SYNTHESIS AND CHARACTERIZATION OF HIGH PERFORMANCE POLYMERIC MATERIALS :

Poly(arylene ethers), Polyamides, Polyesters and Liquid Crystalline Polyarylates

by

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ABSTRACT

Poly(arylene ether)s (PAEs) were synthesized via the silyl ether displacement route. Both AA, BB, and AB silylated monomers were prepared by partial or complete hydrolysis of the dihalide using potassium hydroxide in aqueous dimethyl sulfoxide followed by silylation with hexamethyl disilazane. Both linear and star-branched structures of PAEs were synthesized and this polymerization route allowed both random and block copolymers to be prepared. Triaryl phosphine oxide containing homo-& co-PAEs exhibited very high char yields, which suggested that these polymers were potentially flame-resistant materials. The AB type halogenophenols were also polymerized in the presence of diphenylsulfone as a diluent and potassium carbonate as a base at elevated temperatures.

Poly(ε-caprolactam) (Nylon 6) copolymers were prepared by the incorporation of controlled molecular weight poly(arylene ether sulfone) (PES) oligomer segments into the polymer backbone which were functionalized with carboxyl end groups. A hydrolytic melt polymerization process was used to copolymerize the oligomers with ε-caprolactam. Two series of the copolymers, with varying weight ratios and PES segment lengths, were investigated. Extensive characterization experiments including thermal analysis, mechanical property measurement, wide angle x-ray diffraction and dynamic mechanical

analysis were performed to illustrate that the copolymers displayed a good balance of properties.

Hydrolytically stable triaryl phosphine oxide containing dicarboxylic acid monomers were synthesized and were chemically incorporated into the poly(hexamethylene adipamide) backbone to produce improved flame-resistant copolymers. The content of triaryl phosphine oxide comonomer in the melt synthesized copolymers was controlled from 0-30 mole%. The copolymers were melt crystallizable only at 10 and 20 mole% incorporation of the phosphine oxide comonomer. Cone calorimetric tests were employed to investigate the fundamental flame retardancy behavior of the copolymers. The tests were conducted in a constant heat environment (40 kW/m^2). Significantly depressed heat release rates were observed for the copolymers containing phosphine oxide moiety. The results of the cone calorimetric tests and TGA data suggested that the triaryl phosphine oxide containing nylon 6,6 copolymers had improved flame resistance properties.

The triaryl phosphine oxide dicarboxylic methyl ester was also introduced into poly(ethylene terephthalate) via melt transesterification to produce copolymers which had increased char yields as the P(O) content increased. However, crystallinity was totally disrupted at 20 mole percent P(O) incorporation in compression molded specimen.

Novel star-branched liquid crystalline polyarylates (LCP) were made via melt acidolysis which were subsequently transformed to liquid crystalline foams by supersaturation of carbon dioxide followed by thermal blowing. It was found that the AB type monomers were essential to generate star shaped LCPs without crosslinking. The branching agents were necessary to control the molecular weights, disrupt crystallinity and to allow for higher gas uptake by the polymer matrix.

Dedication

to my

wonderful wife Mei-Yu

dear parents Ya-Min and Lian-Shi

Their love, support and understanding have
been a great source of inspiration and comfort for me

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1. INTRODUCTION

Poly(arylene ether)s (PAEs) such as poly(arylene ether ketone)s (PEK), poly(arylene ether sulfone)s (PES), and poly(arylene ether phosphine oxide)s (PEPO) are a desirable class of high performance engineering thermoplastics. Their excellent hydrolytic, thermal and dimensional stability along with good mechanical properties are receiving increasing interest. The generalized synthesis of PAEs involves the nucleophilic aromatic substitution of activated halides by alkali metal phenates in an aprotic dipolar solvent. Electrophilic processes are also very common methods to prepare PAEs. Kricheldorf and co-workers[24, 25] introduced a variation to the nucleophilic process by condensing activated dihalides with trimethylsilyl derivatives of bisphenols. The authors believe that this route has advantages because no transetherification occurs during polymerization and the polymers can be directly used after polymerization. An important feature of this route is that block copolymers can be made. In this thesis, several new polymers have been synthesized by using this silylated phenol process.

The PAEs offer a wide range of glass transition temperatures(Tg) depending upon the structure of the backbone[5, 102]. Incorporation of the ether linkage along the polymer backbone will lower the Tg of the polymer by increasing the flexibility. PEKs are often semicrystalline polymers and their ordered morphology enables them to be continuously used in the presence of organic liquids, even at high temperatures. However, some PEKs have very high crystalline melting transitions(Tm), which can make synthesis and melt processability difficult. In this study, the Tg of the PAEs was increased by reducing the number of ether linkages and to depress the Tm to an acceptable range by synthesizing random or statistical copolymers. To accomplish this, several activated dihalides were partially or fully hydrolyzed by potassium hydroxide in aqueous dimethyl sulfoxide. The synthesized halogenophenols and bisphenols were then converted to the corresponding silylated monomers by the use of hexamethyldisilazane. The silylated AB monomers can self polymerize or copolymerize with other AB monomers via release of trimethylsilyl fluoride. Several multi-functional monomers were synthesized and used as branching agents for the AB monomer systems. A series of PAE copolymers containing the ether phosphine oxide and ether ketone ketone linkages were prepared by using silylated bisphenols with activated dihalides. Block copolymers were also prepared via this route. The prepared halogenophenols were optionally polymerized at elevated temperatures in the presence of diphenyl sulfone as a diluent and potassium bicarbonate as a base.

Polyamides (nylons) are also known to be high volume engineering thermoplastics as well as synthetic fibers. Many advances have been made to improve the performance and usefulness of these products by various engineering innovations as well as by polymer modification. This includes the introduction of reinforcing fillers, toughening agents, heat stabilizers etc. These modifications attempt to provide new levels of strength, modulus, and thermal stability to nylons. In this research, two of the important polyamides, nylon 6 and nylon 66 were modified by different approaches and for different purposes. Both copolymers were synthesized under melt conditions in a pressure reactor[122-131].

In the first approach, segmented nylon 6/PES copolymers were synthesized in order to enhance the solvent resistance of the PES and the mechanical properties of the nylon 6. The synthetic processes employed include the preparation of carboxy functionalized PES which was subsequently used to copolymerize with ε-caprolactam by a hydrolytic melt polymerization technique. The semi-crystalline, segmented or block copolymers could be of interest in a number of areas, including interleaf materials for composites and/or materials for polymeric adhesive components.

For the second approach, the triaryl phosphine oxide containing monomers were chemically incorporated into nylon 6,6 to improve the flame retardancy. In general, the triaryl phosphine oxide moiety affords thermal and oxidative stability coupled with high glass transition temperatures. Amorphous morphological structures are normally produced from triaryl phosphine oxide containing homopolymers. However, semicrystalline copolymers can also be prepared by controlled incorporation of the non-coplanar triaryl phosphine oxide comonomer. This strategy has been extended to synthesize crystallizable high volume copolymers based on nylon 6,6. This approach has some promise of affording new high performance flame-resistant materials in numerous potential textile and engineering applications.

PART I

Poly(arylene ether)s, Nylon 6 / Poly(arylene ether sulfone) Segmented Copolymers and Triaryl Phosphine Oxide Containing Nylon 6,6 Copolymers

2. LITERATURE REVIEW

2.1 INTRODUCTION

Plastics manufacturers today are expanding applications into areas associated with ceramics and specialty metals. Electronic and auto applications especially have spurred the development of these high performance plastics [1], which are also called engineering thermoplastics. Poly(arylene ether)s (PAEs), –(O–Ar–O–Ar')–, are important members of this class of materials. They can be tailored to be amorphous or semicrystalline materials. In many cases PAEs offer outstanding chemical resistance, good mechanical properties and weather resistance. Some PAEs offer unusually good flame-retardency, solvent resistance, and excellent electrical properties[2-4].

PAEs are phenylene rings linked together by an ether group (–O–) with other groups like sulfone ($-SO_2-$), ketone (–CO–), arylphosphine oxide (–P(O)(Ph)–), or imide. The ether linkage of PAEs provides chain flexibility, thereby imparting good impact strength and toughness. The inert nature of the ether linkage arises from the resonance of the aryl ether bond. The sulfone or ketone groups para to oxygen atoms tend to attract electrons from the phenyl rings and to enhance the resonance of the ether bond. This results in enhanced bond strengths and contributes to the polymers good thermal stability and rigidity at high temperatures.

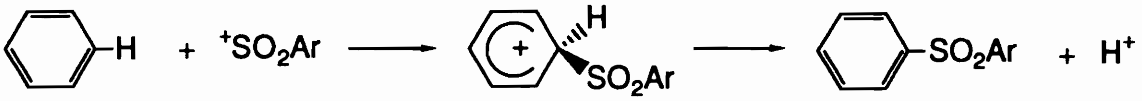
Several synthesis methods have been developed for the synthesis of PAEs and a large number of research results have been published. Among these methods, nucleophilic aromatic substitution and electrophilic aromatic substitution are the two major synthetic routes employed[3-6]. Other methods like oxidative coupling, Ni, Pd or Cu coupling[7-9], ring-opening polymerization[10-16] and silyl ether displacement[17-25] have also received certain attention. In this research, nucleophilic aromatic substitution and silyl ether displacement routes were used to prepare various homo- & co-polymers of PAEs. Carboxyl terminated poly(arylene ether sulfone) oligomers with different chain lengths were synthesized by the nucleophilic substitution reaction using m-hydroxybenzoic acid as the end capper.

2.1.1 Synthesis of poly(arylene ether sulfone)s

In general, poly(arylene ether sulfone)s (PAEs) are amorphous materials, which can be synthesized by either polysulfonylation or polyetherification (i.e. electrophilic or nucleophilic aromatic substitution). However, the polyetherification route is a prefered process in commercial applications. The first patents on polysulfone synthesis were disclosed in the early 1960's by Union Carbide, 3M and ICI [26]. Since then, extensive research on PES has been conducted. Several review articles based on the preparation, properties, processing and applications of PES are available in the literature[2a, 3, 6, 26-30, 60, 61, 64]. In the next two sections, the synthesis of PES based on polysulfonylation and polyetherification will be discussed.

§ Polysulfonylation

Polysulfonylation is an electrophilic aromatic substitution reaction in which the aromatic substrate is attacked by some form of an arylsulfonylium cation and hydrogen is displaced as a proton (Scheme 2.1).



Scheme 2.1 Electrophilic aromatic substitution reaction for poly(arylene ether sulfone)

The general equations of polysulfonation are illustrated below:

$$n\,XO_2SArSO_2X + n\,HAr'H \xrightarrow{MXm} \text{—}(ArSO_2Ar'SO_2)_n\text{—} + 2n\,HX \tag{1}$$

$$2n\,HArSO_2X \xrightarrow{MXm} \text{—}(ArSO_2ArSO_2)_n\text{—} + 2n\,HX \tag{2}$$

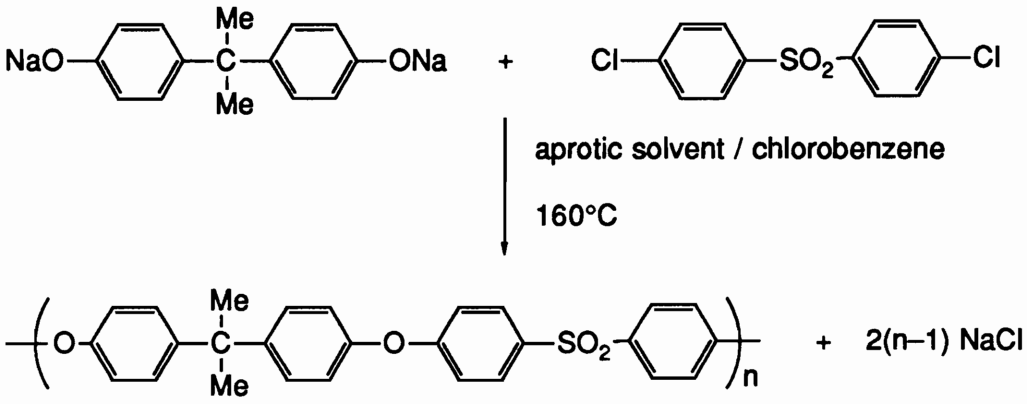
$$n\,HO_3SArSO_3H + n\,HAr'H \longrightarrow \text{—}(ArSO_2Ar'SO_2)_n\text{—} + 2n\,H_2O \tag{3}$$

Here X is a halogen (commonly chlorine) and MXm is a Friedel-Crafts type metal-halide catalyst. Equations (1) and (2) are representative of Friedel-Crafts sulfonylation reactions. Lewis acid catalysts such as $AlCl_3$, $FeCl_3$, $SbCl_5$, and BF_3 can be used to facilitate the reaction[31]. Since more than one site of aromatic hydrogens, which can be replaced by electrophiles, is commonly present in the reacting molecules, different repeat-units can arise from the same polycondensation. This structural irregularity is due to possible sulfonylation at those various sites of the benzene ring, or disulfonylations on the same benzene ring (result in branching or crosslinking) [33,34]. Some side reactions promoted by the catalysts are also observed[32].

The equation (3) is a polycondensation of di-arylsulfonic acid with aromatics(eg. diphenylether)[35]. This route need to remove water between aromatic hydrogen and sulfonic acid groups. It has been reported that this route is easily conducted in either strongly acidic or dehydrating media[6].

§ Polyetherification

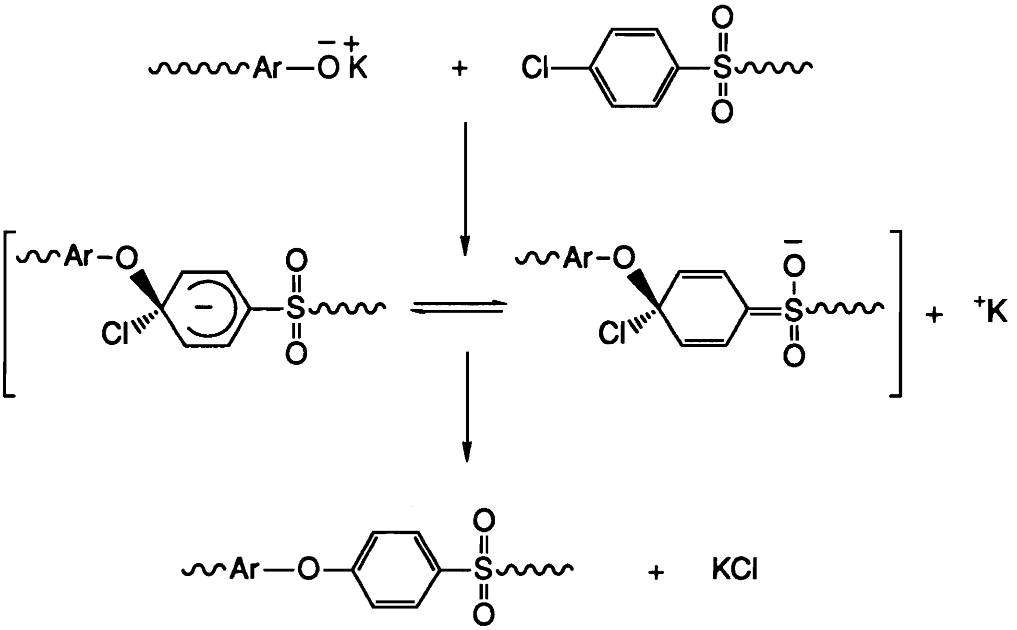
The synthetic method most commonly used to produce PAE is polyetherification, which is a nucleophilic aromatic substitution reaction. In this route, an activated aromatic dihalide is reacted with a phenate to generate the ether bond. This technique was disclosed by Johnson in 1967[36]. Johnson, et al particularly emphasized the need for anhydrous reaction conditions. The disodium salt of bisphenol-A was reacted with 4,4'-dichlorodiphenylsulfone(DCDPS) in a dipolar aprotic solvent such as dimethyl sulfoxide(DMSO) or l-methyl-2-pyrrolidone (NMP)(Scheme 2.2). The experimental procedure description for this reaction[36] is a good example of the synthesis of PES under laboratory or even industrial scale conditions.



Scheme 2.2 Synthesis of polysulfone by polyetherification route [36]

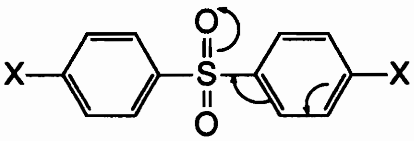
The mechanism and kinetics of polyetherification have been investigated in detail for the polymerization of AA/BB type monomers [36-38] and AB monomers [38-40]. The polymer-forming reaction is via the nucleophilic displacement of a phenate and an activated dihalide system in a two step addition-elimination reaction. The attacking nucleophile first adds to the electron-deficient site of aryl halide, forming a negatively charged Meisenheimer complex intermediate. The halide is then eliminated resulting in the formation of an aryl-ether linkage(Scheme 2.3).

Aromatic halide reactivity and phenoxide basicity are strongly influenced by the electron affinity, the position and other substituents in the aromatic ring, conjugation, inductive and steric effects[40]. Electron-withdrawing groups (EWG) such as sulfone group enhance the halide reactivity. The ease of displacement of the different halogens by nucleophiles can be expressed as F(312) >> Cl(1) ≥ Br(0.74) ≥ I(0.36). The numbers in parentheses are the relative reaction rates for the etherification[41]. The reactivity of the activated halide can be measured by ^1H, ^{13}C and ^{19}F NMR. Since the nucleophilic

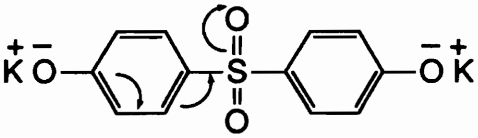


Scheme 2.3. Nucleophilic aromatic substitution mechanism for PES

substitution reaction only proceeds if the EWG substituent is located in the ortho or para position to the halide, ^1H NMR chemical shift data for the protons ortho or para to the EWG can be used to judge the reactivity of the monomer indirectly [42]. (The actual reaction site is occupied by the halide). Both ^{13}C and ^{19}F NMR can be used to probe the chemical shift at the actual site of nucleophilic reaction. In general, lower chemical shifts correlate with lower monomer reactivity. It has been reported that if the ^{13}C chemical shift of an activated fluoride ranges from 164.5 to 166.2 ppm in $CDCl_3$ the compound may be an appropriate system for nucleophilic displacement[43]. An EWG depresses the basicity of phenoxide by delocalization of the negative charge of the phenoxide anion and results in lower nucleophilicity. Because the sulfone group is a powerful EWG, bis(4-hydroxyphenyl) sulfone is recognized as one of the least reactive bisphenols, thus requiring a relative high temperature reaction. The alkali metal cations may also influence the rate of the nucleophilic substitution reaction in the order Cs > K > Na > Li [5].



