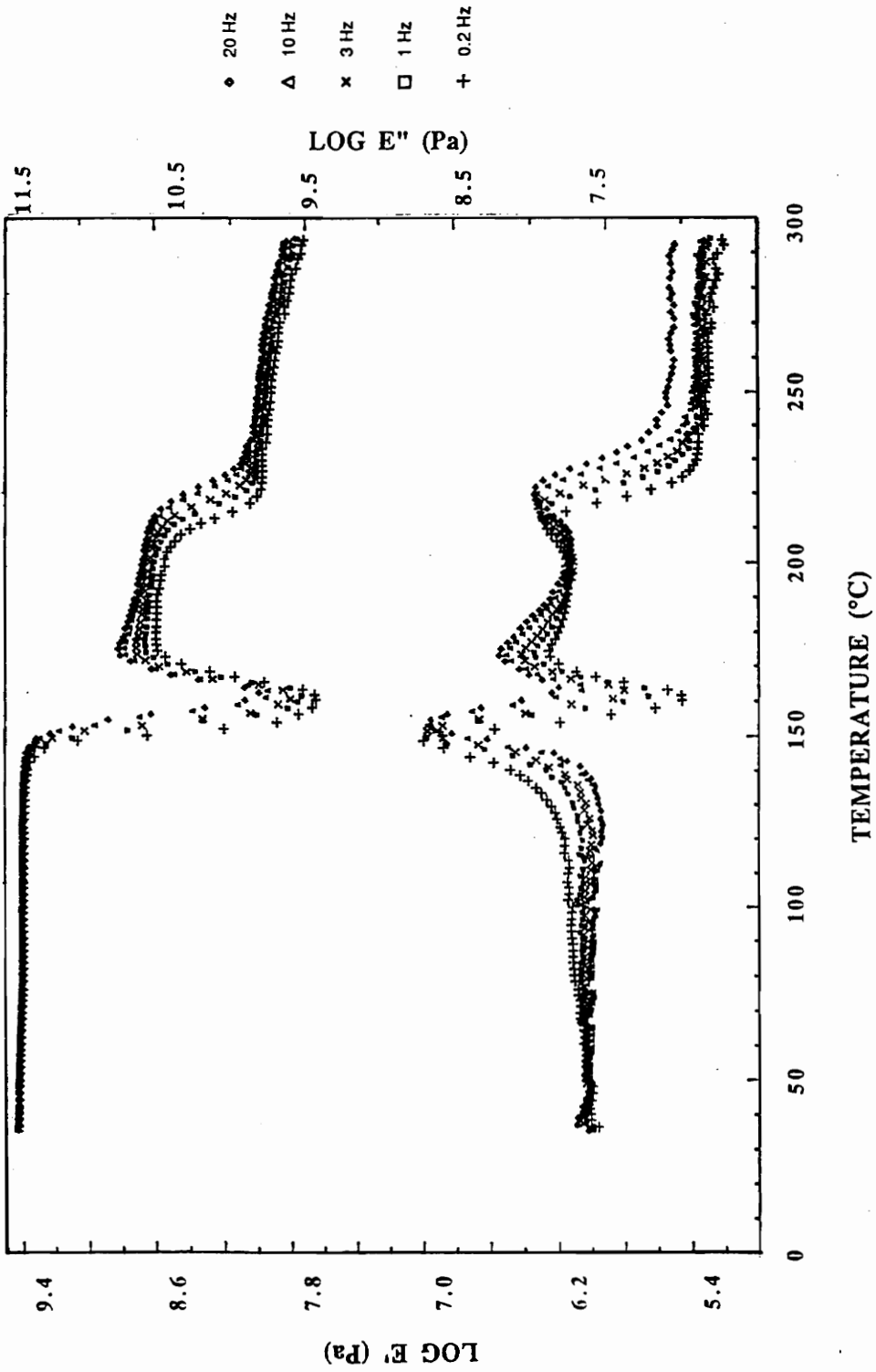


Figure 45. DMTA thermogram of amorphous 30% HQ PEPO blend with PEEK.

Table 18. Char yields of PEPO blends and copolymers.

BLEND COMPOSITION (% PEPO)	800°C CHAR YIELD IN AIR
0 (PEEK)	0
30 (BP)	10
30 (HQ)	14
100 (BP PEPO)	17
COPOLYMER COMPOSITION (% PEPO)	
70	12
60	22
50	13
30	6

CARBON	$\delta$ (calculated) ppm	$\delta$ (found) ppm
A	160.9	159.9
B	118.8	119.1
C	131.3	132.3
D	128.7	128.2
E	133.7	134.4
F	129.7	128.8
G	128.2	127.1
H	131.7	132.1



Unfortunately, only low molecular weight was accomplished as judged by an intrinsic viscosity in methylene chloride of only 0.2 dL/g. The glass transition temperature was 236°C and the material showed 5% weight loss at 495 °C in air. At the time this research was conducted, monomer supply was quite low, and therefore, these experiments are in the process of being completed by other workers in this laboratory.

An alternate approach for the preparation of this identical polymer structure was from the polycondensation of BHPPPO with BFPPPO. At the time of the writing of this thesis, research was underway for exactly this approach. In fact, a recent publication [308] seems to strongly suggest a third method for the synthesis of this polymer from BFPPPO alone with other simple reagents. This approach would be the most facile procedure leading to the desired structure. Basically, the research involved the reaction of an activated dihalide with an alkali metal carbonate in the presence of silica gel and an optional copper catalyst (see Scheme 38). The polymerization involved high temperatures (300-320°C) in diphenylsulfone, probably due to the nature of the monomers used by the authors. Since the targeted polymers for their research were semicrystalline PEK, no attempts at the reaction in solvents such as DMAC or NMP were made. Additional benefits included fast reaction times (30 minutes for PES, four hours for PEK) and simple reaction procedures. Also, stoichiometry of dihalide to oxygen donor (metal carbonate) was not crucial. Therefore, several colleagues have attempted to repeat this work, but have had no success for a number of activated dihalides. Since the reagents used are very common, with the exception of the specific