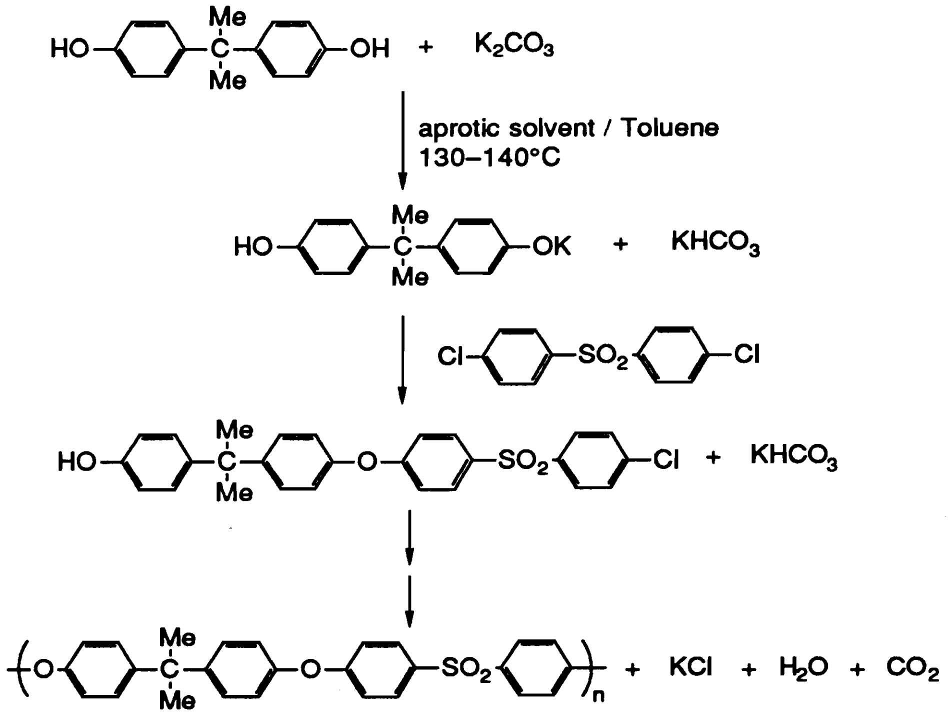
activated dihalide



deactivated phenate

To prepare phenoxide monomers using alkali metal hydroxides requires careful stoichiometric control. If the salt formation is carried out *in situ* by reaction of the phenol with alkali metal carbonate[44-50], the amount of alkali metal carbonate is not extremely critical. This is because the excess carbonate (unlike hydroxide) does not readily lead to hydrolysis of the activated dihalide monomer.

As illustrated in the proposed mechanism(Scheme 2.4), bisphenoxides usually are not formed in the carbonate process. Therefore, this process greatly improves solubility and stability of the salts. Once the mono-salt is formed, it next reacts with dihalide compound to form a soluble phenol ether. This process may also suffer from disadvantages[51]. A finite concentration of phenolic hydroxyl group is present throughout the polymerization. This acidic hydroxyl group may cause decomposition of DMSO [51], and the phenol itself may undergo decomposition if the reaction temperature is raised too high or too rapidly. In addition to DMSO, several other dipolar aprotic solvents, such as N-methyl-2-pyrrolidone(NMP), N,N-dimethylacetamide(DMAc) and cyclohexylpyrrolidone (CHP) have been found to be suitable solvents for many different polymerization systems [46-49] when K_2CO_3 is used as the base.



Scheme 2.4. Proposed mechanism for the synthesis of poly(arylene ether sulfone) via the potassium carbonate process (47)

Although diaryl ethers are known to be very stable towards attack by base, ethers activated by electron-withdrawing groups can be cleaved by nucleophilic reagents readily [52]. This fact has been proved by a kinetic model study of a sulfone-ether compound [40]. Residual water present during the polymerization may cause hydrolytic side-reactions [36, 53]. Such reactions either directly hinder high molecular weight formation or cause cleavage of the formed polysulfone.

$$\text{—ArOK} + H_2O \longleftrightarrow \text{—ArOH} + \text{KOH} \qquad (4)$$

As illustrated in equation(4), water reversibly hydrolyzes the phenate salt and produces potassium hydroxide. The equilibrium concentration of the potassium hydroxide depends mainly on the acidity of the phenol. The hydroxide anion in turn can lead to irreversible halogen-displacement from the dihalides [40, 53-55]. This event offsets the intended halide/phenate stoichiometry, which results in low molecular weight polymers. The hydroxide anion may also attack the polymer chain, cleave the ether linkage (Equation 5), and also generates low molecular weight products.

$$\sim SO_2Ar{-}O{-}ArSO_2Ar\sim \; + \; ^{-}OH \; \rightleftharpoons \; \sim SO_2Ar{-}O^{-} + HO{-}ArSO_2Ar \sim \qquad (5)$$

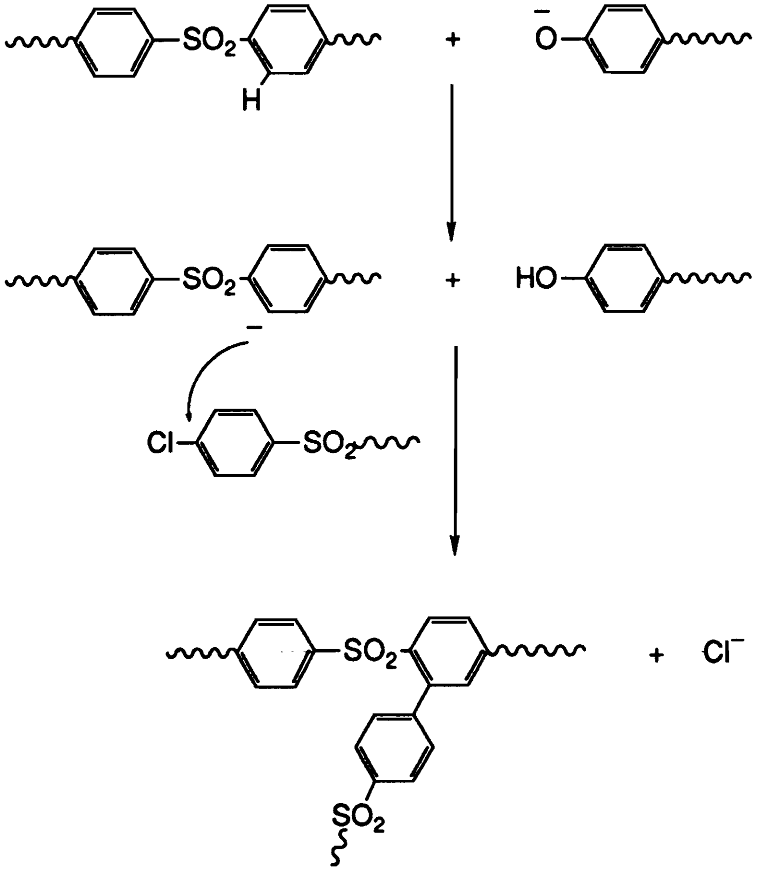
$$\sim SO_2Ar{-}O{-}ArSO_2Ar\sim + \; ^{-}O{-}Ar'\sim \; \rightleftharpoons \; \sim SO_2Ar{-}O{-}Ar'\sim \; + \; ^{-}O{-}ArSO_2Ar\sim \qquad (6)$$

Transetherification virtually proceeds without any influence on the molecular weight(Equation 6); however, it can disrupt a semi-crystalline morphology. The rate of the transetherification increases with temperature.

Fluoride ion is a powerful nucleophile and it may also cleave activated ether linkages[38, 56-58], especially in dipolar aprotic solvents [59](Equation 7). It has been intentionally used as a base[39], but it also may cause molecular weight to decrease[38,59]. In contrast to fluoride anion, other halide ions are much less powerful nucleophiles. Alkali or alkaline earth metal salts such as LiCl have been used as inhibitors for this cleavage reaction [56].

$$\sim ArO\,K \; + \; F{-}Ar'SO_2\sim \; \xrightleftharpoons[k_2]{k_1} \; \sim ArOAr'SO_2\sim \; + \; KF \qquad (7)$$

The low solubility of potassium fluoride in dipolar aprotic solvents permits the synthesis of high molecular weight poly(arylene ether sulfone) from activated fluoride compound. The polymerization reaction can be considered to be an equilibrium process(Equation 7), where [KF] is a constant which reaches a saturation concentration in the earliest stages of the step polymerization reaction.

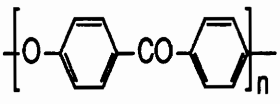


Scheme 2.5. Proposed mechanism for the formation of branched PES[60]

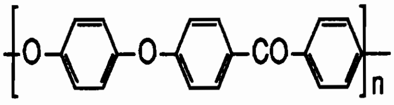
The poly(arylene ether sulfone) synthesized by nucleophilic aromatic substitution route has the possibility of generating a slightly branched fraction of polymer. Attwood[26, 60] proposed a mechanism to account for the generation of the branched fraction(Scheme 2.5). The branching was proposed to occur via a side reaction of a growing chain-end, eg. the phenate attacks the hydrogen ortho to the sulfone group. This side reaction supposedly becomes important as the polymerization temperature is increased, and it was considered responsible for the small amount of gel formation in melt polyetherification conducted above 300°C.

2.1.2 Synthesis of poly(arylene ether ketone)s

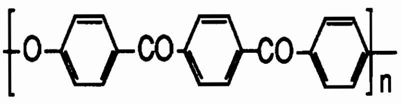
Poly(arylene ether ketone)s (PAEK) may be semicrystalline polymers if an appropriate "rigid" monomer are employed. The acronyms to be used to represent their structure are shown below.



PEK



PEEK



PEKK

The synthesis methods for PAEK are analogous to the poly(arylene ether sulfone)s. The properties, synthesis and development of PEK has been reviewed [2b, 5, 7, 60-64]. The semi-crystallinity of PAEK provides them excellent thermal properties (melting points generally above 300°C[5]). However, the synthesis is much more difficult than for analogous PES. The major problem is to keep the growing chains in solution in order to obtain high molecular weights. Strategies employed to overcome this problem include:

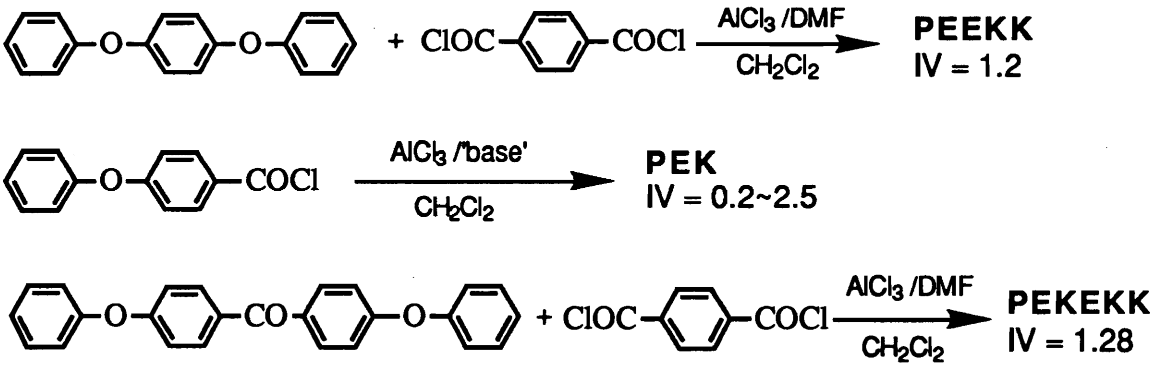
(1) very high temperature by nucleophilic process [36]

(2) strong acidic media by electrophilic process (in which the carbonyl groups are protonated, allowing the polymer to remain in solution [66])

(3) synthesis of PAEK amorphous precursor first at relative low temperature process then, converting the precursor to semicrystalline polymers.[67-73]

§ Polyacylation (Electrophilic Aromatic Substitution)

PAEK was first reported by DuPont scientists in 1962 [5]. Relatively low molecular weight(intrinsic ~ 0.18) PEKK was made from isophthaloyl chloride or terephthaloyl chloride with diphenyl ether in nitrobenzene using $AlCl_3$ as catalyst. Similar techniques have been used in different solvents such as dichloromethane[74], 1,2-dichloroethane, carbon disulfide, etc, and in each case only low molecular weight products resulted. However, high molecular weight PAEK can be made by the use of large amount of $AlCl_3$ (eg. $AlCl_3$ to acid chloride ratio 2.6 - 5.6) and in the presence of a Lewis base (which can be lithium chloride, tetramethylammonium chloride or DMF)(Scheme 2.6)[75-78]. The $AlCl_3$ route appears now to be a very good method at least for academic research and may also be a possible commercial process for PAEK production.



Scheme 2.6 Synthesis of PAEK by electrophilic process [75]

A mixture of HF/BF_3, solvent/catalyst, was another more effective acidic system, which usually results in high molecular weight PAEK[66, 78-81]. In this solvent system, BF_3 was used in the ratios of BF_3/carbonyl group = 2~3 and HF/BF_3 = 2~10. It was suggested that the molecular weight can be controlled by varying the reaction time[79]. This reaction technique has been extensively studied by Du Pont and Raychem and claimed in several patents [66,79-81]. According to the results illustrated, this route is versatile and has been used to prepare many different PAEK material systems. However, it is environmentally very undesirable. Trifluoromethanesulfonic acid (triflic acid) is also an acidic solvent for the synthesis of poly(arylene ether ketone). For example, the polymerization of arylacidchloride[82], and aromatic carboxylic acids[83,84] have been reported by using triflic acid as the solvent.

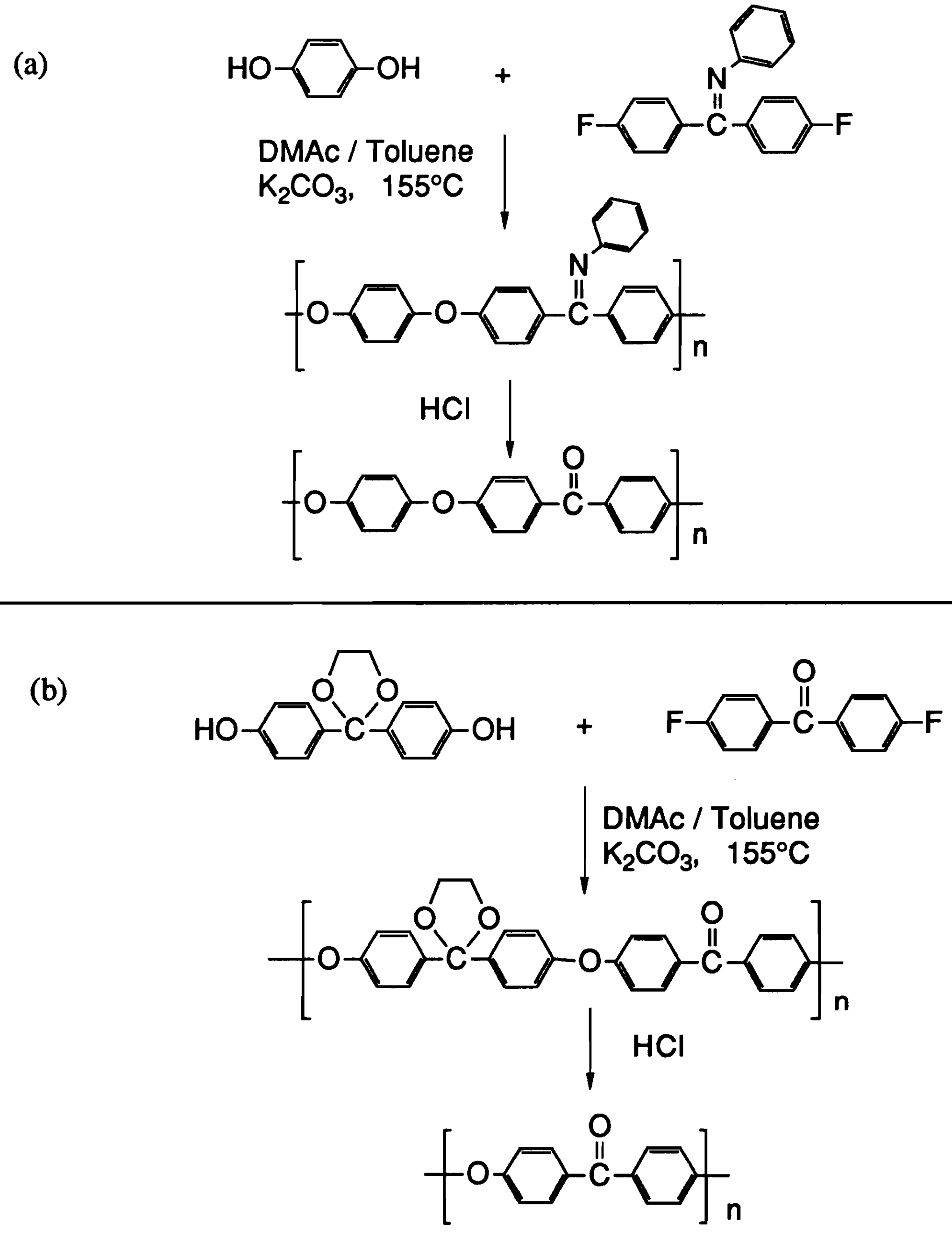
§ Nucleophilic route for PAEK synthesis

The nucleophilic displacement process originally developed for the PES has been successfully adapted to produce PAEK by ICI [85]. A high temperature solvent such as diphenylsulfone is required for this process due to the crystallinity of PAEK to avoid oligomers prematurely precipitating from the solution. However, for amorphous PAEK, common dipolar aprotic solvents are favored [86, 87]. Unlike the sulfone group, the carbonyl group is usually not sufficient to activate the chlorine, so fluorine is necessary as the halide[85]. Using chloro-monomers generally results in low molecular weight and/or some irregular branching product.

A special technique to prepare semicrystalline PAEK has utilized an amorphous precursor, which can then be transformed to semicrystalline products [67-73]. As illustrated in Scheme 2.7, (a) via ketimine intermediates[69-73] and (b) via acetal derivatives[67,68], both processes leading to semicrystalline PAEK. The major advantage of these processes is that the reaction can be conducted at mild temperatures (155 °C), and a "defect free" PAEK can be synthesized.

2.1.3 Poly(arylene ether)s via silyl ether displacement

Silylation of organic compounds has found for many years wide application as an aid for separation procedures through conversion of organic compounds into volatile



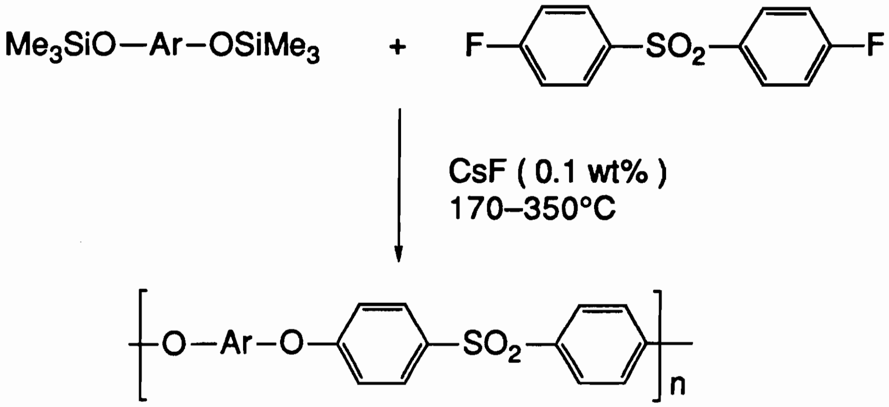
Scheme 2.7 Synthesis of semicrystallinePAEK via amorphous precursors
a). PEEK[71] b). PEK[67, 68]

derivatives. During the last two decades, the silylation method has become not only a new organic synthesis tool but also a new route to synthetic polymers. After pioneering research work conducted by Klebe in the mid 1960's [88], the real major progress in the silylation method to synthesize polymers was demonstrated by Kricheldorf in the late 1970s and the early 1980s for polyesters[89, 90] and for poly(arylene ether)s[24, 25] synthesis. It has also been demonstrated that the silylation method is very versatile and promising for the synthesis of polyamides[91], polyimides[92, 93], polyureas[88, 93], and polybenzoxazoles[94] by using N-silylated diamines.

Silylation followed by distillation is an efficient method for the purification of bisphenols, aminophenols and diamines. Silylation may also activate functional groups for the condensation process or protect functionalities against undesired side reactions[17]. Silylated bis-phenols protect the oxygen containing monomers against electrophilic attack even above 300°C. However, some anions such as carbonate, chloride and in particular, fluoride may easily activate the siloxy group and generate phenoxide anions(Equation 8).

$$\mathrm{Ar{-}O{-}SiMe_3} + \mathrm{X^-} \longleftrightarrow \mathrm{Ar{-}O^-} + \mathrm{X{-}SiMe_3} \qquad (8)$$

The silylated bisphenols may react with various activated aromatic difluorides in bulk[24, 25] (Scheme 2.8). These polymerizations were successful only when



Scheme 2.8. Synthesis of poly(arylene ether)s via. silylated bisphenol route[24, 25]

potassium or cesium fluoride was used as a catalyst at temperatures in the range of 270-350°C. They produced aromatic polyethers with number average molecular weight up to 17,500 [24]. This silyl ether displacement route has three advantages. Firstly, no solvent is involved as the reaction medium. Secondly, the highly volatile fluorotrimethylsilane is the only by-product of the reaction and third, transetherification is minimized; Therefore, after the completion of polymerization, purification or separation of the resulting polyethers from inorganic salts is not required. The polymers synthesized in this manner may have controlled morphology and various random or block copolymers may be feasible. The main disadvantage is that these reaction conditions are limited to activated fluoro compounds. Activated chloro compounds, such as 4,4'-dichlorodiphenyl sulfone are not reactive enough. However, it has been reported by Kricheldorf that the activated dichloro-compound can be successfully polymerized in NMP and in the presence of equimolar amounts of K_2CO_3[19].

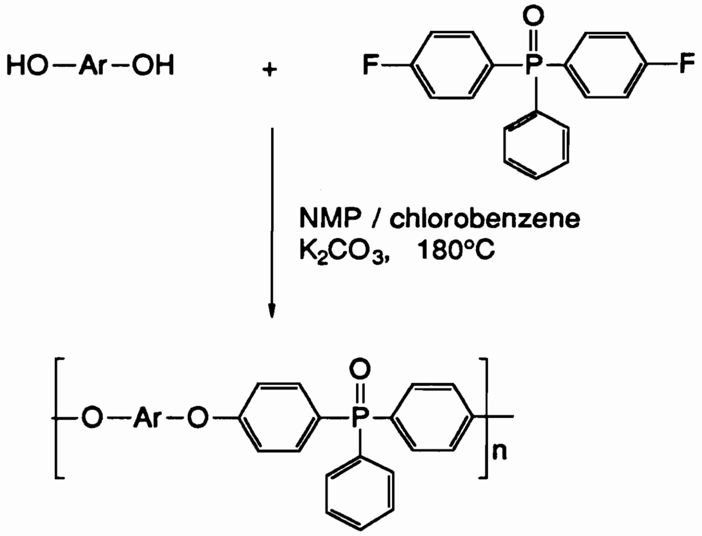
$$\mathrm{Ar{-}OSiMe_3} + \mathrm{Cs^{-}F^{+}} \longrightarrow \mathrm{Ar{-}O^{-}Cs^{+}} + \mathrm{F{-}SiMe_3}\uparrow \qquad (9)$$

$$\mathrm{Ar{-}O^{-}Cs^{+}} + \mathrm{F{-}Ar'} \longrightarrow \mathrm{Ar{-}O{-}Ar'} + \mathrm{CsF} \qquad (10)$$

In the mechanism of the silylated route, the fluoride anion converts the trimethyl siloxy group into a phenate salt, which then attacks the activated fluoro-compound to form an ether linkage. (Equation 9 & 10). A very low level of the catalyst is required for the reaction (ca. 0.1 wt%). Without the catalyst present, the reaction is inert even up to 350°C[25]. This route has been successfully employed to synthesize random copolymers[24, 25] as well as block copolymers[20, 25, 95, 96].

2.1.4 Poly(arylene ether)s with triaryl phosphine oxide groups

Phosphine oxide containing poly(arylene ether)s or PEPOs have attracted considerable attention in recent years. In general, homo-PEPOs are amorphous and they are potentially useful as flame retardant polymeric materials due to their high char yields at high temperatures[55, 97, 99]. Semicrystalline co-poly(arylene ether)s containing the phosphine oxide moiety can be synthesized [55]. It has been reported that the PEPO containing phenolphthalein or its derivatives exhibit higher Tg as well as higher moduli[100].



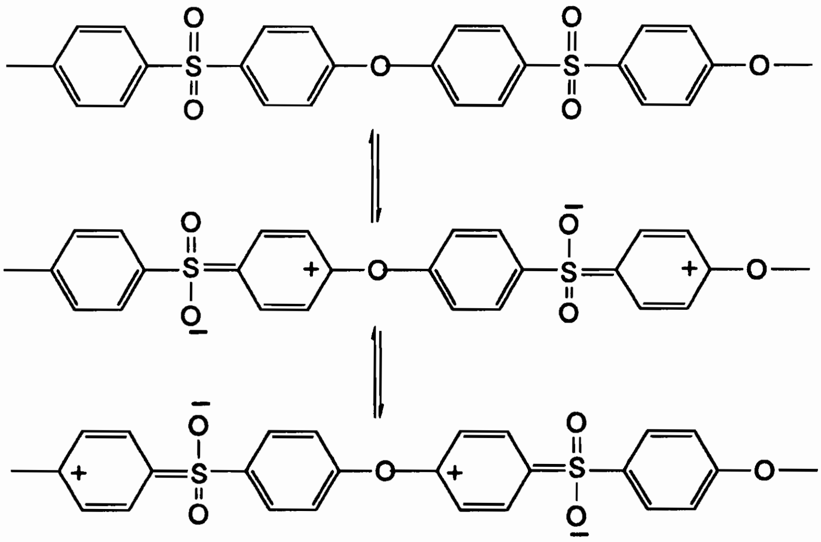
Scheme 2.9. Poly(arylene ether phosphine oxide) synthesis via nuclcophilic displacement [99]

Unlike PES and PAEK, PEPOs can only be prepared by nucleophilic polyetherification route(Scheme 2.9). There are no reported successful examples of PEPO synthesis via the electrophilic route. This is likely because the catalyst, commonly AlCl3, is known to complex with the phosphine oxide bond. Therefore, the system either gels or becomes non-reactive. In contrast, the phosphine oxide group activates the halide in the para position by virture of its electron withdrawing nature and allows polymerization to take place via nucleophilic substitution process[101]. The fluoro monomer was the preferred monomer for this reaction. The corresponding chloro monomer usually results in low molecular weight products, since it does not activate sufficiently as discussed earlier.

2.1.5 Properties of Poly(arylene ether)s

Poly(arylene ether)s PAEs can be either amorphous or semicrystalline as mentioned earlier. Both categories of PAEs may exhibit good mechanical, electrical and thermal properties. The semicrystaline PAEs such as PAEKs have good solvent resistance and long term stability. The closest competitive commercial thermoplastic in terms of solvent resistance is poly(phenylene sulfide), which is also a semicrystalline polymer[63]. The amorphous PAEs are usually soluble in chlorinated solvents such as dichloromethane and chloroform and in dipolar aprotic solvents such as NMP, DMSO and DMAc. The non-coplanar triaryl phosphine oxide group of PEPO polymers enhances the solubility in these solvents.

The glass transition temperature depends on both chain rigidity and polarity [102, 105]. For example, the sulfone group has high polarity and large electronegativity and consequently the electron withdrawing ability of the sulfone group delocalizes the π electrons from the aromatic rings. The neighboring links can develop some double bond character (Scheme 2.10). Such a delocalization considerably enhances the rotation barrier around the C-S linkage and consequently increases chain rigidity. The ketone groups have the same effect analogous to the sulfone linkage. However, because of the lower polarity (or electron withdrawing ability) of the ketone group, this effect is much smaller than in the sulfone. Thus, PAEK exhibits a lower Tg than PES in general and this can be seen by comparing Table 2.1 and Table 2.2. From these two tables, the influence of the ether linkage as a flexible unit on the Tg can also be seen. As the concentration of the ether linkage increases, the chain rigidity decreases so, the Tg decreases. On the other hand, both the ketone and sulfone group are polar and rigid groups; therefore, the Tg increases as their concentration increases. By using the rigidity and polarity concept, the Tg as well as the Tm of PAEK and PES can be predicted accurately [102].



Scheme 2.10. Electron-withdrawing effect in PES [102]

Toughness or the impact strength is an important characteristic property of PAEs. One of the most important factors in determining the toughness of a polymer is the structural symmetry of the polymer chains[103]. Toughness is reduced as the symmetry of the polymer chain is disrupted. The symmetric nature also influences the Tg, which is a transition associated with intermolecular barriers to motion and the inherent stiffness of an isolated chain [104]. Increasing rigidity of the polymer chain, increases the Tg[105]. For example, symmetric substitution of methyl groups on the phenyl rings of polysulfone (or polycarbonate) increases the barrier of the phenyl ring to rotate and raises the Tg of the polymers[36, 106]. Polymers with an unsymmetric

Table 2.1 Thermal transition of poly(arylene ether sulfones)s[102]

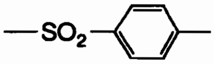
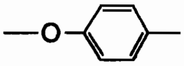
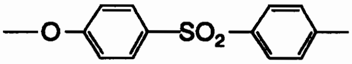
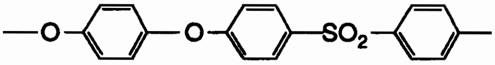
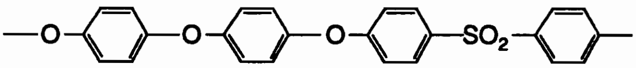
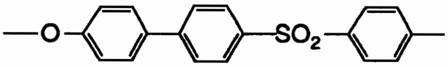
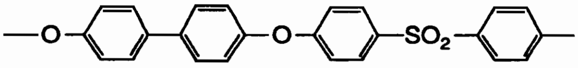
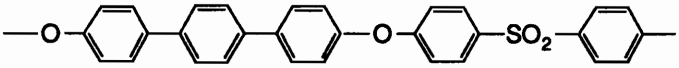
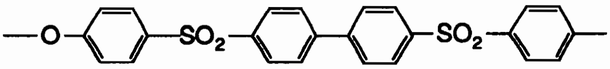
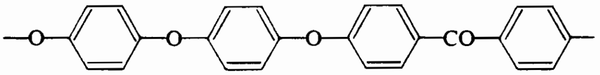
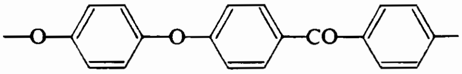
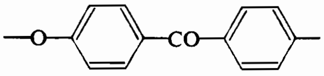
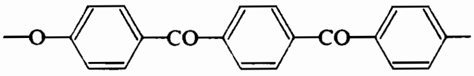
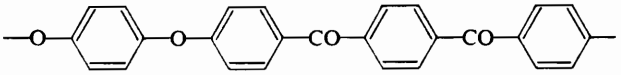
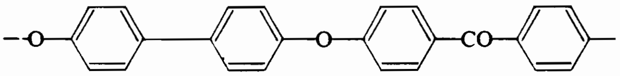
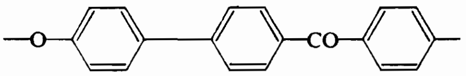
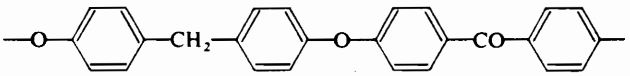
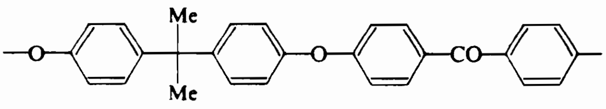
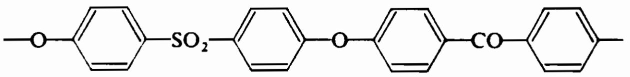
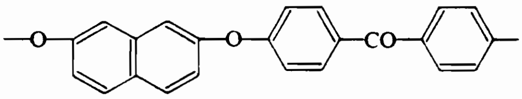
Structure	Tg (°C)	Tm (°C)
	350	>520, >580
	110	285
	223-230	—
	217	—
	180	—
	265	—
	232	—
	251	389
	280-290	395

Table 2.2 Thermal transition of poly(arylene ether ketone)s[5]

Structure	T_g (°C)	T_m (°C)	*Ref.*
	129	324	a
	144	335	b
	154	367	b
	165	391	a
	150	365	c
	167	416	b
	210	440	d
	123	f	e
	155	f	e
	181	f	e
	155	f	e

[a] J. E. Harris and L. M. Robeson, *J. Polym. Sci., Polym. Phys. Ed.*, 1987, **25**, 311.
[b] T. E. Attwood, P. C. Dawson, J. L. Freeman, L. R. J. Hoy, J. B. Rose and P. A. Staniland, *Polym. J.*, 1981, **22**, 1096.
[c] K. J. Dahl and V. Jansons (Raychem Corp.), *US Pat.* 3 956 240 (1976) (*Chem. Abstr.*, 1976, **85**, 63 655).
[d] K. J. Dahl (Raychem Corp.), *Br. Pat.* 1 383 393 (1975) (*Chem. Abstr.*, 1973, **78**, 98 766).
[e] Author's unpublished results.
[f] Does not crystallize on cooling at 20 °C min^{-1} from the melt.

nature have more densely packed chains, less free volume and suppressed Tgs[106]. This is in contrast with aliphatic carbon chain polymers,(eg. vinyl versus vinylidene) for which the unsymmetrical polymers usually have a higher Tg[107].

A variety of techniques have been employed to study the origin of the toughness caused by molecular motions. These techniques include dielectric relaxation[108], nuclear magnetic resonance spectroscopy[109, 110] and dynamic mechanical analysis[104, 106, 111, 112]. Though some different explanations may be proposed, it appears that the phenylene motions are the primary origin of the sub-Tg relaxation, (also called as secondary relaxation or ß-relaxation) which is directly related to the toughness of the polymers. The phenylene motions under 180° or π flips can be detected by Deuterium NMR techniques [109, 113]. Some other theories may include intermolecular as well as intramolecular factors to explain the origin of the secondary relaxation [106]

2.1.6 Molecular weight control and functionalization of poly(arylene ether)s

The molecular weight of step-growth polycondensation polymers can be controlled by two methods. Firstly, off-set the 1:1 stoichiometry of the functionality by adding one monomer with calculated amount more (or less) than another monomer may be employed. Secondly, addition of a stoichiometric amount of a monofunctional monomer or functionalized monomer to control the molecular weight, as well as the chain end can be utilized. Both methods are illustrated in appendix I & II (I for AA/BB monomer systems and II for AB monomer system).

PAE can be synthesized with controlled functionality and molecular weight. Several different functionalized PAEs have been reported, which include carboxyl[114-117], amine[118, 119] and hydroxyl[120] chain ends. The carboxyl terminated PES may further copolymerize with other monomers to make segmented PAE/polyarylate[114-

116] or PES/nylon 6 copolymers[117]. The amine chain ends may also be derivatized to maleimide[120].

2.2 Polyamides

Polyamides contain the amide group, –NH-CO–, in the main chain. Commercial products are frequently referred to as nylons, which is now a generic name. Nylons were perhaps the first materials to be recognized as an engineering thermoplastics. The two different types of nylons are pragmatically named according to the number of carbon atoms in the main chain. Thus, nylon 6 or polyamide 6 is poly(ε-caprolactam), which can either be prepared from amino acid by a self-condensation reaction or from cyclic lactams. The second series of nylons have two numbers; the first number refers to the number of carbon atoms in diamine component and the second number refers to the carbon atoms in the dicarboxylic acid moiety. Therefore, nylon 6,6 is poly(hexamethylene adipamide). Letters are often used to designate cyclic units, eg. T for the terephthalic acid moiety. Many review articles have been written on polyamides and their synthesis[122-131].

The commercially important routes to polyamide synthesis include melt step polycondensation, ring-opening polymerization and low temperature solution polymerization (important for aromatic "aramide" systems). For the nylon series, the nylon 6 and nylon 6,6 are the most important polyamides and both represent a part in this thesis. Therefore, the synthesis methods and the properties of these two nylons will be briefly reviewed.

2.2.1 Principles of polyamidation

An amide linkage is formed by the condensation of an amine with a carboxylic acid to form an amide bond and water(Equation 11). This equilibrium nature of the polyamidation has been thoroughly investigated [129,132,133].

$$\text{—COOH} + \text{H}_2\text{N—} \longleftrightarrow \text{—CONH—} + \text{H}_2\text{O} \qquad (11)$$

$$\frac{[\text{—CONH—}]\,[\text{H}_2\text{O}]}{[\text{—COOH}]\,[\text{—NH}_2]} = K = B \exp \frac{-\Delta Ha}{RT} \qquad (12)$$

Here B is the temperature independent constant and ΔHa is the enthalpy change of the reaction(Equation 12). This polyamidation is an exothermic reaction. The reported values of ΔHa are around –25~ –29 kJ/mol[129,130,132]. This means that a decrease in temperature shifts the equilibrium to higher molecular weights at constant water concentration[125,130]. The equilibrium constant K has been found to be dependent on the water concentration[131]. However, it is also found that at high water content, K seems to be independent of water concentration[135](Figure 2.1). When steric effects are present, such as some lactam ring structures, the equilibrium constant, K, can be changed[124,129].