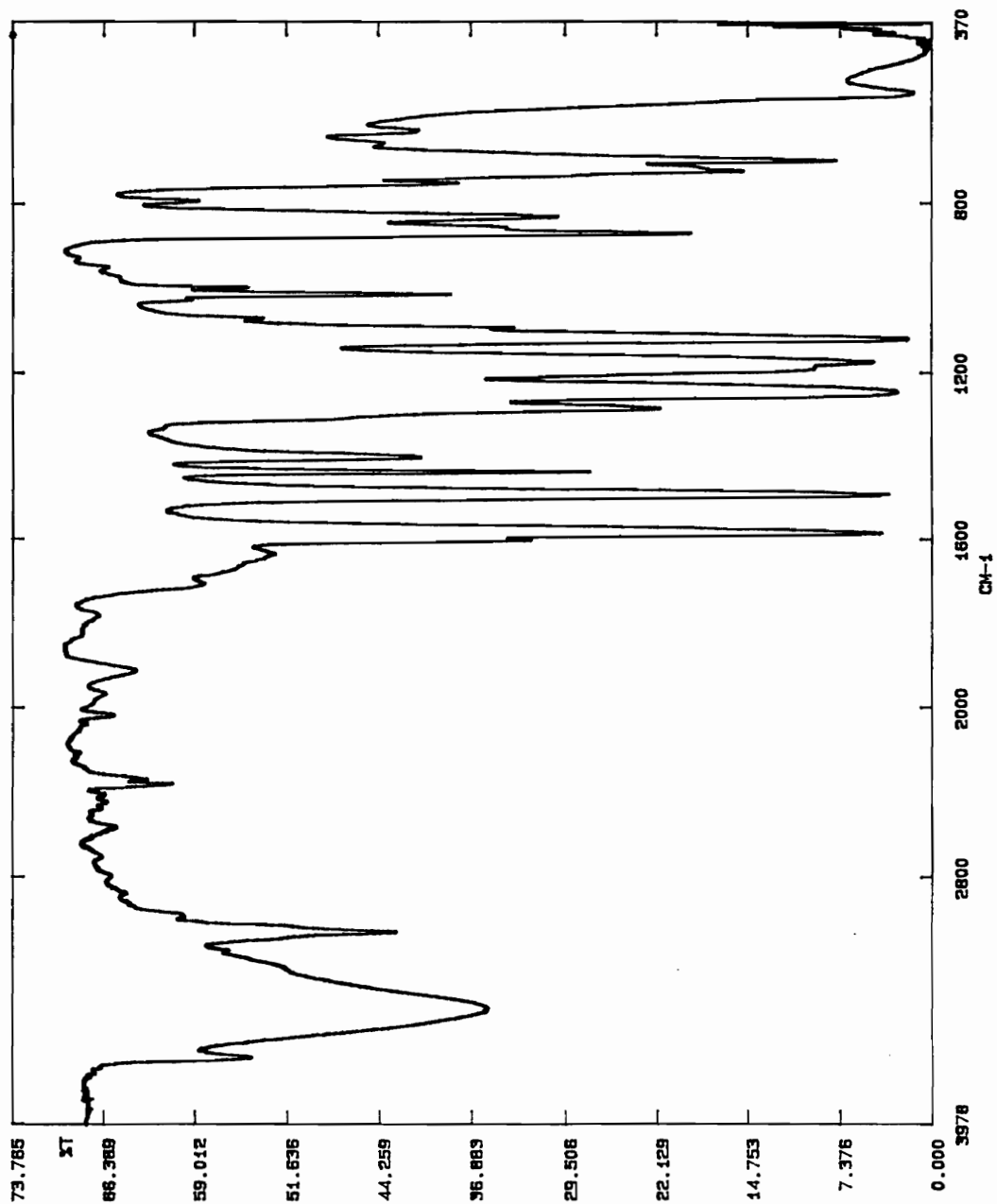


Figure 46. FTIR spectrum of "poly(ether triphenyl phosphine oxide)."

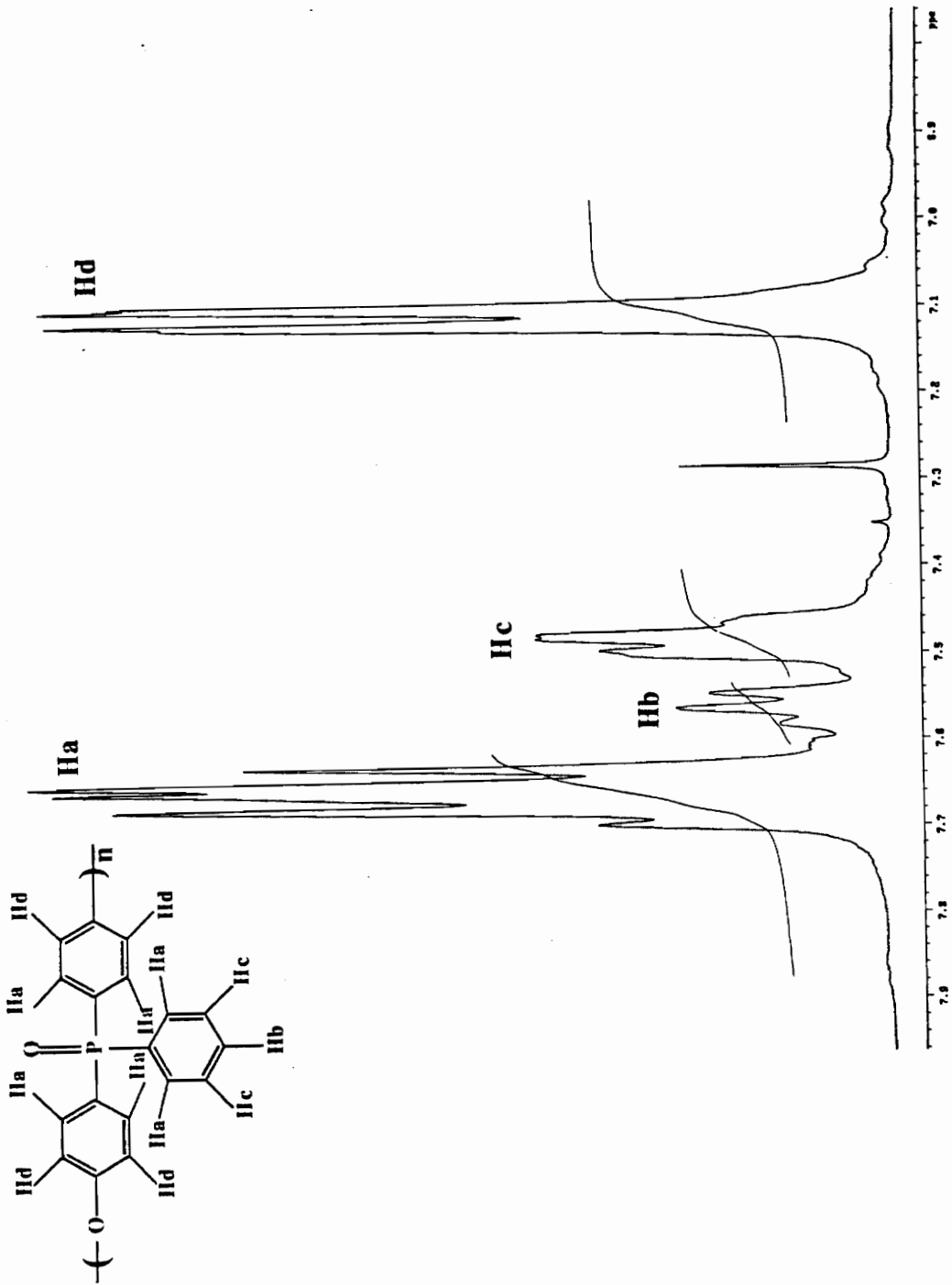


Figure 47.  $^1\text{H NMR}$  spectrum of "poly(ether triphenyl phosphine oxide)."