Amide-interchange is a side reaction of polyamidation reaction and its equilibrium value is usually not important. However, for a ring-opening polymerization under the hydrolytic process, the equilibrium value determines the content of the cyclic monomer, which is ~8% for nylon 6 at 250°C and even higher for some other lactam polymers[130]. In the later sections, the process for nylon 6 synthesis will be discussed

2.2.1.1 Polymerization of nylon 6,6

Nylon 6,6 can be produced by either batch or continuous processes. The necessary functional group equivalence required for the polycondensation is achieved by first producing the salt from the 1,6-hexamethylene diamine and adipic acid. The formed

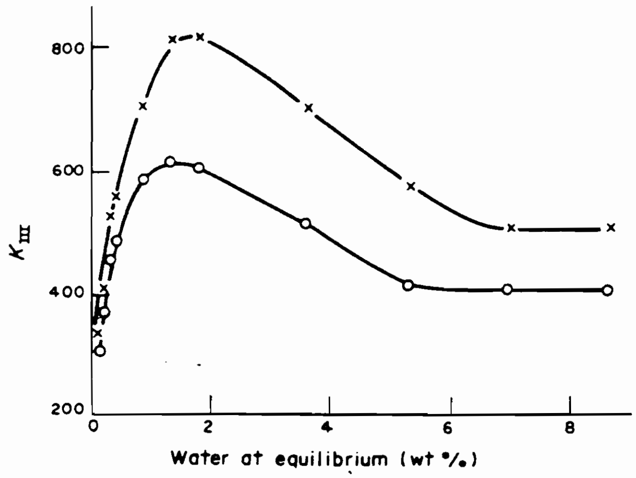


Figure 2.1 Equilibrium constants K vs. equilibrium water content (x) 240°C, (o) 260°C[130, 135]

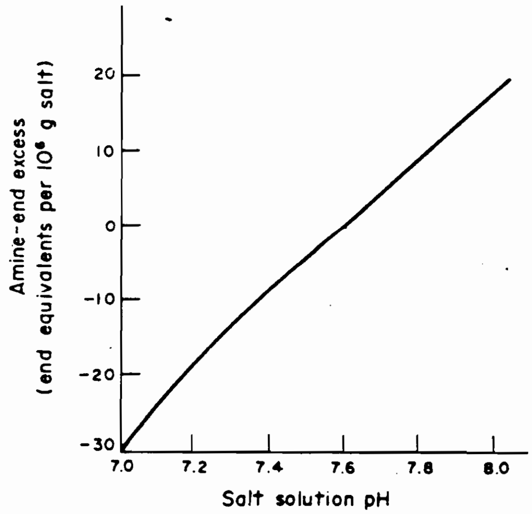
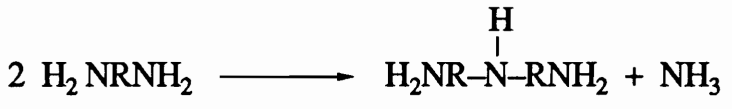


Figure 2.2 Relation of free amine group concentration vs. pH of nylon 6,6 salt in aqueous solution[130, 137]

nylon 6,6 salt is stoichiometrically equivalent in functionality of both monomers. If the salt is not isolated, the stoichiometric balance can be controlled by adjusting the pH of an aqueous solution of the reaction by addition of one or another of the two reactants. The reported pH value for the exact stoichiometric balance of the two reactants is about 7.6[125]. The change in end-group balance to pH unit is about 4/0.1(end group change/pH change). The end group vs. pH change relationship is shown in Figure 2.2[130,137]. Since the salt has very low solubility in methanol or ethanol(eg. in methanol it is only 0.4% at 25 °C[125]), the salt prepared in these solvents can be easily separated and purified at the same time(excess monomers as well as impurities stay in the solution) However, the salt can also be recrystallized in water/alcohol solution and the pure salt has a melting point of 195°C.

Nylon 6,6 is mainly produced by a batch method. The polymerization is conducted by heating an aqueous slurry of approximately 60-80% of the salt, at above 200-210°C. During the polymerization, pressure is maintained at 1.4-1.8 MPa(or 250 psi) and the temperature is raised to 250-275°C. Pressure is employed to exclude oxygen, to prevent the volatile diamine from evaporating[136] and to keep water in the system, so that the mass remains in liquid state below its melting temperature[130]. The high water concentration limits molecular weight, so that only prepolymers are produced. At the second stage of the polymerization, the pressure is slowly reduced to atmospheric pressure over 1-1.5 hours, then under an inert gas purge or reduced pressure, the reaction is completed in about an hour.

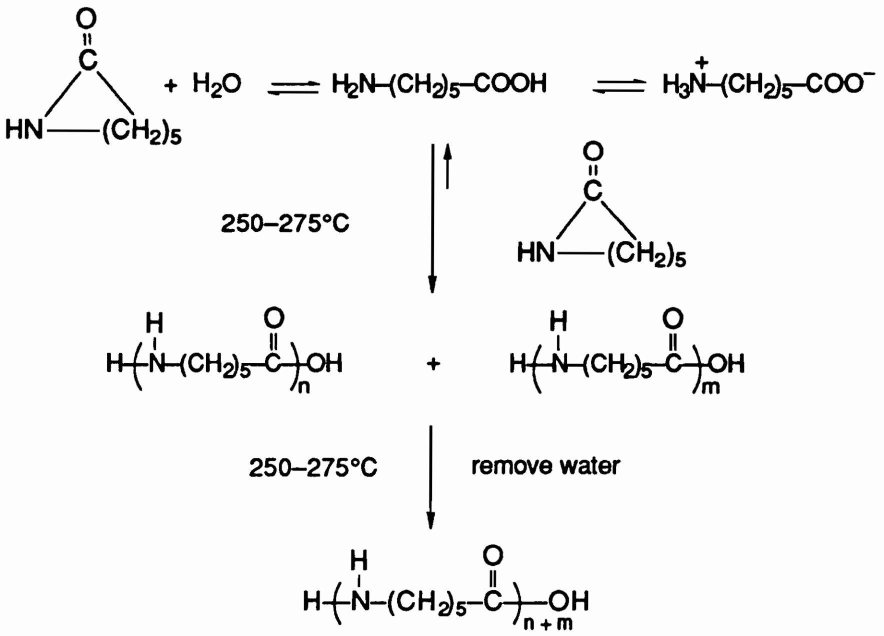


$$2\ H_2NRNH_2 \longrightarrow H_2NR\text{–}\overset{H}{\overset{|}{N}}\text{–}RNH_2 + NH_3 \qquad (13)$$

It has been reported that the nylon 6,6 is susceptible to gelation at high temperature and reduced pressure in a long reaction process. The gelation may be a result of the reaction of diamine produce a triamine(equation 13)[137]. Therefore, high temperatures and long reaction times should be avoided. At the end of the second stage, the system is pressured by an inert gas and the polymer is extruded out of the reactor. For high molecular weight nylons, a solid state polymerization process can be employed after the batch autoclave processes[138]. In the second half of this dissertation(Part B section 2.5), solid-state polymerization will be discussed more thoroughly.

2.2.1.2 Polymerization of Nylon 6

Nylon 6 can be synthesized by either a hydrolytic ring-opening polymerization or an anionic ring-opening route. The ring-opening polymerization of ε–caprolactam is favored from thermodynamic considerations[124]. However, because of the equilibrium between the cyclic monomer and the polymer, the residual monomer in the hydrolytic process is about 8-9% (and 1-2% cyclic oligomers at 250°C), and about 2% monomer is left in the anionic process[124,125].

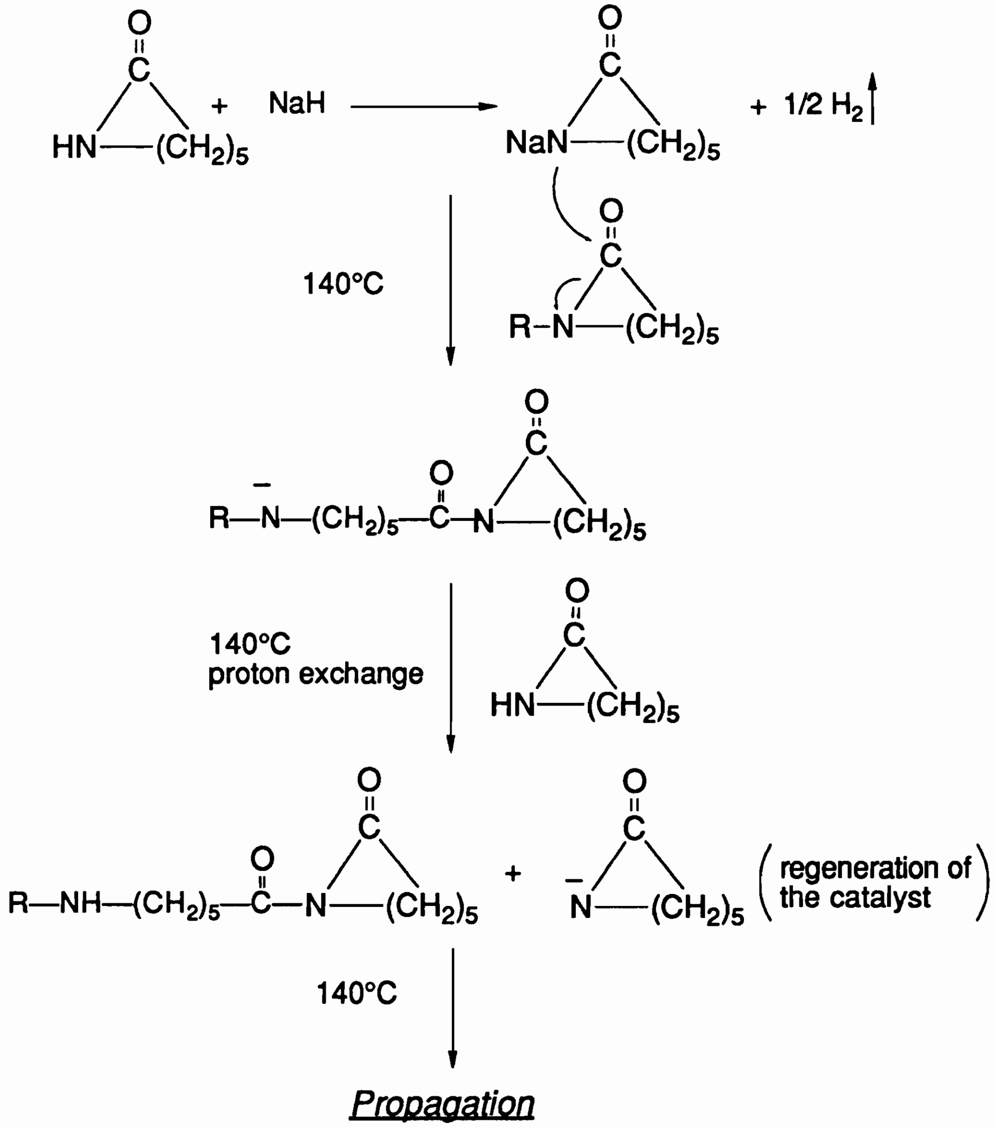


Scheme 2.11. Hydrolytic polymerization of ε–caprolactam[124]

Hydrolytic polymerization of ε–caprolactam can also be conducted in both batch and continuous processes by heating the monomer in the presence of 5-10% of water at 250-270°C. The overall processes are outlined in Scheme 2.11. Dry ε–caprolactam will not polymerize[139]. With water present, a small amount of the ε–caprolactam is hydrolyzed to the corresponding amino acid under the reaction conditions. The generated amino acid facilitates the polymerization of the lactam. This ring-opening polymerization reaction is about one order of magnitude faster than the polymerization of the corresponding ε–aminocaproic acid. In the second stage, water is removed by reduced pressure and the conversion reaches about 90%. The extractable contents can be removed by hot water extraction.

Anionic ring-opening polymerization of ε–caprolactam is a very fast reaction and it is used industrially to fabricate molded objects. This technique is called reaction injection molding (RIM) of nylon 6[140]. The anionic polymerization is catalyzed by alkali metals or metal hydrides such as sodium hydride and the lactam anion is formed *in situ*. The lactam anion may be considered to be a catalyst, which attacks the initiator, which is generally a lactam derivative with electron attracting substitutents on the N atom. The use of an initiator allows the polymerization to take place at temperatures as low as 140°C[124]. This low temperature process has advantages in terms of low residual monomer concentration and fewer side reaction(Scheme 2.12).

The equilibration of monomer and oligomer contents in the anionic and hydrolytic processes are identical at the same reaction temperature. However, when polymers are prepared at temperatures lower than the melting temperature(ca. 220°C for nylon 6), the monomer content is favored to be much lower than would be expected from extrapolation of the monomer content vs. temperature relationship(Figure 2.3). From Figure 2.3, it is clear that the monomer of the anionic polymerization is excluded from the crystalline



Where : R = CH_3CO-, R'–NHCO–, or other electron withdrawing groups

Scheme 2.12 Anionic initiated polymerization of ε-caprolactam[124]

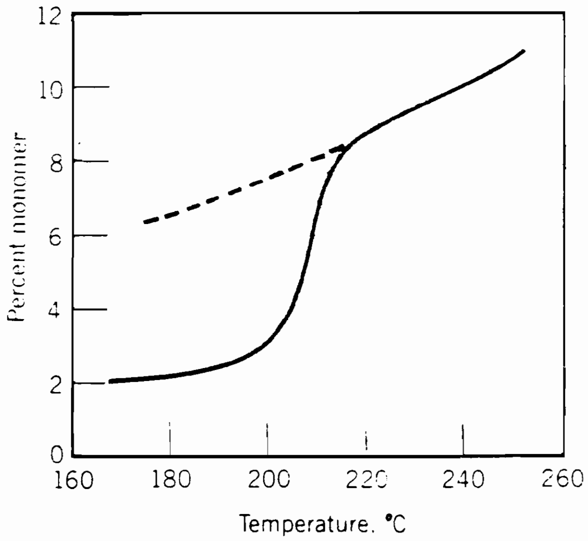
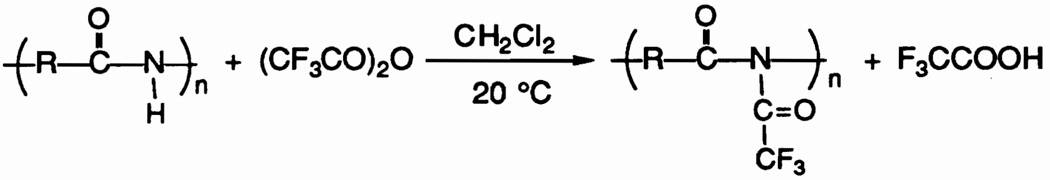


Figure 2.3 Dependence of the equilibrium of caprolactam on temperature for polycaprolactam (The dash line is the percent monomer on the basis of fully amorphous phase)[125]

regions of the polymer[125]. This is similar to the end groups in solid-state polymerization. The low content of the monomer in the polymer is crucial for this type of process to yield high performance products. The monomer remaining in the polymer can act as a plasticizer and it may also deteriorate the properties or the stability of the polymers.

2.2.2 Characteristics of Nylon 6 and Nylon 6,6

Both nylon 6 and nylon 6,6 are semicrystalline polymers. They are soluble in strong acid such as mineral acids, formic acid, m-cresol and phenols at ambient temperature[122,125]. Intrinsic viscosity measurement is usually conducted in formic acid or m-cresol. Although gel permeation chromatography(GPC) can be used to study the molecular weight of polyamides in m-cresol at 100°C[141], another elegant method developed by Schulz et al in 1980 of great interest[142]. This analysis method has further proved applicable for polyureas, as well as for polyamides[143] and it can be extended to polyurethane[142]. In this technique, polyamides are derivatized via an N-trifluoroacetylation reaction. Through this N-trifluoroacetylation reaction, the H-bond is disrupted(Equation 13) and the resulting analogous polyamide can be easily dissolved and analyzed in common GPC suitable solvents such as CH_2Cl_2, $CHCl_3$, THF, 1,4-dioxane, acetone and DMAc.



$$\left(R-\overset{\overset{O}{\|}}{C}-\underset{H}{\underset{|}{N}} \right)_n + (CF_3CO)_2O \xrightarrow[20\ ^\circ C]{CH_2Cl_2} \left(R-\overset{\overset{O}{\|}}{C}-\underset{\underset{CF_3}{|}}{\underset{C=O}{\underset{|}{N}}} \right)_n + F_3CCOOH \qquad (13)$$

Polyamides usually exhibit fast crystallization rates(Table 2.3), which are facilitated by the essentially linear character of the polymer chain, H-bonds and symmetrical structures. Crystallinity allows for polyamides of increased tensile strength, flexural modulus, creep resistance and hardness, accompanied by some loss in elongation and impact resistance. Although high crystallinity (~80%) has been reported under laboratory conditions(131), the maximum crystallinity of nylon 6 and nylon 6,6 under practical molding condition is around 40-60%[122,125]. Wide angle x-ray scattering (WAXS) has been an important tool in assessing the degree of crystallinity, although it is not the best quantitative method, and in determining the crystal lattice of polymers. Both nylon 6,6 and nylon 6 are known to exhibit polymorphism. Nylon 6,6 has both α and β crystal forms[145-147]; and nylon 6 exhibits α, β and γ crystal forms, depending on processing[145]. Only the α and γ crystal forms of nylon 6 are the reported stable crystal forms[125]. Figure 2.4 and Figure 2.5 show the crystal structures for nylon 6[148] and nylon 6,6[125].