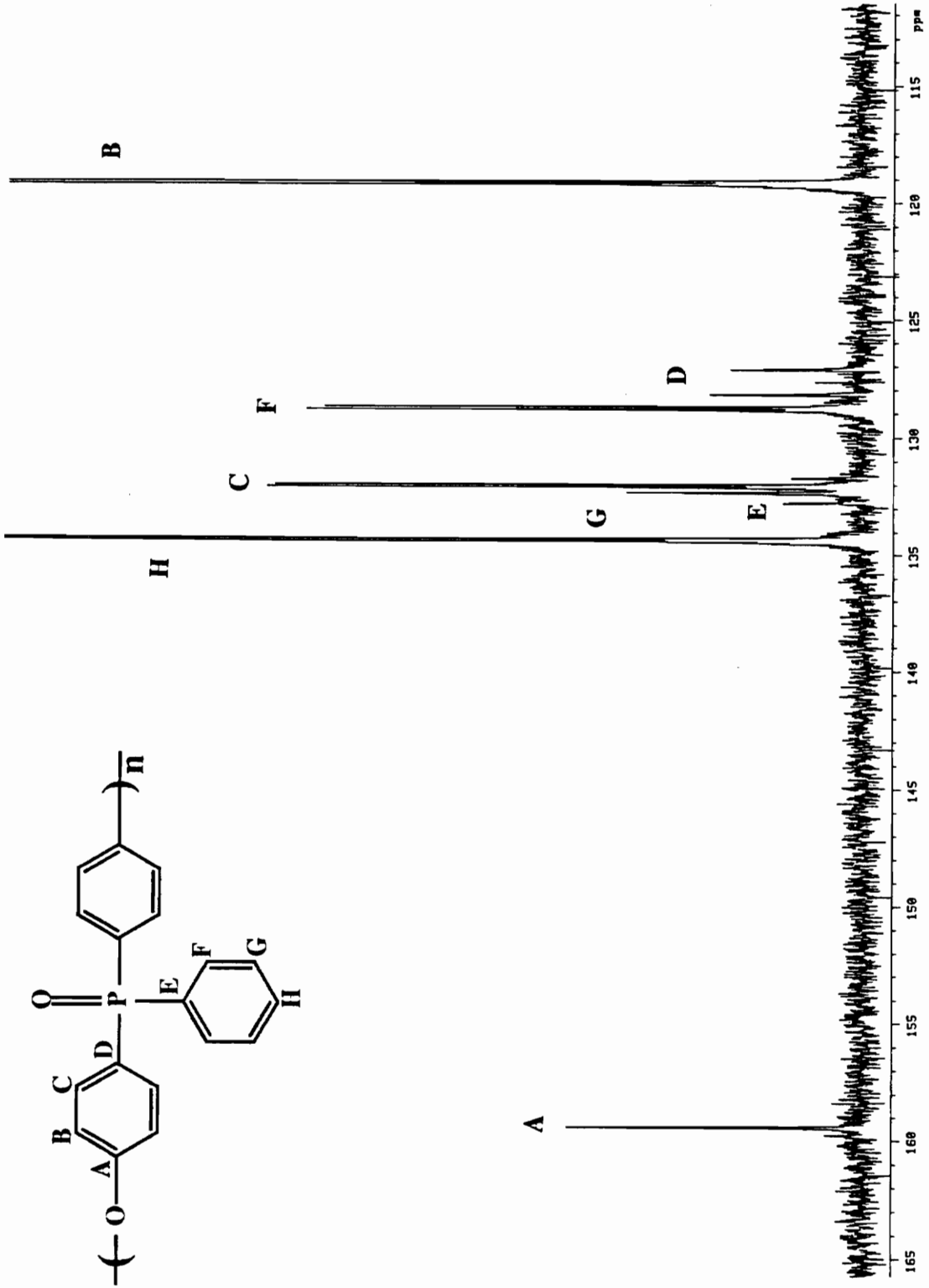


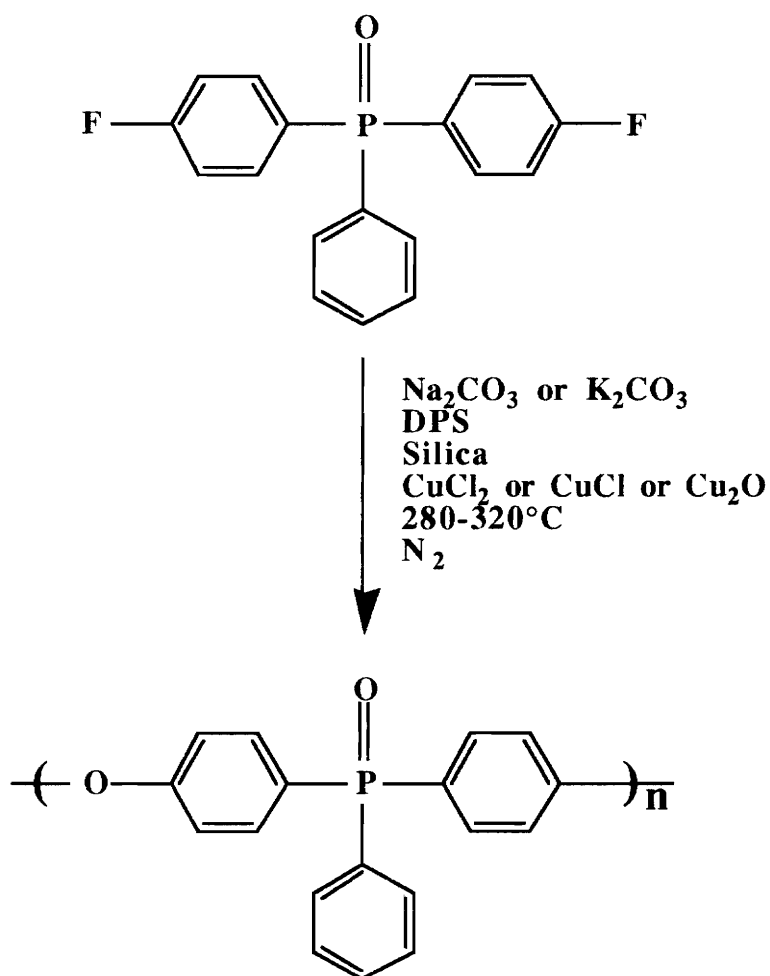
Figure 48.  $^{13}\text{C}$ NMR spectrum of "poly(ether triphenyl phosphine oxide)."

silica utilized by the authors, it can be concluded that this polycondensation requires specific silica catalysts, and is not general to any commercial silica gel. This work will undoubtedly continue in our laboratory due to the unique structures which can be prepared by quite simple techniques.

The advantages of preparing the polymer formed by any of the three routes described above would be increased phosphorus content, which should lead to increased char formation, which certainly would afford excellent fire resistance. Additionally, this polymer has not been reported in the literature in terms of any physical characteristics.

#### 4.2.6 Melt Transesterification Polycondensation with Bis(4-carboxyphenyl) phenyl phosphine oxide

For comparison purposes, a polyester containing the triphenyl phosphine oxide moiety was desired. As described in the experimental section and in Scheme 36, this polymer was prepared by a typical melt transesterification polycondensation of bis(4-carboxyphenyl) phenyl phosphine oxide with the diacetate of BIS A. Several problems were encountered with this polymerization. Small amounts of chlorobenzene had been utilized in the past for this reaction in order to reduce sublimation of the diacetate and to insure homogeneous mixing of the two reactants. However, since the diacid was not soluble in this solvent and since the initial temperature used was much higher than the boiling point of chlorobenzene, severe bumping was observed, and probably led to loss of some reactants along the walls of the flask or in the condenser.



Scheme 38. Proposed preparation of "poly(ether triphenyl phosphine oxide)" [308].

Nevertheless, the reaction was continued and the resulting brown glassy material was analyzed. A disappointing 0.1 dL/g intrinsic viscosity in methylene chloride indicated low molecular weight; however, the oligomer did display a glass transition temperature of  $229^\circ\text{C}$  and an impressive 5% weight loss in air at  $445^\circ\text{C}$ , with 30% char yield at  $800^\circ\text{C}$ . Further work on this project centering on optimizing reaction conditions could lead to improved molecular weights and thermal behavior.

### 4.3 UNIQUE CHARACTERISTICS OF PHOSPHORUS CONTAINING POLY(ARYLENE ETHER)S

#### 4.3.1 Oxygen Plasma Resistance

The area of oxygen plasma resistance has been of extreme interest for the past eight years in the field of material degradation by atomic oxygen (AO) while in low earth orbit (LEO). Many polymers used on the space shuttle missions have been seriously degraded, and much of the data has been reviewed and tabulated [309-314]. Plasma chemistry is an inexpensive source of "AO" and oxygen plasmas have been used extensively since the discovery of unacceptable levels of material etching by AO in LEO. In efforts to overcome this potentially disabling problem on future space station missions of many years in LEO, many workers in the field have attempted one of several methods to reduce material loss. These approaches include copolymerizations or coatings with semi-inorganic polymers, typically silicon based materials [139, 315-320], or coatings with metallic materials [321]. An interest in this area was generated by the non-volatile oxidized species of phosphorus which could form at the surface, thereby protecting the underlying PEPO material, similar to what was observed for the siloxane copolymerized or coated systems in which it was theorized that silicate type structures formed at the surface [139, 322]. Additionally, other workers have reported somewhat lower etch rates for low glass transition temperature phosphorus containing polyphosphazene systems [323, 324].

From observations of the presence of char yield in all PEPO systems, and from previous experience with siloxane containing polyimide materials, a hypothesis was drawn that PEPO should be quite resistant to

oxygen plasma environments (and therefore, atomic oxygen). In order to investigate the effects of oxygen plasma upon PEPO and related PAE, three polymers were chosen in which the only difference in polymer structure was the presence of the phosphine oxide unit along the backbone. BIS A PEPO, UDEL PSF and BIS A PEK were chosen as representative samples.

Ellipsometry was utilized as a quantitative tool to observe the decrease in height of around 1000Å films over time in a radio frequency generated oxygen plasma. Results were plotted as percent polymer height remaining vs. time in the oxygen plasma and representative curves are shown in Figure 49. It is clear that the PEPO material outperformed both the PEK and PSF by quite a large margin. While the UDEL and PEK films were totally volatilized after only 15 minutes in the oxygen plasma, the BIS A PEPO material still maintained 80% of its original height. Behavior such as this for such a small chemical difference in polymer structure is quite amazing and has been pursued to a large extent for many phosphorus containing engineering thermoplastics synthesized in our laboratory. Again, this behavior was observed to be generic for all phosphorus containing engineering thermoplastics. In fact, all non-phosphorus or silicon containing engineering polymers utilized for this experiment, including commercial polyimides and other polyarylene ethers, were completely volatilized after 15 minutes in the plasma. Direct comparisons between the PEPO homopolymers and the polysiloxane (PSX) copolymers were not made because of problems associated with the



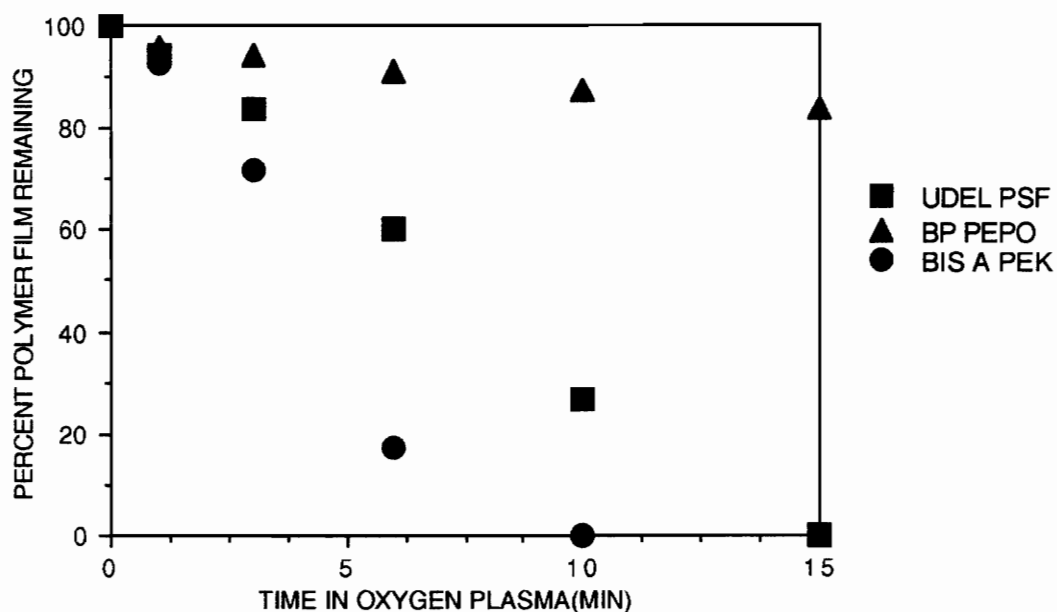


Figure 49. Oxygen plasma etching of several poly(arylene ether)s.

ellipsometer. Since the PSX phases of the copolymers were etching at a much different rate than the thermoplastic phases, laser scatter probably resulted as etching occurred. Nevertheless, both approaches for protection of organic polymers from atomic oxygen seem reasonable.

A method for determining the chemistry which takes place at the polymer surface during etching by oxygen plasma is XPS. Some of the data acquired by this technique will be presented to confirm the protective layer forming at this surface. Table 19 shows the atomic concentrations for the BIS A PEPO, BP PEPO, and polysulfone films before and after a 5 minute oxygen plasma exposure. Before exposure, the atomic concentration ratios of all polymers were in good agreement with the structures of the polymers. After a five minute oxygen plasma exposure, however, all

samples displayed a large increase in the oxygen content. For both PEPO samples, there was also an increase in phosphorus content, while the polysulfone showed little change in the sulfur atomic concentration. The presence of nitrogen was observed for both the PEPO and polysulfone samples after exposure to the plasma which is not present in the

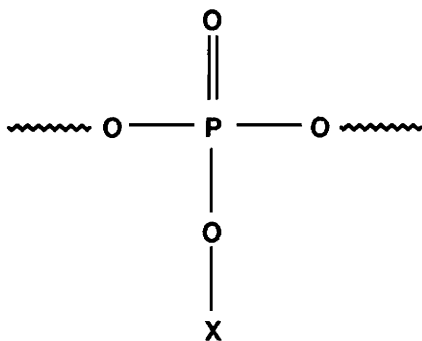
Table 19. XPS analysis of PEPO and UDEL polymer films before and after a 5 minute oxygen plasma treatment.

ELEMENT	ATOMIC CONCENTRATIONS (BEFORE/AFTER) PLASMA TREATMENT		
	BP PEPO	BIS A PEPO	UDEL
CARBON	88.3/46	89.2/42	84.0/63
OXYGEN	8.5/40.6	7.6/43.0	13/32.3
SULFUR	-----	-----	3.0/3.2
PHOSPHORUS	3.2/10.4	3.1/11.3	-----

original backbone structure. This finding may be attributed to the reaction of excited species on the plasma treated surface with air during sample transfer or may be due to the relatively low vacuum used in the reaction chamber.