Table 2.3 Linear crystallization rates of various polymers from the melt (30°C below Tm)[144]

Polymer	Crystallization rate in μm/min
Poly(ethylene)	5000
Poly(hexamethylene adipamide)	1200
Poly(oxymethylene)	400
Poly(caprolactam)	150
Poly(trifluorochloroethylene)	30
it-Poly(propylene)	20
Poly(ethylene terephthalate)	10
it-Poly(styrene)	0.25
Poly(vinyl chloride)	0.01

For nylon 6, both α and γ crystal forms are monoclinic structures[125,148]. The α form consists of fully extended antiparallel chains and the γ form has hydrogen bonds

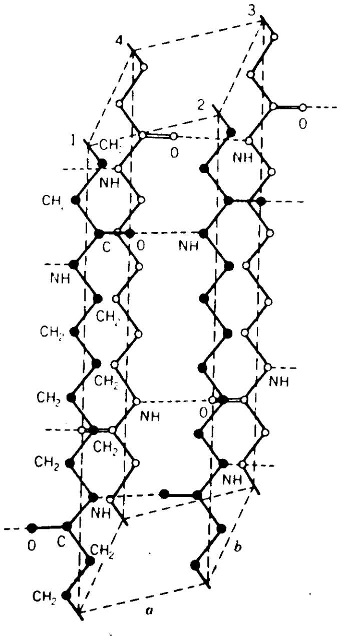


Figure 2.4 Unit cell of nylon 6,6 (α-form) [125]

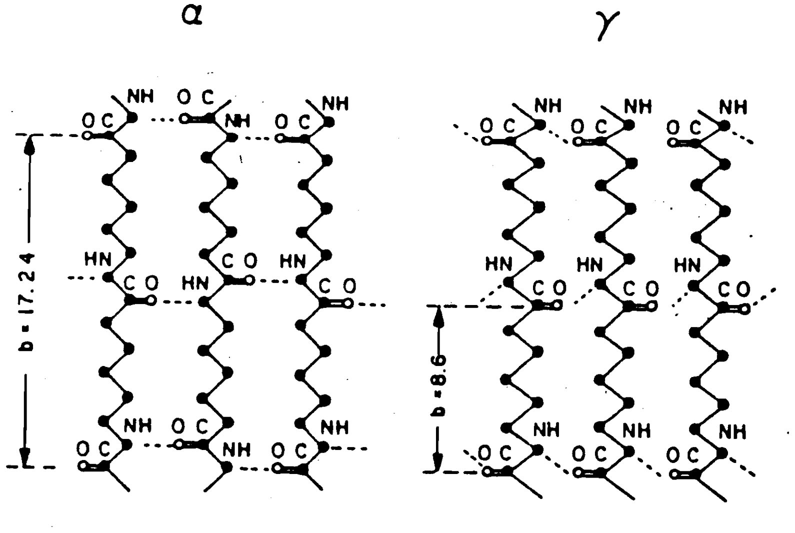


Figure 2.5 Crystallographic unit cells of the α & γ-forms of nylon 6[148]

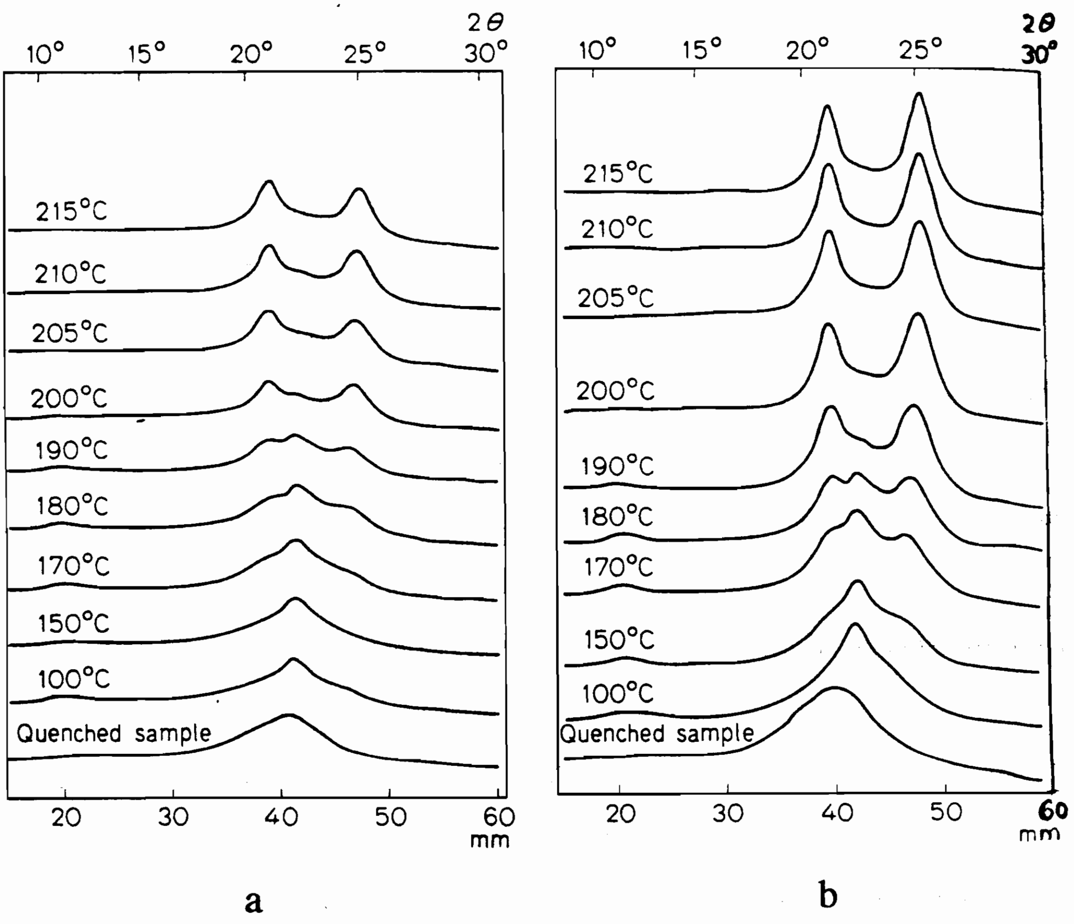


Figure 2.6 Annealing of quench cooled nylon 6 samples a). Renyl MV® (anneal 1 hr.) b). BBV®(anneal 24 hrs.) [152]

between parallel chains[148,149]. The γ form has a shorter c-axis, and it is observed in spun-drawn fibers, particularly at high spinning speeds[150] or fibers drawn without lag time[151]. It can also be obtained by treating yarns in KI-I_2 solution[151] or by quenching from the melt[152]. Nylon 6 fibers drawn in warm and humid condition or annealed result in the α form, which is more stable than the γ form. Upon annealing, the γ form partially (or totally) transforms to the α form[149-153].(Figure 2.6)

All nylons absorb moisture from their immediate environment, eventually reaching a level that is in equilibrium with the relative humidity of the atmosphere. Moisture has a plasticizing effect on nylons that decreases Tg, increases flexibility and impact resistance[131]. The rate of moisture absorption depends on temperature, crystallinity, humidity and thickness.

3 EXPERIMENTAL

3.1 Purification of Solvents

Pure solvents for polymerization reactions obtained by distillation prior to use. Some high boiling point solvents such as NMP, DMAc and DMSO, were distilled under reduced pressure, using either a water aspirator or a rotatory vacuum pump.

Dimethylsulfoxide (DMSO) : DMSO (bp 190°C) was distilled over calcium hydride under reduced pressure (bp 76°C / 12 mmHg) and stored in a septum sealed flask purged with nitrogen

N-methyl-2-pyrrolidone (NMP) : NMP (bp 202°C decomposition) was distilled under reduced pressure (bp 81°C / 10 mmHg) and then stored under nitrogen

N, N-dimethylacetamide (DMAc) : DMAc (bp 160°C) was also distilled over calcium hydride under reduced pressure (bp 58°C / 11.4 mmHg).

Chlorobenzene : Chlorobenzene (bp 132°C) was distilled over calcium hydride and stored under nitrogen.

o-Chlorobenzene : o-Chlorobenzene (bp 180°C) was distilled over calcium hydride and stored under nitrogen.

Diphenylsulfone (DPS) : DPS (bp 379°C) was purified by recrystallization from acetone. Active charcoal was used to decolorize the solution and colorless crystals were recovered.

3.1.2 Monomers

2,2'-Bis(4-hydroxyphenyl)propane (Bisphenol A or Bis A): Bis A (Mp 155°C, MW 228.27g/mol) was obtained as monomer grade material from DOW Chemical. It was used without purification.

4,4'-Difluorobenzophenone (DFBP): DFBP (Mp 105°C, MW 218.20) was provided as monomer grade material from ICI and used as received.

4,4'-Dichlorodiphenyl sulfone (DCDPS): DCDPS (Mp 147°C, MW 287.16) was provided as monomer grade material from Amoco and used as received.

4,4'-Difluorodiphenyl sulfone (DFDPS): DFDPS (Mp 98°C, MW 254.25) was purchased from Aldrich and used as received.

Bis(4-fluorophenyl)phenyl phosphine oxide (BFPPO): BFPPO was synthesized and purified in our laboratory [97]. (Mp 124-126°C MW 314.27)

3-Hydroxybenzoic acid: 3-Hydroxybenzoic acid was purchased from Aldrich and was purified by converting it to disodium salt using aqueous sodium hydroxide. The solution was then acidified with HCl to regenerate the monomer (Mp 202°C, MW 138.12)

1,3 & 1,4-Bis(4-fluorobenzoyl)benzene (BFBB): BFBB was provide as monomer grade material from BASF and was used as received(MW 322.31).

ε-Caprolactam: High purity monomer grade 99+% of ε-caprolactam was purchased from Aldrich. It was used without purification.(Mp 70-72°C, MW 113.16)

Adipic acid: High purity monomer grade 99+% of adipic acid was obtained from DuPont. It was used without purification.(Mp 152-154°C, MW 146.14)

Hexamethylene diamine (HMDA): HMDA was obtained from DuPont. It was used without purification.(Mp 42-45°C, Bp 204-205°C, MW 116.21)

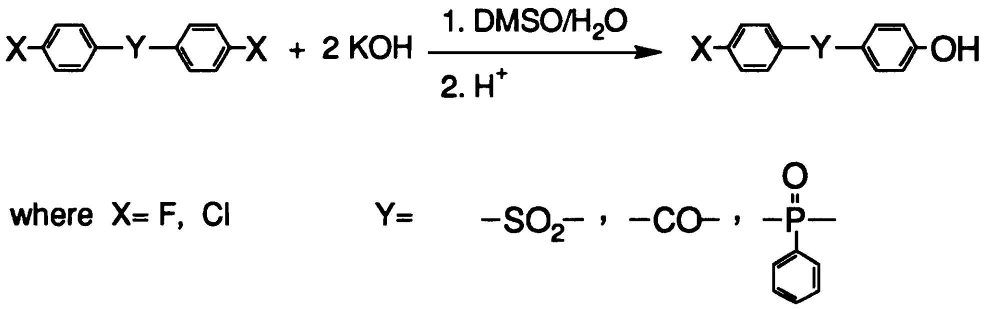
Nylon 6,6 salts: Nylon 6,6 salts were prepared from adipic acid and HMDA in ethanol. The resulting product was recrystallized in H_2O/EtOH mixture. The pH value of the salt in water was 7.5(lit. 7.6). (Mp ~195°C)

1,1,1,3,3,3-Hexamethyldisilazane(HMDS): HMDS was purchased from Aldrich. It was distilled before use.(Bp 125°C, FW 161.4)

3.2 Synthesis of Monomers

3.2.1 AB Type Halogenophenols

Four halogenophenols were prepared by partial hydrolysis of the corresponding activated dihalides. The electron withdrawing groups on the dihalides included sulfone, ketone and phenylphosphine oxide.



Scheme 3.1 Synthesis of Halogenophenols

3.2.1.1 4-Fluoro-4'-Hydroxydiphenyl Sulfone (FHDPS)

4,4'-Difluorodiphenyl sulfone (DFDPS) (83.5g, 328.4 mmole) was charged into a stainless steel vessel fitted with an efficient stirrer made of stainless steel. DMSO (80ml) was added into the vessel under nitrogen and the reaction vessel was heated by a oil bath at 60°C. After DFDPS was completely dissolved in the DMSO, aqueous KOH solution (36.8g or 655.9 mmol in 25ml of water) was added into the vessel. The reaction solution changed from clear to turbid and was allowed to reach completion under the described conditions in 24 hours. The reaction mixture was then cooled and poured into ice water, filtered to remove unreacted DFDPS and slowly acidified with concentrated hydrochloric acid to a pH~5. A white precipitate was formed immediately upon acidification which was filtered, washed with water and dried. The yield of the product, FHDPS, was about

63g (87~90%). The FHDPS was purified by recrystallization from a mixture of ethanol/water which first produced an oily layer and later crystallized on standing. Another way to purify the FHDPS was to dissolve the crude product into aqueous KOH, treat with active charcoal at 0°C and then, acidify again. The yield of FHDPS after purification was about 85%. The melting point of FHDPS was 152-153°C (lit. 155°C)[54].

3.2.1.2 4-Chloro-4'-Hydroxydiphenyl Sulfone (CHDPS)

CHDPS was prepared by the same method described for the FHDPS preparation. Thus, 4,4'-dichlorodiphenyl sulfone (DCDPS) (71.8g, 250 mmole), 50% aqueous KOH (28.05g, 0.5 mole) and DMSO (80ml) were charged into a stainless steel vessel, which was equipped with a mechanical stirrer and nitrogen inlet. The vessel was heated to 110°C (**oil bath temperature**) for 24 hour. Then the reaction mixture was cooled, poured into ice water, filtered, acidified, washed with water, dissolved into aqueous KOH, treated with active charcoal and then acidified again. A very pure product was obtained. The yields of CHDPS is about 56g (82%) and its melting point is 149-150°C (lit. 150°C).

3.2.1.3 4-Fluoro-4'-Hydroxybenzophenone (FHBP)

FHBP was also prepared by the similar method as described for the FHDPS preparation. 4,4'-Difluorobenzophenone (DFBP) (50g, 229.1 mmole) and DMSO (50ml) were heated to 75°C (**oil bath temperature**) under nitrogen. Then, aqueous KOH (25.15g, 448 mmole) was added into this clear solution, which turned to light yellow right after the addition. The temperature of the oil bath was raised to 95°C for 24 hours. After the reaction was completed and cooled, the solution was poured into ice water, and the filtered, clear light yellow solution was acidified by using concentrated HCl to afford a pale yellow to white product (FHBP). The yield of FHBP was 37g (~76%). As with the other monomers, FHBP was dissolved into an aqueous KOH solution followed by active charcoal. It was then filtered, acidified and collected. The melting point of FHBP was 166~167°C.

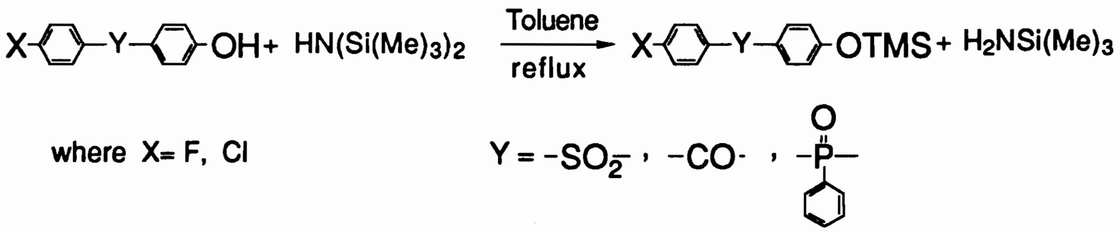
3.2.1.4 4-Fluorophenyl-4'-Hydroxyphenyl Phenyl Phosphine Oxide (FHPPO)

Again, this AB type halogenophenol was prepared by partial hydrolysis of the corresponding active dihalide. For example, bis(4-fluorophenyl) phenyl phosphine oxide (BFPPO) (30g, 95.5 mmole) was dissolved into DMSO(55ml) and heated to 70°C (oil bath temperature). Aqueous KOH (10.5g KOH in 9 ml H_2O) was added and stirred for 24 hours. At the end of the reaction, the reaction solution was treated by the same method as discussed previously. The yield of the FHPPO was 20g (~68% yield). FHPPO can be crystallized in EtOH/H_2O mixture at a very slow rate.

3.2.2 Silylation of Halogenophenols

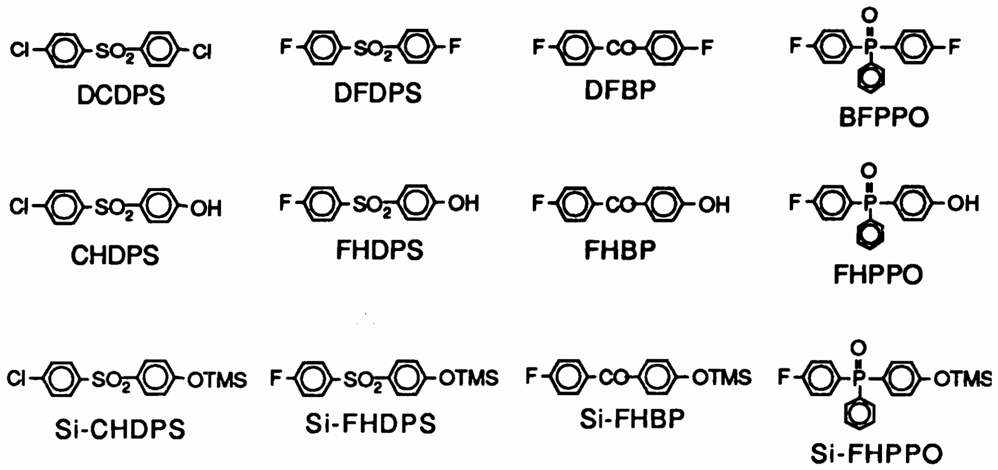
The four halogenophenols obtained (FHDPS, CHDPS, FHBP and FHPPO) were silylated by using the same reaction condition. The silylated products are as follows:

4-fluoro-4'-trimethyl siloxy diphenyl sulfone (Si-FHDPS)
4-chloro-4'-trimethyl siloxy diphenyl sulfone (Si-CHDPS)
4-fluoro-4'-trimethyl siloxy benzophenone (Si-FHBP)
4-fluorophenyl-4'-trimethylsiloxy phenyl phenyl phosphine oxide (Si-FHPPO)



Scheme 3.2 Silylation of Halogenophenols

For example, FHBP (10g, 46.3 mmole) was refluxed in 1,1,1,3,3,3-hexamethyldisilazane (HMDS) and toluene mixture at the volume ratio of 10ml/30ml for 24 hours. Initially, the FHDPS was not soluble in the solution but a clear solution was obtained upon heating. At the end of the silylation reaction, the toluene and excess HMDS were removed by using a rota-vap (or by distillation). The resulting products were liquids at room temperature.(Scheme 3.2) Both silylated FHDPS and FHBP (ie. Si-FHDPS and Si-FHBP see Scheme 3.3) were be purified by vacuum distillation. The distillation conditions for Si-FHDPS was 210-220°C at 150-200 mtorr and for Si-FHBP was 180-190°C at 160-180 mtorr. Freshly distilled silylated products are colorless; however, upon standing for a two days, the Si-FHBP turns very light yellow color.

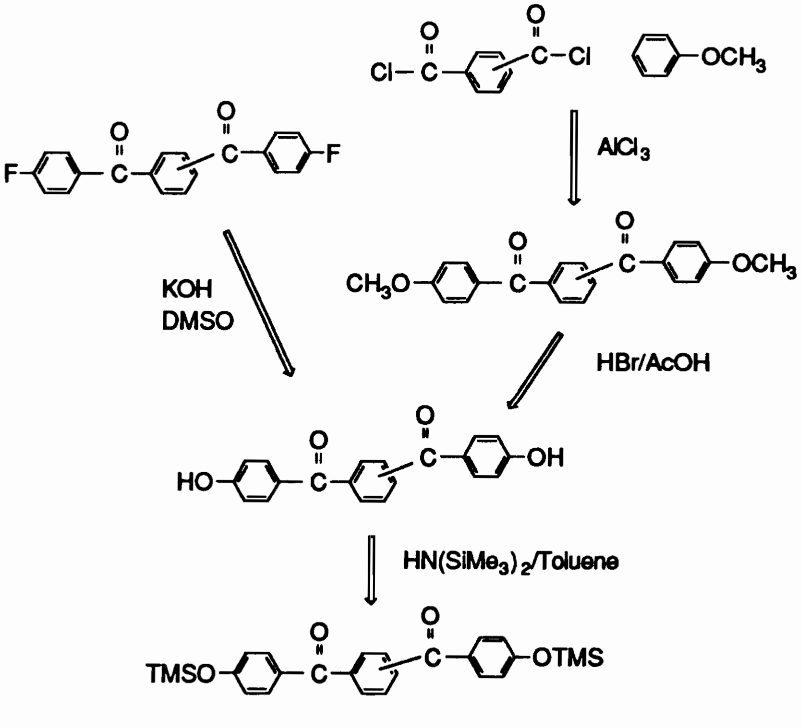


Scheme 3.3 Monomer acronyms

Silylated CHDPS and FHPPO, in contrast to the previous two monomers are very difficult to purify by distillation due to their higher boiling points.

3.2.3 1,3 & 1,4-Bis(4-hydroxybenzoyl)Benzene (BHBB) and 1,3 & 1,4-Bis(4-trimethylsiloxybenzoyl)Benzene (Si-BHBB)

1,3 & 1,4-Bis(4-fluorobenzoyl)benzene (BFBB) (30g, 93 mmole), KOH (24g, 428 mmole), water(200ml) and DMSO (100ml) were refluxed in a stainless steel vessel under nitrogen for 30 hours. The temperature of the heterogeneous reaction mixture was about 110°C. Upon completion of the reaction, the color of the solution changed to light yellow. At the end of the reaction, the mixture was cooled to room temperature and



Scheme 3.4 Synthesis of 1,3 & 1,4-Bis(4-hydroxybenzoyl)benzene and their silylated derivatives

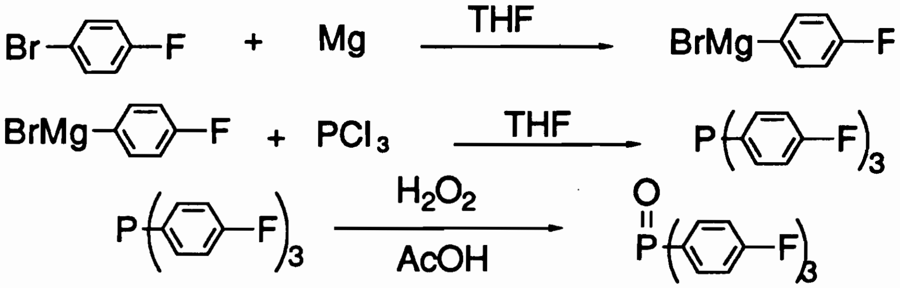
treated by the similar processes as for the halogenophenols. The products were light yellow in color and the yields were 60% and 78% for 1,3 & 1,4-BHBB respectively (Scheme 3.4).

Since monomer grade 1,3 & 1,4-BFBB were available, the bis(4-hydroxybenzoyl) benzene (BHBB) were directly prepared from BFBB. In an alternative route to prepare BHBB, terephthaloyl chloride (or isophthaloyl chloride) (10g, 49.2 mmole) was reacted with anisole(50ml), which is a reactant as well as a solvent(Scheme 3.4). During the course of the reaction $AlCl_3$ (14g, 105 mmole) was added in 3 aliquots over 1 hour. The temperature of the reaction was maintained at 100-110°C for 8 hours. At the end of reaction, the solution mixture was poured into ice water. Chloroform was used to extract the organic layer, which was then washed twice with aqueous K_2CO_3 and the chloroform was removed under reduced pressure. The yield of the product, bis(4-methoxybenzoyl)benzene, was usually around 70%. Cleavage of the methyl group was done in hydrobromic acid (48%, 15ml) and acetic acid (50ml) mixture. About 8.8g (86%) of BHBB was obtained from 11g bis(4-methoxybenzoyl)benzene.

BHBB was silylated in refluxing HMDS/toluene mixture for 24 hours. The excess HMDS and toluene were removed under reduced pressure. The silylated materials were purified by sublimation(180°C, 150 mtorr). At room temperature, the 1,3-bis(4-trimethylsiloxybenzoyl)benzene (Si-BHBB) is a viscous liquid and 1,4-Si-BHBB is a pale-yellow to white solid with a melting point at 126-127°C.

3.2.4 Tris(4-fluorophenyl)Phosphine Oxide (TFPPO)

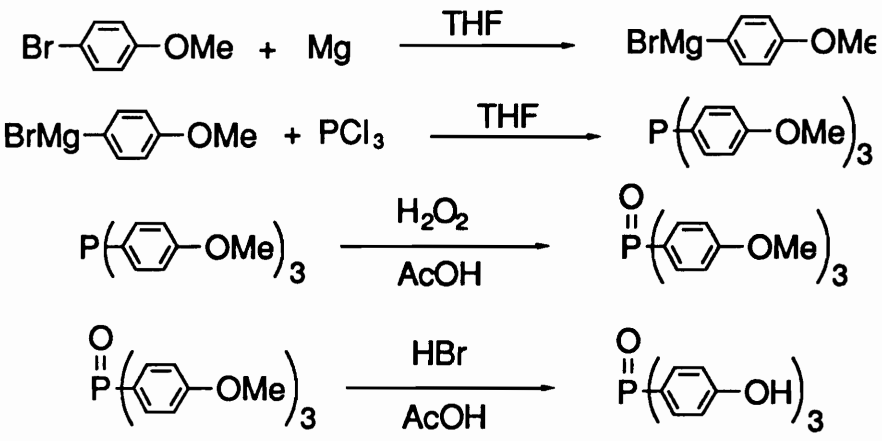
4-Bromofluorobenzene (46g, 266 mmole) was diluted with dry THF (50ml) and slowly added to a flask with Mg(6.4g, 263mmole) and some THF over 1 hour. The mixture was stirred for another 3~4 hours. Then phosphorus trichloride (12g, 87 mmole) diluted with THF was added to the Grignard reagent dropwise. After the PCl_3 was added, the mixture was stirred overnight at room temperature. The product was extracted with diethylether and recrystallized from ethanol. Needle-like white tris(4-fluorophenyl)phosphine was obtained (81% yield). This product was oxidized in acetic acid by 50% H_2O_2 followed by recrystallization in toluene. The needle-like white tris(4-fluorophenyl)phosphine oxide was synthesized with a mp. 122-123°C (88% yield).



Scheme 3.5 Synthesis of tris(4-fluorophenyl)phosphine oxide

3.2.5 Tris(4-hydroxyphenyl)Phosphine Oxide (THPPO)

This monomer was synthesized by a method similar to TFPPO. 4-Bromoanisole(42g, 224.6 mmole) was diluted with dry THF (30ml) and added dropwise to a flask with Mg(5.4g, 222mmole) and dry THF (40ml) over 1 hour. The mixture was stirred for another 5 hours. Then, PCl_3 (10g, 72.8 mmole) diluted with dry THF (30ml) was added to the Grignard reagent dropwise, and stirred overnight at room temperature. The product was extracted with diethylether. After the solvent was removed, the product was washed with aqueous KOH solution to afford an off-white product in ~72% yield. The product was oxidized to phosphine oxide by refluxing in 50% H_2O_2 (8ml) and acetic acid (60ml) mixture for 6 hours. After the solution was cooled, water was added and the precipitate was collected. The synthesized tris(4-methoxyphenyl)phosphine oxide (TMPPO) was purified by dissolving into chloroform, washing with sodium hydroxide solution and water, dried and then refluxed in toluene with a small amount of active charcoal. The solution was then filtered and the toluene was distilled off. TMPPO was obtained in 85% yield from the last step.

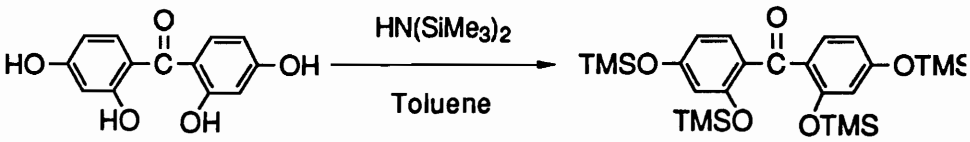


Scheme 3.6 Synthesis of Tris(4-hydroxyphenyl)phosphine oxide

The methoxy group of TMPPO was cleaved by refluxing in HBr (48%) and acetic acid mixture for 8 hours. After cooling, water was added and an off-white powder was formed. The final product THPPO was purified by converting to triphenate in aqueous KOH, filtering through celite, followed by acidification back to THPPO. An off-white product with high purity resulted. Yield ~86% (mp > 260°C).

3.2.6 2,2',4,4' Tetra(trimethylsiloxy)Benzophenone (Si-THBP)

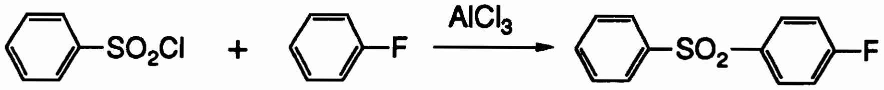
2,2',4,4'-tetrahydroxybenzophenone (THBP) (4.2g, 17.1 mmole) was refluxed in the HMDS/toluene (10ml/30ml) mixture 24 hours. The excess HMDS and toluene were distilled off and the product was purified by vacuum distillation at 215-220°C and 210-250 mtorr.



Scheme 3.7 2,2',4,4' Tetra(trimethylsiloxy)benzophenone

3.2.7 4-Fluorophenylphenyl Sulfone (FPPS)

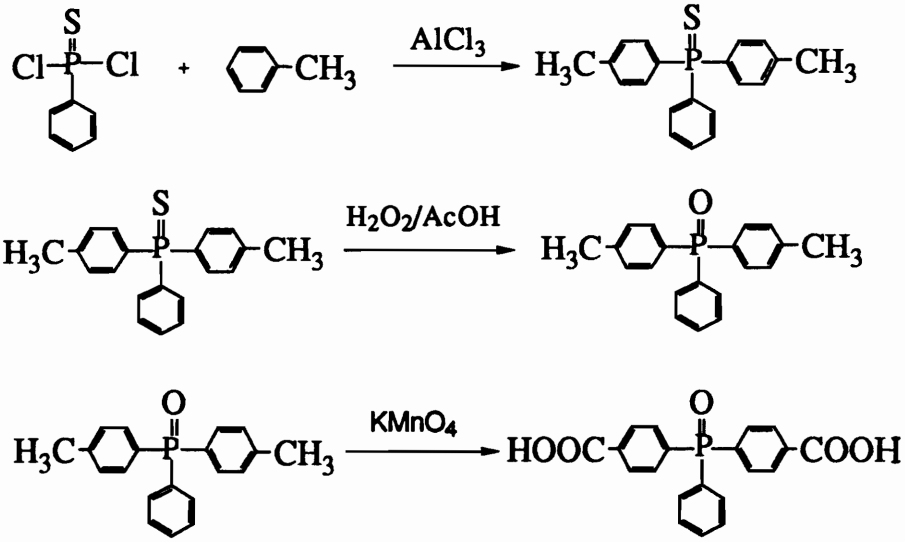
Benzenesulfonyl chloride (15g, 84.9 mmole) and fluorobenzene were charged into a 3-neck flask equipped with a nitrogen inlet and a condenser. $AlCl_3$ (6g, 45 mmole) was added in the mixture in two aliquots and refluxed for over 6 hours. At the end, the mixture was diluted with chloroform, poured into ice water, followed by extraction, separation, washing with potassium carbonate aqueous solution and then water. The chloroform was stripped off and the resulting product was obtained in high purity. The yield was 17.5g (87%). Recrystallization in toluene resulted in a white product (total yield 80%) with mp. 107-108°C.



Scheme 3.8 Synthesis of 4-fluorophenylphenyl sulfone

3.2.8 Bis(4-carboxyphenyl)Phenyl Phosphine Oxide (BCPPO)

Bis(4-carboxyphenyl)phenyl phosphine oxide was synthesized by a series of three step reactions starting from dichloro phenyl phosphine sulfide. The first step was a Friedel Craft reaction, which is described as follows. Thus, dichlorophenyl phosphine sulfide(160g, 758 mmole) and toluene (300 ml) were added in a 4-neck flask and heated to 70°C under nitrogen flow. At this temperature $AlCl_3$ (210g, 1.755 mole) was added into the flask in 6 aliquots over 1 hour. Then, the temperature was raised to 110°C and stirred for 7 hours. After the reaction was completed and cooled, the mixture was poured into ice water. Chloroform was used to extract the product, and the organic layer was washed twice with potassium carbonate solution. Magnesium sulfate was used to dry the organic layer, which was then filtered and the chloroform was stripped off. A brown-yellow product was slowly formed after the solvent was removed. The product was then washed with hexane several times to decolorize it. The yield of the product, bis(4-methylphenyl)phenyl phosphine oxide, was about 80%.



Scheme3.9 Synthesis of bis(4-carboxyphenyl)phenyl phosphine oxide

The second step was to oxidize the phosphine sulfide group to phosphine oxide. This reaction was almost quantitative. For example, the phosphine sulfide monomer (186g, 576 mmole) was dissolved in acetic acid (750 ml) and the 50% hydrogen peroxide (80g) was added into the solution dropwise. The temperature was raised to 85~90°C then decreased to 70°C after the addition of hydrogen peroxide. The reaction was allowed to continue for another 2~4 hours. The solution was filtered through celite to remove precipitated particles. Chloroform was used to extract the product, followed by washing with water and drying with magnesium sulfate. The solvent was removed and a viscous fluid, bis(4-methylphenyl)phenyl phosphine oxide resulted.

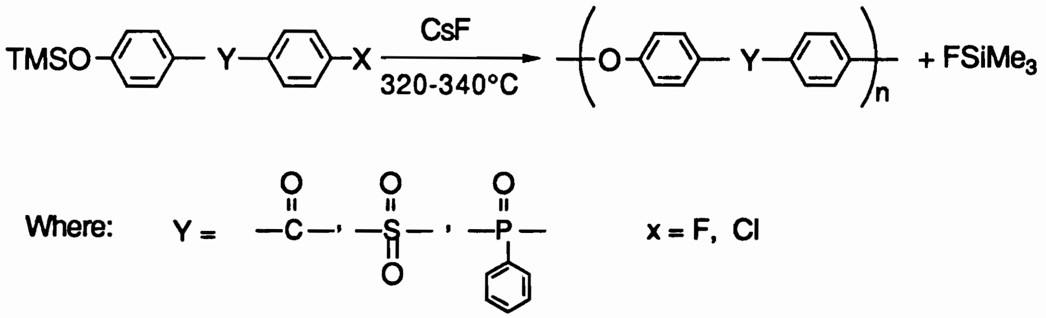
The next step was to oxidize the methyl group to a carboxylic acid group by using potassium permanganate. Thus, BMPPO(152g, 496.2 mmole) was added in a 4-neck 2 liter flask equipped with an overhead stirrer and a condenser. Pyridine (600ml) and water (300ml) were added into the flask and the temperature was raised to 70°C. The $KMnO_4$ (580g, 3.7 mole) was added in 6-8 aliquots at 30 minute intervals and after the last addition, the temperature was raised to 80-90°C for 12 hours. At the end of the reaction, the mixture was allowed to cool to room temperature and the excess $KMnO_4$ was filtered off. The red solution was then acidified with concentrated HCl to pH~5. The collected bis(4-carboxyphenyl)phenyl phosphine oxide (BCPPO) is a white product. Since there is a small amount of residual methyl group in the product and this incompleted oxidation species is very hard to separate from the diacid, a second oxidation is frequently needed. This second oxidation was conducted in a stoichiometric amount of aqueous sodium hydroxide solution. The sodium hydroxide was used to dissolve the diacid (BCPPO) as the dicarboxylate salt. A slight stoichiometric excess (by diacid NMR spectra) of $KMnO_4$ was added into the solution and the reaction was allowed to proceed at 80°C for 6~8 hours. Then, the solution was filtered, acidified and the product was collected. Yields of the BCPPO were about to 74% after two oxidations.

3.3 Synthesis of Poly(arylene ether)s Oligomers, Homopolymers and Copolymers

The PAEs described in the following several sections were mainly synthesized from the silylated monomers. The AB type halogenophenols can also be polymerized directly in the presence of diphenylsulfone (as a diluent) and potassium carbonate (as a base). The last section describes the carboxyl terminated poly(arylene ether sulfone)s (PES), which was used to prepare segmented PES/nylon 6 copolymers.

3.3.1 Linear Homo-Poly(arylene ether)s via AB Type Silylated Monomers

In this section, a description of the step polymerization of several silylated halogenophenols via silyl ether displacement in a neat melt reaction is provided(scheme 3.10).



Scheme 3.10 Synthesis of PAEs via AB type silylated monomers[55]

The typical reaction conditions are described as follows. The A-B monomers 4-Fluoro-4'-trimethyl siloxybenzophenone (Si-FHBP) (5g, 17.3 mmole) and a small amount of cesium floride (~0.5wt%) were weighed into a 3-neck melt reaction vessel equipped with a mechanical stirrer and heated to 260~270°C for 1 hour. At this stage fluorotrimethylsilane was evolved. Then, the reaction temperature was raised to 340°C for 2 hours and a solid powder was formed at this temperature. This product is poly(arylene ether ketone), which is often described by the acronym PEK and it is known to display a crystalline melting point(Tm) of about 367°C.

The poly(arylene ether phosphine oxide), (PEPO), was prepared by a method similar to that described for PEK and the reaction conditions are shown in Table 3.1. The Si-FHPPO was used directly after the silylation of the FHPPO and evaporation of excess silylation reagent to produce an amorphous polymeric material. By the end of the reaction, the melt was allowed to cool to room temperature to produce a light gray colored transparent solid. The Si-CHDPS was polymerized by the same method as the Si-FHPPO. Unfortunately, no polymerization took place and this demonstrates that the Si-CHDPS is non-reactive. In contrast, the Si-FHDPS was reactive and the reaction conditions for the synthesis of poly(arylene ether sulfone) (PES) are also shown in Table 3.1.