Figure 50 illustrates the phosphorus 2p spectrum for both the control and 5 minute oxygen plasma treated BP-PEPO samples. As can be seen from this figure, the peak maximum shifts from a binding energy of 132.5 eV due to the original triphenyl phosphine oxide moiety in the

polymer backbone, to a much higher binding energy peak at 135.0 eV due to some highly oxidized form of phosphorus. This phosphorus peak position compares well with a binding energy of 134.8 eV found for the phosphorous 2p photopeak in a triphenyl phosphate standard, indicating the possible formation of a surface phosphate layer. To investigate the evolution of the surface layer, the O 1s / P 1s ratio was monitored over a wide range of exposure times ranging from 5 seconds to 15 minutes, and the results are shown in Figure 51. This plot shows evidence that after an initial high O 1s/P 2p value, this ratio decreases to a plateau value of approximately 3.4, which is consistent with a surface phosphate layer of the structure:



where the X moiety may represent a variety of carbon containing groups. The C 1s/P 2p ratio of between 3-4 after 15 minutes exposure time may represent an average of many carbon containing substituents. For comparison, Figure 51 also shows the O 1s/S 2p ratio for UDEL polysulfone which displayed a plateau value of 12-14 almost immediately after the initial 10 second exposure. The formation of a steady state surface concentration with polymer ablation has been shown in a number

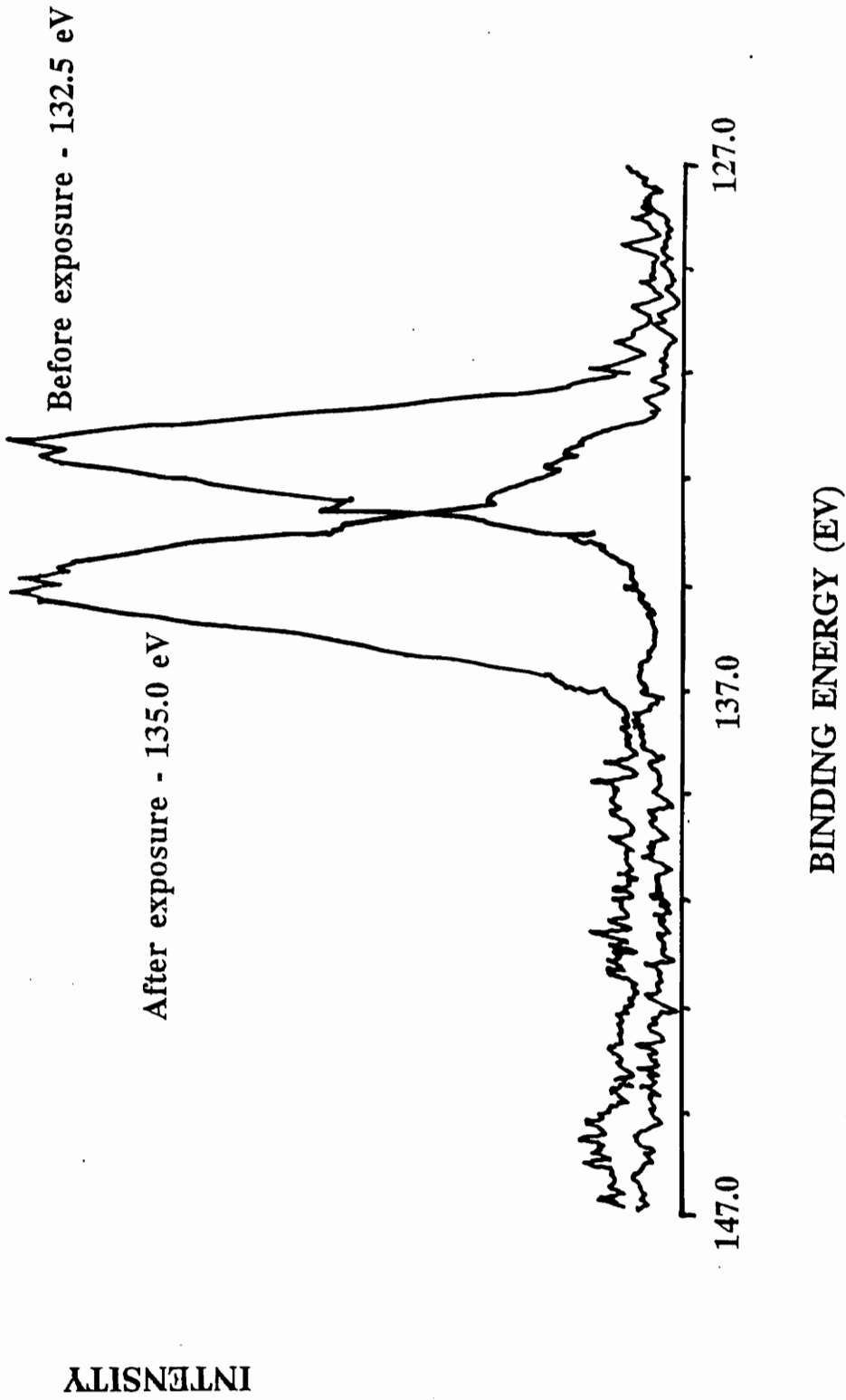


Figure 50. XPS analysis of the phosphorus 2p spectrum for the control and the 5 minute oxygen plasma treated BP PEPO films.

of plasma treated polymer systems including oxygen plasma treatment of polyphenylene sulfide [325].

To examine the surface changes further, Figure 52 shows the carbon 1s spectrum for a control BP-PEPO film, a film with a 10 second exposure, and sample with a 15 minute exposure. Even without the use of curve fitting techniques, it can be easily seen that the 10 second treatment results in the formation of many types of highly oxidized carbon species. After a 15 minute exposure, however, many of these species have disappeared. This seems to indicate that much of the polymer is initially oxidized with eventual loss of oxidized carbon species as  $\text{CO}_2$  and the surface enrichment of oxidized phosphorus species. The continuing presence of a high binding energy shoulder at 286.3-286.5 eV indicates that C-O type functionality remained even after plasma treatment, and this would be consistent with the proposed phosphate structure with the X moiety of an oxidized hydrocarbon type. The evaluation of standards is needed, however, to determine the exact chemical structure. The additional presence of the  $\pi$  - $\pi^*$  shake-up satellite at approximately 292 eV also indicates that some aromatic functionalities are still present in the surface layer after oxygen plasma exposure.

These important findings could be utilized in fields other than aerospace applications. For example, a recent review focused on some applications in the areas of solid state electronics, where plasma etch resistant materials could be used as plasma etching masks or plasma developed resists [326]. Future investigations should focus on the exact

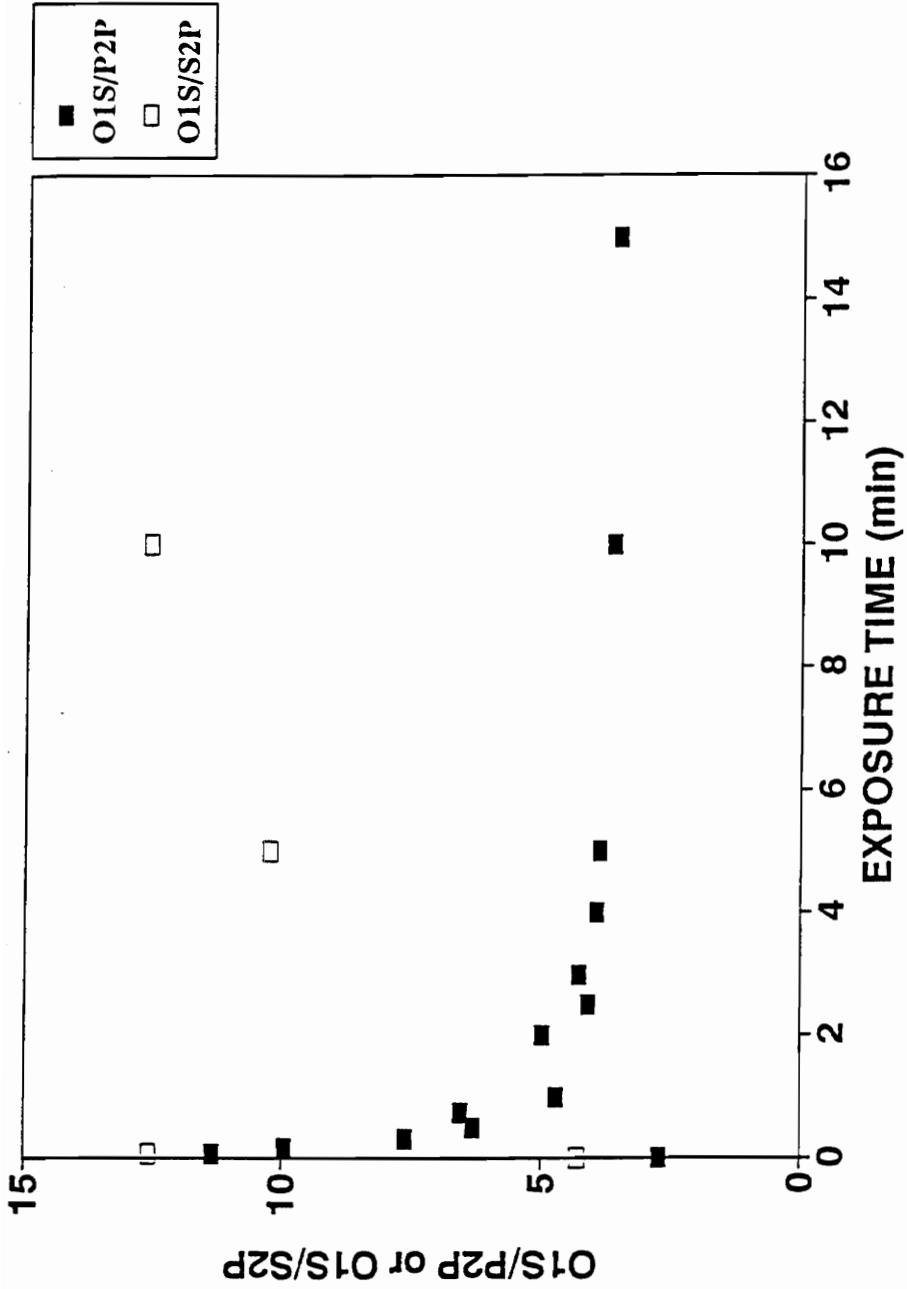


Figure 51. XPS analysis of the O 1s/P 2p and O 1s/S 2p ratio as a function of oxygen plasma treatment time.

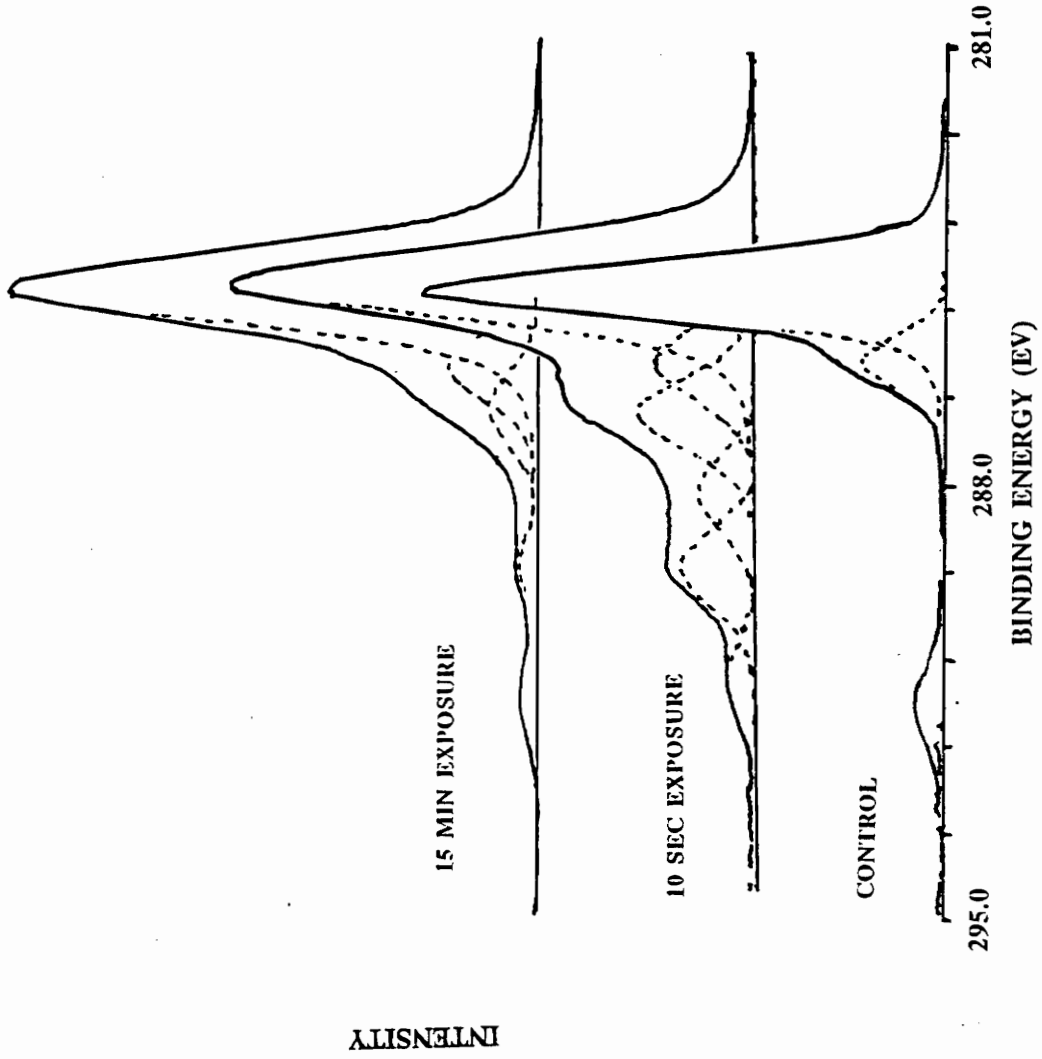


Figure 52. XPS analysis of the C 1s spectrum for control, 10 second and 15 minute oxygen plasma treated BP PEPO.

identity of the surface layer, the structural integrity of the modified layer, and the resistance of this modified layer to other agents, such as solvents, temperature, etc.

#### 4.3.2 Metal Complexation Behavior

For over 100 years, metals have been known to form adducts with phosphoryl group containing organic compounds, such as triphenyl phosphine oxide [327]. Since the phosphine oxide group can act as a Lewis base (electron-pair donor) toward inorganic Lewis acids (electron pair acceptors), many metals have been reported to form complexes with organophosphine oxides. Almost any metal in the periodic table, from 3d-5d metal ions to the lanthanide and actinide series to lithium, sodium, etc., etc. has been reported to form some type of complex with phosphine oxide containing ligands. Thus, it was a simple transition from inorganic complexation chemistry to organic polymer modification which lead to the newest and one of the most intriguing areas of research on this project.