Table 3.1 Reaction conditions of AB silylated monomers

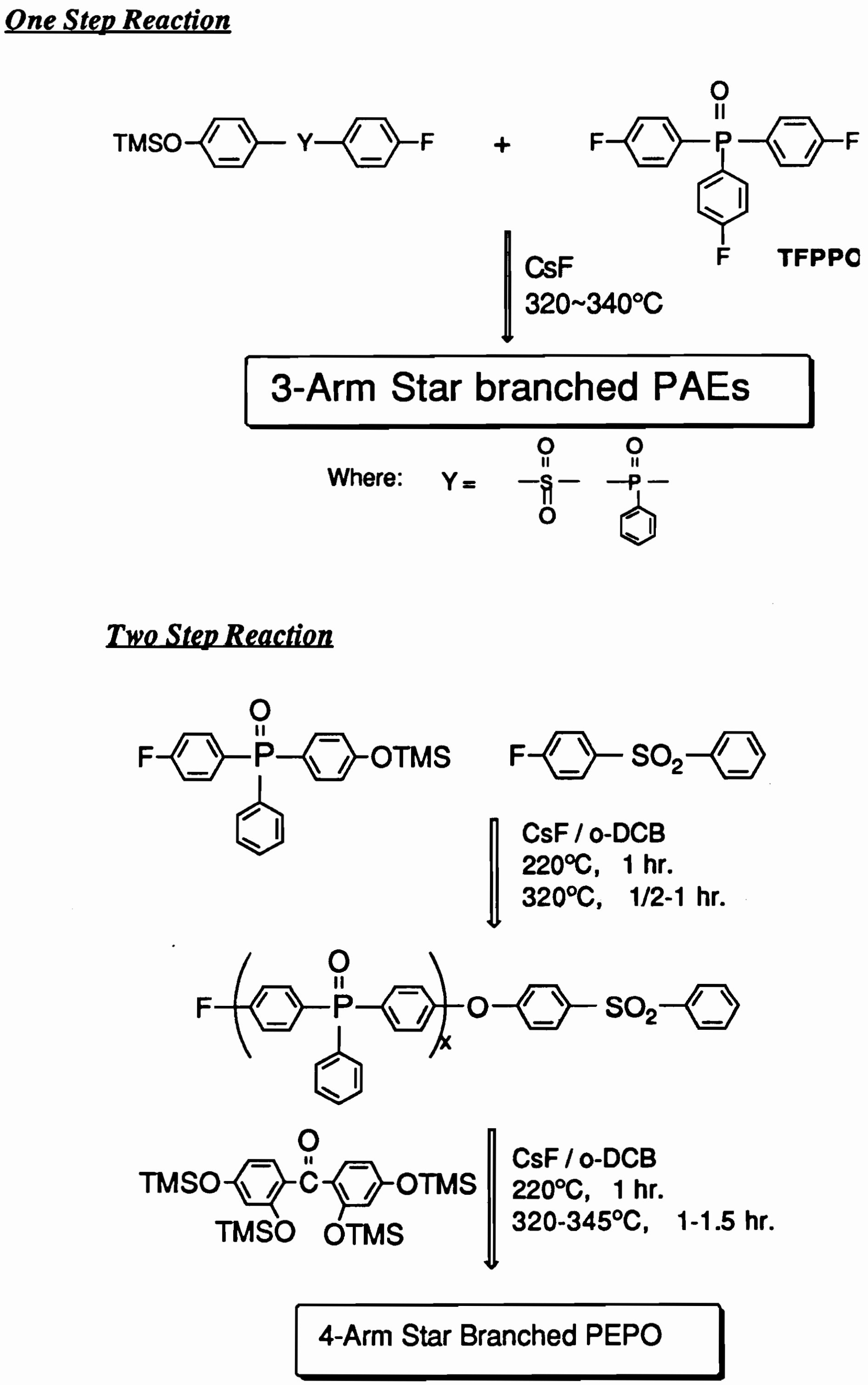
Monomers	T_i(°C)	Time (hr)	T_f(°C)	Time(hr)	Polymer
Si-FHBP	250~270	0.5	340	2	PEK
Si-CHDPS	220, 250	20min, 1hr	320	2.5	no reaction
Si-FHDPS	220, 250	20min, 1hr	320	2.5	PES
Si-FHPPO	270	0.5	340	40min	PEPO

T_i : Initial reacrion temperatutes T_f : Final reaction temperatures

3.3.2 Star-Branched Poly(arylene ether)s via AB Type Silylated Monomers

The AB type monomers can be used, in principle, to synthesize star-branched PAEs. Two kinds of star-branched PAEs (3-arm & 4-arm) were synthesized by either one step or two step reactions as shown in the reaction Scheme 3.11.

The one step reaction used tris(4-fluorophenyl)phosphine oxide(TFPPO) as the



Scheme 3.11 Synthesis of star branched PAEs via one step or two step reactions

branching agent. Two silylated AB monomers have been used to synthesize the 3-arm PAEs. For example, a 23K 3-arm PES was synthesized as follows: Si-FHDPS (8.2g, 25.3 mmole) and TFPPO (83mg, 0.25 mmole) and cesium fluoride about 1 wt% (82mg) were weighed into a 3-neck melt reactor. The mixture was heated up to 220°C for 20 minutes, 250°C for 1 hour and finally 320°C for another 2.5 hours. After cooling, a light gray colored solid with 3-arms, in theory, polymeric material was obtained.

For 3-arm PEPO(30K) polymerization, the Si-FHPPO (5.75g, 14.96 mmole) was directly used after the silylation reaction and evaporation of the solvents. The branching agent TFPPO (48.9mg, 0.147mmole) and catalyst CsF (0.5 wt% of monomer) were weighed in the 3-neck melt reactor and then about 1.5ml dry o-dichlorobenzene was added. The initial temperature was 220°C for one hour which afforded a viscous fluid at this stage. The temperature was then raised up to 320°C for 40 minutes. By the end of the reaction, vacuum was applied to the system at this temperature for 20 minutes to remove the solvent. After cooling, the polymer was recovered as a transparent gray colored solid.

A two step reaction was used to synthesize a 4-arm PEPO. The first step was to prepare a controlled molecular weight PEPO, followed by coupling with a tetrafunctional monomer. A typical example is illustrated in the following section: A PEPO oligomer with 5000 g/mole was synthesized by using Si-FHPPO (6.5g, 20.8 mmole), 4-fluorophenylphenyl sulfone (0.3g, 1.27 mmole) CsF (0.3 wt%) and dry chlorobenzene (1.5ml). The above mixture was heated to 220°C for 60 minutes, followed by 320°C for 30 minutes. Then, vacuum was applied to the system for 20 minutes in order to remove chlorobenzene. The resulting oligomer was removed from the flask and some of it was used for characterization. The remaining PEPO (5K) was reacted with a tetrafunctional monomer, Si-THBP. For example, 5K PEPO (4.5g) was heated to 175°C in the presence of dry o-dichlorobenzene(2ml) to produce a viscous fluid after 1 hour. At this stage, Si-

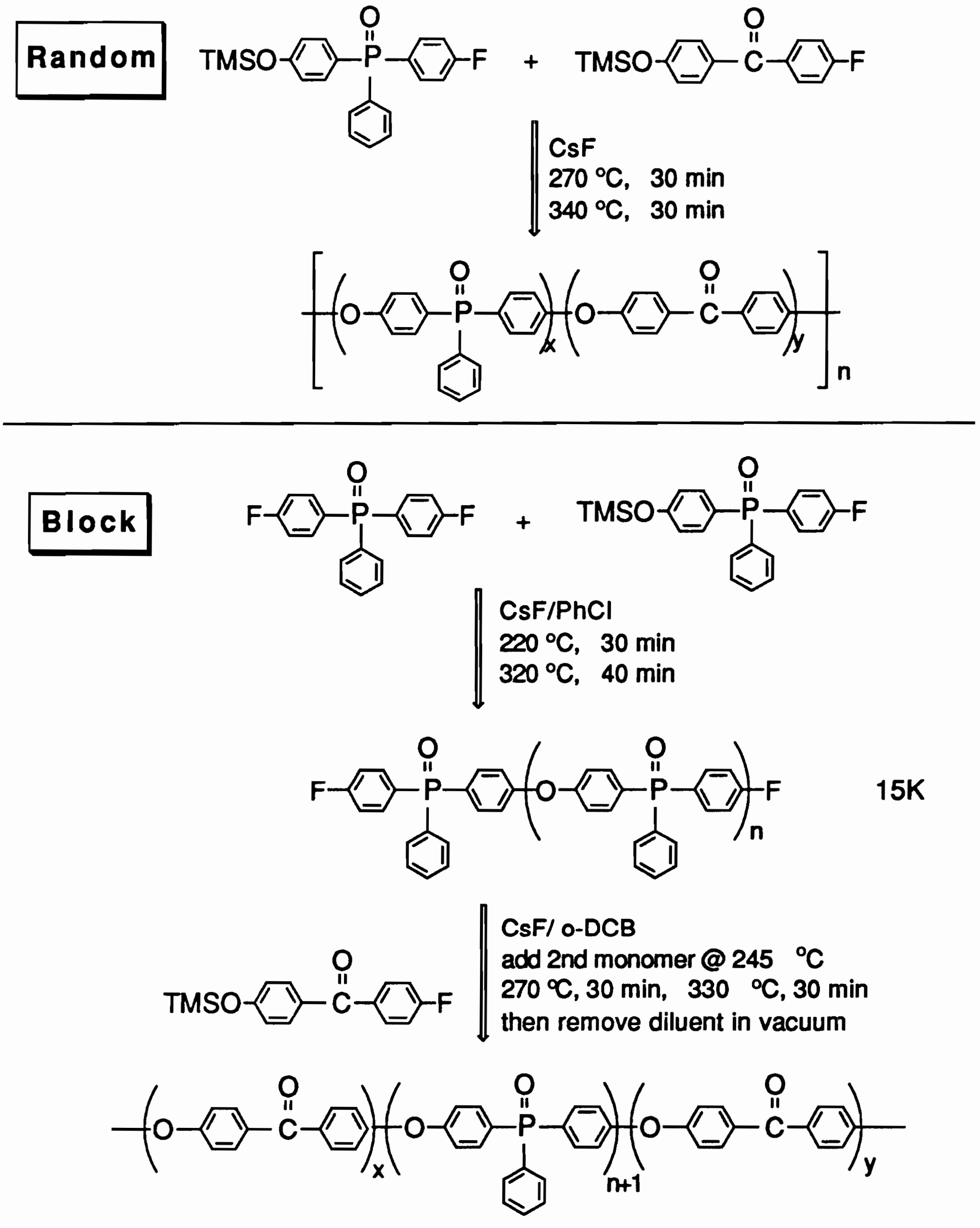
THBP (0.13g, 0.24 mmole) was diluted with chlorobenzene (2ml) and was then added to the melt reactor. The temperature was raised to 270°C for 1 hour, then 320°C for 40 minutes. Finally, vacuum was applied to the system to remove the solvent. A theoretical 4-arm PEPO polymer with 20K molecular weight was obtained.

3.3.3 Random or Statistical Copolymers of PEK-co-PEPO via AB Type Silylated Monomers

In this section, the synthsis of a statistical PEK-co-PEPO copolymer is described(Scheme 3.12). For example, the FHPPO (35g, 11.2 mmole) was refluxed in HMDS/toluene (10ml/20ml) mixture for 24 hours, then the excess HMDS and toluene were removed by vacuum distillation. Next, the Si-FHBP (3.23g, 11.2 mmole) and CsF (0.01g) were added to the above melt reactor along with Si-FHPPO. Fluorotrimethylsilane evolution started at 260~270°C and the temperature was maintained at this stage for 30 minutes which produced a viscous fluid. The temperature was then raised to 340°C for another 30 minutes, which produced a highly viscous reaction mixture. The copolymer was dissolved into hot NMP, precipitated into methanol, boiled in water and dried in vacuum at 100°C for 48 hours.

3.3.4 Tri-Block PEK/PEPO/PEK via AB Type Silylated Monomers

The block copolymer was synthesized in a one pot two step reaction (Scheme 3.12). The first step was to prepare an amorphous central block. Thus, FHPPO (4g, 12.8 mmole) was refluxed in HMDS/toluene (10/20) mixture for 24 hours and the excess solvent was then removed by vacuum distillation. A stoichiometric amount of BFPPO(0.08g, 0.25 mmole) was added into the reactor to control the molecular weight of the central block (~15,000 g/mole). A small amount of CsF (0.01g) catalyst along with dry o-dichlorobenzene (1 ml) was also added into the reactor. The initial temperature was



Scheme 3.12 Synthesis of 50/50 mole percent composition PEK/PEPO random and block copolymers

220°C for 30 minutes and which was then raised to 320°C for 40 minutes. Before the second AB monomer, Si-FHBP, was added, the temperature was reduced to 240-250°C. After the Si-FHBP (3.69g, 12.8 mmole) was added, the reaction mixture was stirred at the same temperature for 20 minutes to provide a homogenous mixture. Then, the mixture was heated to 270°C for 30 minutes, and 330°C for 30 minutes. The resulting copolymer solidified at this temperature. Any remaining o-dichlorobenzene was removed by applying a vacuum to the system which produced a copolymer which was yellow to light brown in color.

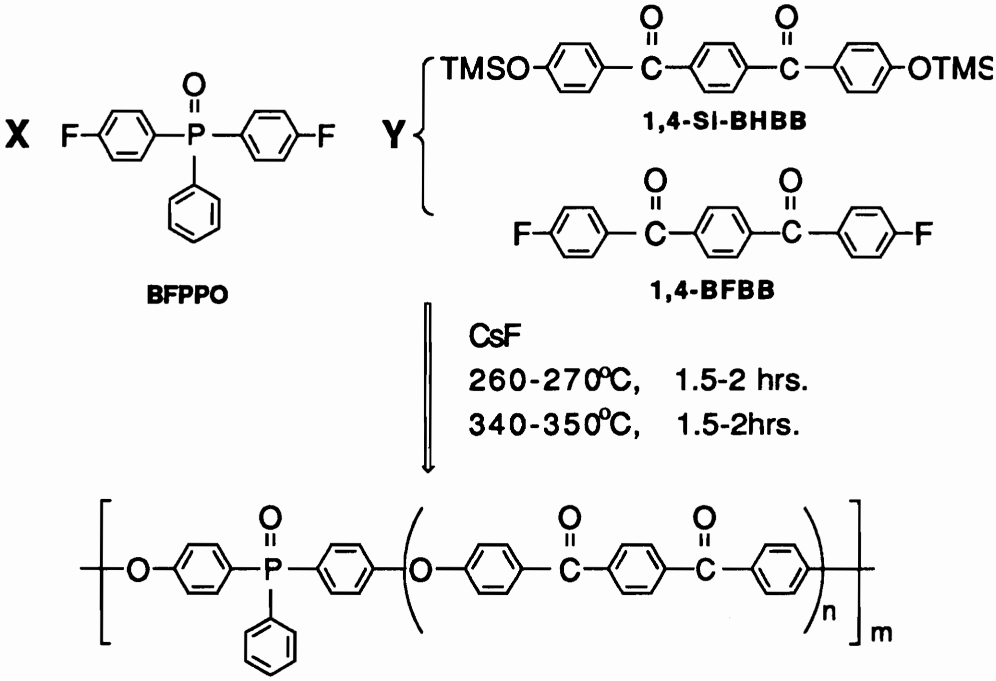
3.3.5 Poly(arylene ether phosphine oxide/arylene ether ketone ketone) Copolymers

AA, BB type of monomers were used to synthesize PEPO/EKK copolymers via the silyl ether displacement process. The two silylated 1.3 & 1.4-bis(4-hydroxybenzoyl) benzene(Si-BHBB) were used to generate copolymers with different compositions, as shown in Scheme 3.13.

A typical example for a 50/50 composition of PEPO/EKK copolymers is as follows (Table 3.2): Stoichiometric amounts of BFPPO (2.037g, 6.48 mmole) and silylated 1,4-BHBB (3g, 6.48 mmole) were added with cesium fluoride (0.07g) into a melt reactor and

Table 3.2 Monomers for PEPO/EKK copolymer synthesis

EPO/EKK	BFPPO(g)	1,4-BFBB(g)	1,4-Si-BHBB(g)	1,3-Si-BHBB(g)	CsF(g)
50/50	2.037	—	3.0	—	0.07
40/60	1.360	0.348	2.5	—	0.08
30/70	1.215	0.836	3.0	—	0.05
20/80	0.692	1.045	2.5	—	0.05
50/50	1.9	—	—	2.8	0.04

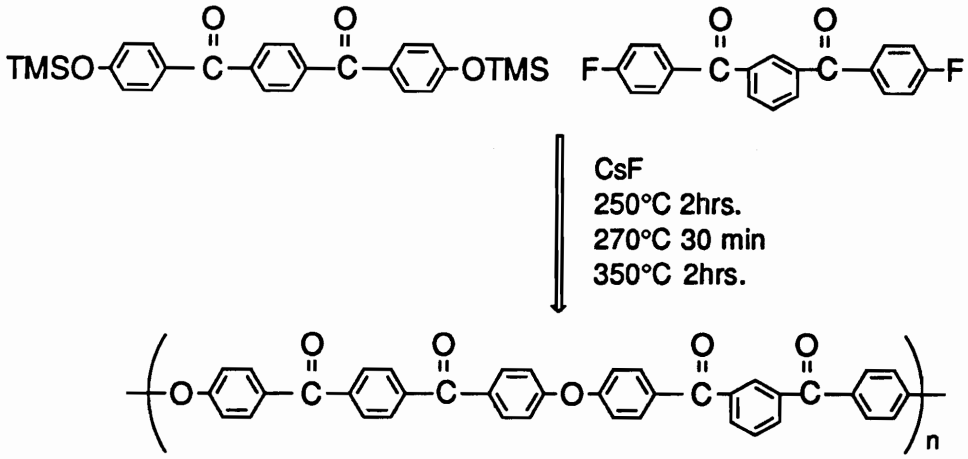


X / Y = 50/50, 40/60, 30/70, 20/80 (mole ratios)

Scheme 3.13 Synthesis of PEPO/EKK copolymers via silylated bisphenols heated up to 260°C for 1.5 hours. Then, the temperature was raised to 340-350°C for another 2 hours. At this temperature, the PEPO/EKK of the ratio 50/50 and 40/60 were very viscous apparently amorphous fluids whereas 30/70 and 20/80 ratios were solids. The copolymers were removed from the reaction vessel while still hot. The synthesis of corresponding PEPO/iso-EKK(ie. the last row of the table 3.2) copolymer in 50/50 ratio by using 1,3-Si-BHBB and BFPPO was similar to the procedures described above.