Metal-containing polymeric systems have been investigated for many years [328, 329]. Particular emphasis has been placed on materials with the possibility of specific interactions with metallic additives, such as poly(vinyl pyridine) [330] and poly(vinyl alcohol) [331]. Additionally, much work has been reported on polyimide based materials doped with many different metallic additives [332-334]; however, it is not clear whether any specific interactions were accomplished or attempted. Therefore, it appears that no high performance material has



been successfully complexed with metal substrates. The potential for important applications in this field is vast, with possible uses for this type including semiconducting high performance polymers, extraction applications, catalytic utility, stealth technology, lightning strike resistant high performance composites, etc.

The actual "research" was initiated by a discovery made by chance. In an effort to find a method by which PEPO could be crosslinked, an idea was proposed to heat a mixture of PEPO with some metal halide at 300°C. Thus, the procedure of such an experiment involved preparing a solution of PEPO with a metal halide, casting a film, and heating to 300°C. Also to be run was a sample of UDEL PSF as control which should not crosslink. The solvent utilized was a 50:50 mixture of THF : CH<sub>2</sub>Cl<sub>2</sub>, since metal halides were not soluble in methylene chloride alone. Ferric chloride was chosen as the metal halide of choice, since it was readily available, and was used as the hexahydrate. Solutions prepared were 2:1 polymer:FeCl<sub>3</sub> by mass. UDEL solutions were clear and orange upon addition of the salt. Upon addition of the ferric chloride to the solution of BP PEPO, immediate gelation of the entire solution occurred. This experiment was repeated several times with many phosphine oxide containing polymers with the identical results.

Separation of this "gel" and drying gave a material with glass transition temperature of 247°C, which was 14°C higher than the control 20000 g/mol t-butyl terminated BP PEPO sample. Water seemed to have no effect on this gel, as boiling water was not discolored at all with this material. Additionally, the product would not redissolve in chloroform,

but would redissolve in NMP or DMAC. Initially these findings were quite puzzling, but upon further consideration, became somewhat more clear.

Since no gelation was taking place in DMAC or NMP, it was thought that perhaps these solvents were interacting with the metal, preventing interactions with the polymer. Search of the literature revealed many references to this fact, e.g. [335]. The data indicated complexation through the carbonyl carbon for many amide solvents. Thus, the overwhelming excess of amide molecules in the PEPO/metal halide/DMAC solution reduced the tendency or availability of the metal salt for interaction with the polymer. Proof of the solvent/metal halide interaction could be observed through  $^{13}\text{C}$ NMR of the solvents with metal halides. Both DMAC and NMP samples gave carbonyl carbon chemical shifts at 170.8 and 202 ppm, respectively; however, upon addition of ferric chloride to the  $\text{CDCl}_3$  solution, these shifts disappeared completely from the spectra while all other shifts remained the same.

Additionally,  $^{31}\text{P}$ NMR studies of BFPPPO in THF gave a single peak at 23 ppm; addition of a 1:1 stoichiometric ratio of  $\text{ZnCl}_2$  to BFPPPO shifted the peak downfield to 32 ppm. On the other hand, excess BFPPPO resulted in a shift of 26 ppm. Two chemical shifts were not observed in the latter sample due to rapid exchange in solution, thus resulting in an averaged peak at room temperature. Reduction of temperature should result in freezing out one of the peaks.  $^{31}\text{P}$ NMR of DMAC solutions of BP PEPO with 55 mole%  $\text{ZnCl}_2$  resulted in a 1.2 ppm downfield shift of the phosphoryl peak.

Thus, a decision was made to prepare films from homogeneous

solutions of PEPO/DMAc/metal halide salts and investigate the resulting film properties. The salts chosen were  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2$  (anhydrous),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ . After preparing 20 mole % salt (based on repeat unit molecular weight) films, and drying at  $150^\circ\text{C}$ , the results were as follows. All films were clear tough and of varying bright colors, with Co salts being deep blue, Ni very light blue, Cu green/yellow and Fe orange. Glass transition temperatures all showed increases, ranging from  $247^\circ\text{C}$  for iron complexes to  $266^\circ\text{C}$  for Co salts. None of the resulting films redissolved in chloroform, but all redissolved in DMAc. Thermogravimetric analysis did not show an appreciable decrease in decomposition onset and showed higher char yields relative to the unmodified polymer. FTIR spectra of films on KBr plates showed a large decrease in the intensity of the P=O stretch at  $1180\text{ cm}^{-1}$ , indicative of complexation through the phosphine oxide bond.

Although more work is continuing on this subject in these laboratories, this is certainly a novel characteristic for PEPO materials and unique to this set of polymers. Future directions in this project should include additional spectroscopic work and the preparation of an extended range of compositions. Thermal and spectroscopic investigations of the series should yield valuable information on this potentially valuable property.

## 5.0 SUMMARY

Poly(arylene ether phosphine oxide)s were successfully prepared by the nucleophilic aromatic substitution polycondensation of aromatic bisphenols with bis(4-fluorophenyl)phenyl phosphine oxide or bis(4-fluorophenyl)methyl phosphine oxide in the presence of potassium carbonate and an aprotic dipolar solvent. In addition to offering hydrolytic, thermal and oxidative stability, with Tg's ranging from about 190-280°C, these materials were more self-extinguishing than any other engineering thermoplastics when burned, due to the presence of phosphorus in the substantial amount of char. Moreover, phosphorus presence played the major role in resisting aggressive oxygen plasma environments by forming a highly oxidized, nonvolatile phosphorus containing surface layer. Finally, complexation of these PEPO materials through the phosphoryl group with metal halides afforded clear tough films with modified thermal and solubility characteristics. These properties were unique to all phosphorus containing poly(arylene ether)s, with important implications in the aerospace and other commercial industries.

Controlled molecular weight oligomers were prepared for several reasons. Amine terminated PEPO were synthesized for incorporation into crosslinked networks and copolymers. Polymers were prepared with t-butyl endgroups for confirmation of molecular weight control.

Compatible blends of PEEK with PEPO were prepared which gave clear amorphous films when quenched from the melt. Although not miscible, the thermal performance of such materials could be expected to surpass those

of PEEK alone. Random PEEK-PEPO copolymers were synthesized by a relatively low temperature technique which showed glass transition temperatures higher than PEEK. Several compositions were crystalline and this crystallinity could be regenerated in the sample by annealing about 50°C below the observed  $T_m$ .

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## 7.0 APPENDIX

### Controlling Molecular Weight of Step-Growth Polymers

Two related methods of controlling molecular weight exist for step growth polymerizations. These methods are off-setting the stoichiometry by a calculated amount or intentionally adding a monofunctional "end-capper." Both processes will be discussed as the latter method cannot be explained independently of the former.

If M is defined as a monomer and p as the fractional extent of reaction ( $0 \leq p \leq 1$ ), then

$$[M]_{(t=0)} = [M]_0$$

$$[M]_t = [M]_0 - [M]_0 p = [M]_0(1-p)$$

where [M] is monomer concentration at times 0 and t.

If  $X_n$  is the number average degree of polymerization and DP the degree of polymerization (number of repeat units), then in our case, since there are two monomer units per repeat unit,

$$X_n = 2 \text{ DP}$$

and, since  $X_n = \text{Total \# initial molecules} / \text{Total \# polymer molecules}$ , then

$$X_n = [M]_0 / [M]_t = [M]_0 / \{[M]_0(1-p)\} = 1/(1-p)$$

Thus, the extent of reaction must be very high (i.e. p must be  $> 0.99$ )

for most applications) for high molecular weight to be achieved. The above equation is often referred to as the Carothers equation since this development was first reported by him in 1936 [61].

In order to control molecular weight, the stoichiometry of the reaction must obviously be controlled. Modifications of the Carothers equation will allow the utilization of either offset stoichiometry or the addition of a monofunctional "impurity." The following discussion assumes an AA + BB type polymerization, but the equations developed are easily modified for other reaction types.

If N is the number of functional groups of a particular monomer (2 times the number of molecules of that monomer), referred to as monomers A or B, and if  $N_B > N_A$ , then the stoichiometric imbalance, r, can be defined as

$$r = N_A/N_B \leq 1$$

and

$$X_n = \text{Total \# initial molecules} / \text{Total \# polymer molecules}$$

then

$$\text{Total \# initial molecules} = (N_A + N_B) / 2$$

$$\begin{aligned} \text{Total \# polymer molecules at any time} &= \text{total \# initial} \\ \text{molecules} - \text{\# reacted molecules at any time} &= (N_A + N_B) / 2 - \\ &\text{\# reacted molecules} \end{aligned}$$

Assuming equal reactivity, # reacted molecules = p (4N<sub>A</sub>) and



$$X_n = [(N_A + N_B)/2] / [(N_A + N_B)/2 - 4pN_A]$$

Dividing all terms by  $N_B$ , gives

$$X_n = [(N_A/N_B) + 1] / [(N_A/N_B) + 1 - 2(N_A/N_B)p]$$

$$X_n = (r + 1) / (r + 1 - 2rp)$$

or, as  $p$  approaches 1

$$X_n = (r + 1) / (1 - r)$$

Rearranging yields

$$r = (X_n - 1) / (X_n + 1)$$

The utility of this equation is best shown by example. If a 5000  $M_n$  BIS A poly(arylene ether sulfone) terminated by aromatic hydroxyl groups was desired, the following manipulations of the above calculations will allow one to calculate the excess of BIS A which must be incorporated into the polymerization. The repeat unit of the BIS A PES has been illustrated throughout the text and has a molecular weight of 442.514 g/mol. Thus,

$$\begin{aligned} DP = \# \text{ repeat units} &= \text{Molecular weight of oligomer} / \text{molecular} \\ &\text{weight of repeat unit} = 5000 \text{ g/mol} / 442.514 \text{ g/mol} = 11.299 \end{aligned}$$

Also,

$$X_n = 2 DP = 2(11.299) = 22.598$$

Thus,

$$r = (X_n - 1)/(X_n + 1) = 21.598/23.598 = 0.91525 = N_A/N_B$$

In this case,  $N_A$  = moles DCDPS and  $N_B$  = moles BIS A. Therefore, instead of the normal 1:1 stoichiometry required for high molecular weight polymer formation, one monomer will be offset by almost 10%. For hydroxyl termination, it is obvious that the bisphenol must be present in excess, and is  $N_B$ . For every one mole of BIS A utilized in this polycondensation, 0.91525 moles of DCDPS will be used.

However, if functionality other than hydroxyl or aromatic chlorine is desired, some other type of monofunctional "impurity" may be utilized in the reaction with appropriate modifications of the above equation. In poly(arylene ether) synthesis, this additive is normally a substituted phenol such as *m*-aminophenol. The substituted group must not be reactive in the polymerization, while the phenolic group must be reactive. In order to arrive at the correct expression for the addition of a monofunctional reagent, several features must be expanded upon regarding the correct choice of monomer ratios. A very small detail on the utilization of modified Carothers equations is normally overlooked in the understanding of the theory at this point. Although all monomers are in practice charged initially into the reaction setup, assume for the sake of discussion here that initially only the difunctional monomers were charged. If again a 5000 g/mol BIS A PES is desired with amine

termination by the controlled addition of *m*-aminophenol, then the functionality at the chain end with which this endcapper must react is the activated dihalide. Therefore, initially, the same calculation performed above for hydroxyl terminated PES can be performed here with DCDPS in excess over BIS A giving the correct activated halide endgroup.

Now to incorporate a monofunctional endcapper to the polymerization, *r* must remain the same number to give the same molecular weight polymer; however, now the phenols are in excess and not the dihalide since phenolic reactivity must be the last link in the polymer chain. Thus, the equation must become, by inspection

$$r = N_B / (N_A + 2N_{A'})$$

where  $N_{A'}$  is the number of monofunctional endcapper molecules added. It is multiplied by two to remind one that two molecules of this reactant must be added for every one of monomer to give a difunctional chain. Rearranging, one obtains

$$2 N_{A'} = (N_B - rN_A) / r$$

Again, the two does not enter into the calculation.

Therefore, the calculation for amine terminated 5000 g/mol BIS A PES is as follows. As calculated above

$$DP = 11.299$$

$$X_n = 22.598$$

$$r = 0.91525$$

$$\text{mol Bis A} = 0.91525 * (\text{mol DCDPS})$$

$$2 \text{ mol m-AP} = \{(\text{mol DCDPS}) - [(0.91525) \text{ mol Bis A}]\}/r$$

This approach can be "normalized" for desired batch sizes.

Slight deviations have actually been observed for the resulting engineering polymer molecular weights due to several slight errors in the above process. In almost all cases, higher molecular weight oligomers have been obtained than theoretically calculated. This phenomenon has normally been attributed to loss of low molecular weight species through filtration. While this may actually be occurring, another source of error has been in the calculation of DP. No dependence for the endgroups is accounted for in the above calculations. If one is preparing a 20000-30000 g/mol polymer, then the additional 400-500 g/mol imparted by the endgroups are a small percentage of the total molecular weight and thus a small error. On the other hand, for the preparation of 3000-5000 g/mol oligomers, the extra 400-500 g/mol for endgroups becomes significant error in the final product. The method to improve the calculations above come in the very first step, determination of DP. Instead of the relation which does not take into account endgroups

$$DP = \text{Molecular weight of oligomer} / \text{molecular weight of repeat unit}$$


the following equation should be used

$$DP = \frac{\text{Molecular weight of oligomer} - \text{Molecular weight of endgroup}}{\text{Molecular weight of repeat unit}}$$

Now the effect of the endgroup mass is taken into account and if any deviation in final product results, it is then probably due to filtration and precipitation difficulties of low molecular weight species. Alternatively, one should consider the possibility of an unknown impurity or side reaction.

## 8.0 VITA

Carrington Duane Smith was born in Halifax County, Virginia on April 7, 1965. He entered Virginia Commonwealth University in August, 1983 and graduated Magna Cum Laude with a B.S. in Chemistry in May, 1987. The author then entered the graduate program in chemistry at Virginia Polytechnic Institute and State University in September, 1987. Under the direction of Dr. James E. McGrath, Mr. Smith began his thesis research centered on the synthesis and characterization of phosphorus containing high performance polymeric systems. Mr. Smith was married to Susan Florence Abenes on July 29, 1989. The author received his Ph.D. in Chemistry with an emphasis in polymer science in August, 1991. Immediate plans for Carrington and Susan include a post-doctoral appointment with Dr. Bernard Sillion at Institut Français du Pétrole in Lyon, France.

A handwritten signature in cursive script, appearing to read "Carrington D. Smith". The signature is written in dark ink and is positioned in the lower right quadrant of the page.