3.3.6 Perfectly Alternating 1,3 & 1,4-PEKK

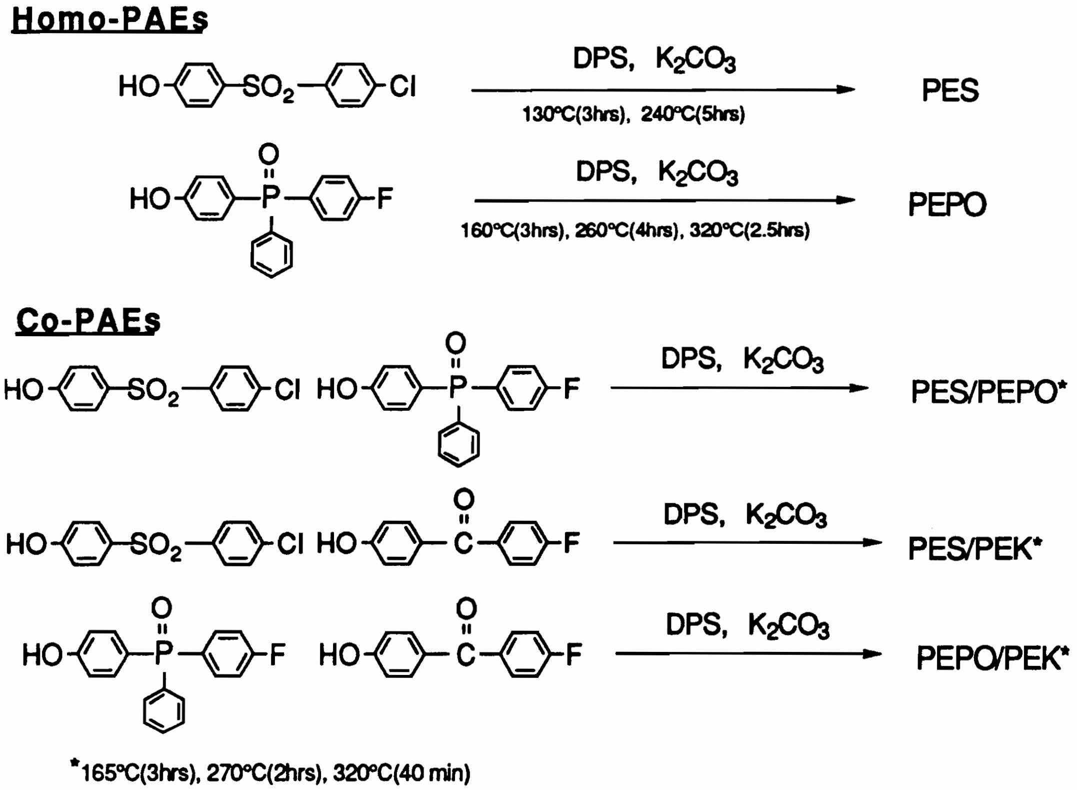
The perfectly alternating 1,3 & 1,4 PEKK was synthesized by the similar method mentioned in the above section. Thus, 1.4-Si-BHBB (3g, 6.48 mmole) 1,3-BFBB (2.01g, 6.48 mmole) and CsF (0.03g) were charged into a melt reactor. The temperature was controlled to 250°C for 2 hours, 270°C for 30 min, and 320 to 350°C for 2 hours. The copolymer at this temperature was a viscous fluid which was removed from the reactor while still hot. (Scheme 3.14)



Scheme 3.14 Synthesis of perfectly alternating 1,3 &1,4 PEKK

3.3.7 Homo and Co-Poly(arylene ether)s from AB Type Halogenophenols

In this section halogenophenols polymerized directly without first silylation of the phenol groups are described. In this case, diphenyl sulfone (DPS) was used as a diluent and potassium carbonate was used as the base. Two homopolymerization and three copolymerization reactions were conducted by this route(Scheme 3.15)



Scheme 3.15 Homo & co-poly(arylene ether)s from AB types halogenophenol

All of these reactions were conducted in a similar way as described earlier, only the reaction temperatures and times were different. During the course of the reaction, a small quantity of chlorobenzene was used to rinse the sublimed diphenyl sulfone back to the reactor. For example, the homo poly(arylene ether sulfone) (PES) was synthesized by using 4-chloro-4'-hydroxydiphenyl sulfone (CHDPS) (7g, 26.1 mmole), potassium carbonate (2.16g, 15.6 mmole) and diphenyl sulfone (7g) in a melt reactor. The temperature was increased to 130°C for 3 hours, the byproduct water was removed by a nitrogen stream. Next, the temperature was increased to 240°C for an additional 5 hours. During the course of the reaction, dry chlorobenzene was added several times in very small quantities (eg. 0.5-lml) to rinse the sublimed diphenyl sulfone back to the reactor. Finally, the polymer was dissolved into NMP, filtered, and precipitated into rapidly stirred methanol. The polymer was collected, washed with methanol, boiled in water to remove NMP and then dried in a vacuum oven at 100°C for 48 hours.

Poly(arylene ether phosphine oxide) (PEPO) obtained from the 4-fluorophenly-4'-hydroxydiphenyl phenyl phosphine oxide(FHPPO) utilized the reaction conditions similar to those described for the poly(arylene ether sulfone) (PES). The major differences were the reaction time and temperature. For example, the monomer was heated to 160°C for 3 hours, 260°C for 24 hours and 320°C for 25 hours. After cooling, the mixture was dissolved into NMP, filtered, precipitated in methanol/water mixture, boiled in water and dried in vacuum at 100°C for two days.

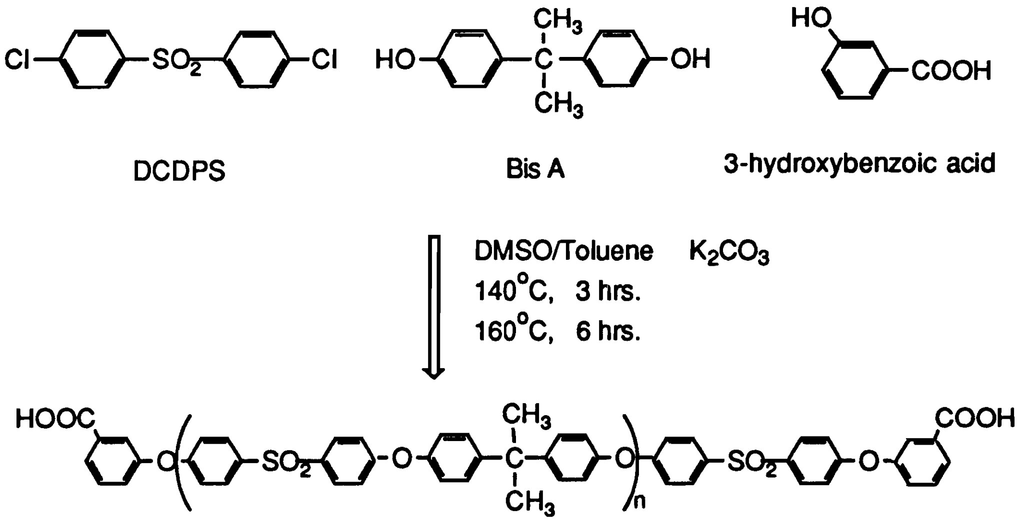
The synthesis of the PEPO/PEK, PEPO/PES and PES/PEK copolymers were similarly conducted. For example, an equimolar mixture of two halogenophenols along with potassium carbonate (~20% excess) and DPS were heated in a melt reactor and a small amount of chlorobenzene was added in during the reaction. The initial temperature was 165°C for 3 hours, then 270°C for 2 hours and 320°C for 40 minutes. The polymer was recovered by dissolving the reaction mixture in NMP, filtering to remove the inorganic salts and precipitating into methanol. The polymer was filtered off, washed with ethanol, boiled in water and dried under vacuum at 100°C for two days.

3.3.8 Solution Polymerization of AB Type Halogenophenols.

The reactivity of the prepared halogenophenols was investigated under relatively mild reaction conditions by polymerization of two AB type halogenophenols, FHDPS and FHPPO, in DMSO and NMP. Potassium carbonate (20% excess) was used as the base and toluene was used as the azeotroping reagent. The reactor was heated to 130-140°C for 3 hours, and then to 170°C for 20 hours. The reaction mixture was then filtered and precipitated into a methanol/water mixture, boiled in water, and dried in a vacuum oven. Very low molecular weight oligomers were recovered for both cases. Apparently, higher reaction temperatures were needed to achieve high molecular weight.

3.3.9 Carboxyl Terminated Poly(arylene ether sulfone) Oligomers

Carboxyl functionalized poly(arylene ether sulfone) (PES-COOH) was synthesized as an intermediate for the purposes of subsequently synthesizing poly(ε-caprolactam) or nylon 6 segmented copolymers. Several carboxyl terminated PES with different molecular weights were investigated. A typical reaction is shown in Scheme 3.16. For the synthesis of PES-COOH oligomer with a number average molecular weight of 10,000 gm/mole, bisphenol A(15.21g, 66.63 mmole), DCDPS(20g, 69.65 mmole), m-hydroxybenzoic acid (0.852g, 6.15 mmole), DMSO(120ml), toluene(50ml) and anhydrous potassium carbonate (13g, 94 mmole) were charged into a 4-neck round flask. The system was maintained under an inert atmosphere with flow of dry nitrogen. The flask was initially heated to 130-140°C for 3 hours, then the temperature was raised to 160-170°C and held there for another 6-8 hours. After the reaction mixture was cooled to 100°C, the salts was filtered and the solution was neutralized with diluted hydrochloric acid, then precipitated in methanol/water(70/30, v/v). The resulting polymer was then dried in a vacuum oven, re-dissolved in chloroform and precipitated into methanol/water. The polymer was finally dried in a vacuum oven at 100°C for 2 days.



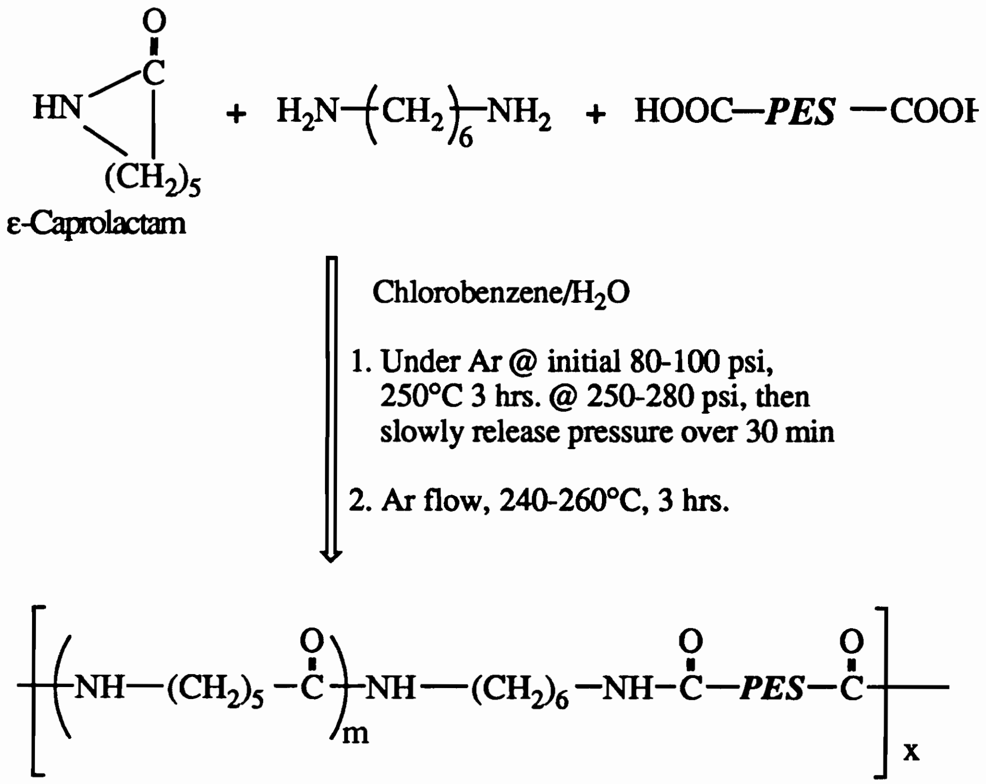
Scheme 3.16 Synthesis of carboxyl terminated poly(ether sulfone) oligomers

3.4 Modification of Polyamides

In this section, two of the important polyamides, nylon 6 and nylon 6,6, were modified by different approaches and for different purposes. Both copolymers were synthesized in a 0.2 liter Parr® reactor using a batch process.

3.4.1 Nylon 6/Poly(arylene ether)Sulfone Segmented Copolymers

Two series of copolymers were synthesized via a hydrolytic melt polymerization techniques. These included variations of the poly(arylene ether sulfone) weight % incorporation and the segmental length at the same weight % incorporation. The copolymerization was conducted in two stages. Firstly, carboxyl terminated PES and a stoichiometric amount of hexamethylene diamine were dissolved in a small amount chlorobenzene(about 30~50 wt% of solid) and mixed well. To this solution, the required amount of ε-caprolactam was added along with 5% of deionized water. The entire

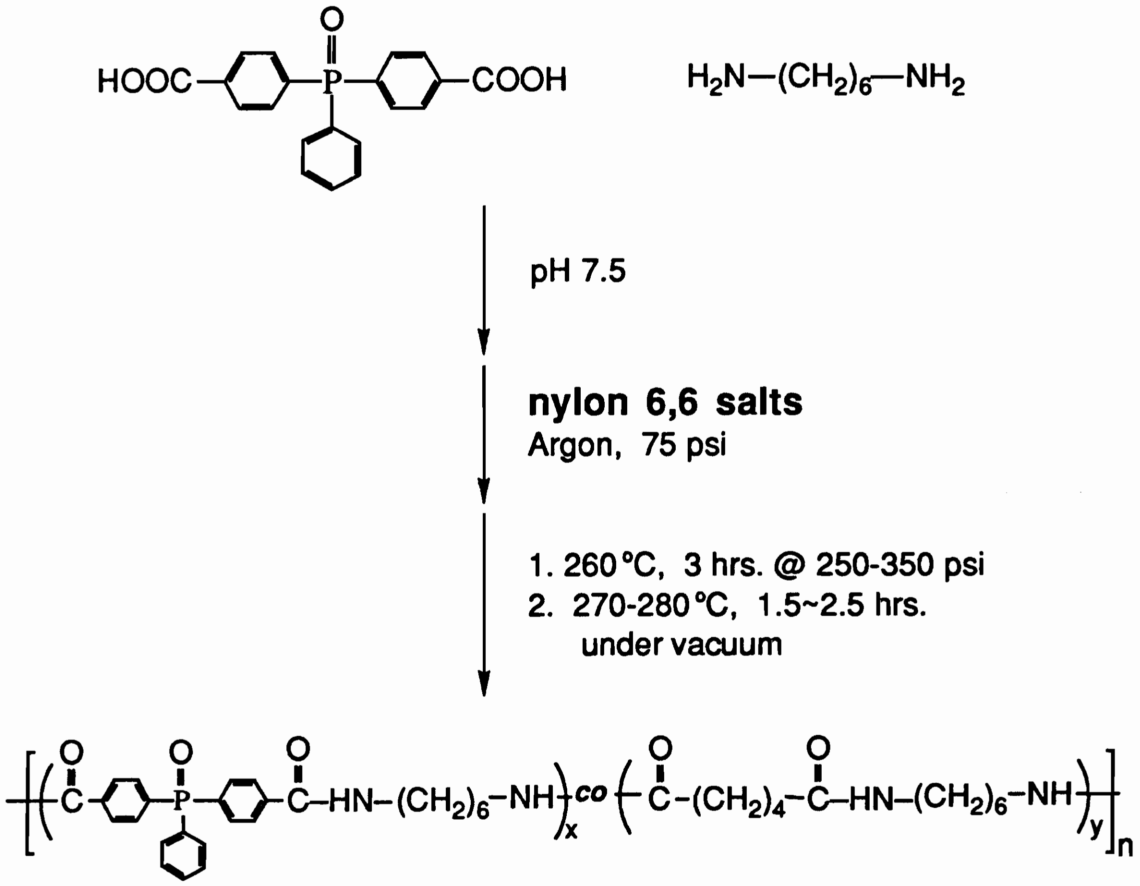


Scheme 3.17 Synthesis of poly(arylene ether)sulfone/ nylon 6 segmented copolymers

mixture was charged into a stainless steel Parr® reactor. The system was then purged with argon for 10 minutes, sealed and pressurized to 60-100 psi with argon and the temperature was slowly raised to 250-260°C. During the course of the reaction, the system was allowed to increase in pressure to 250-280 psi and was held for 2.5 hours. In the second stage, the pressure was slowly released in 30 minutes to atmospheric pressure and was then held under constant argon flow. The reaction was considered complete after been held at 250-260°C for another 3 hours. The resulting copolymer was obtained as a fused off-white mass. The polymers were ground and extracted in a Soxhlet apparatus with boiling water to remove cyclic oligomers and unreacted ε-caprolactam.(Scheme 3.17)

3.4.2 Triphenyl Phosphine Oxide Containing Nylon 6,6 Copolymers

The triphenyl phosphine oxide dicarboxylic acid was incorporated into nylon 6,6 copolymers at 0, 10, 20 and 30 mole% incorporation. In a typical copolymerization reaction, pure nylon 6,6 salts were prepared from adipic acid and hexamethylene diamine in ethanol followed by recrystallization in methanol/water mixture. Then, the triphenyl phosphine oxide dicarboxylic acid monomer and an equimolar amount of hexamethylene diamine were dissolved into water in a glass vessel. The pH value of this solution was adjusted to 7.5 by adding one or the other monomer. Next, a controlled amount of the nylon 6,6 salt was added into the solution and the concentration was adjusted to about 60~70%. Copolymerization was conducted in a two stage reaction. In the first stage, the glass vessel was transferred into a Parr® reactor, purged with argon, pressurized to 75 psi, and then slowly heated to 250~260°C. During the course of the copolymerization, the pressure increased to 250~350 psi and it was maintained at this pressure for 2~3 hours. For the second stage, the pressure was slowly reduced to



Scheme 3. 18 Synthesis of triarylphosphine oxide/nylon 6,6 copolymers

atmospheric over 1 hour and then, vacuum (0.5 torr) was applied to the system at 270~280°C. After 1~2 hours, a light yellow nylon 6,6/triphenyl phosphine oxide co-polyamide was formed(Scheme 3.18).

3.5 Analysis and Characterization of Monomers, Oligomers and Polymers

3.5.1 Monomer Analysis(NMR, FTIR, MS, Elemental analysis)

1. Nuclear magnetic resonance spectroscopy (NMR)

The structural and compositional analyses of monomers were determined by solution ^{1}H, ^{13}C and ^{31}P-NMR. The spectra were obtained using a Varian 400 MHz spectrometer.

2. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectra were obtained using a Nicolet MX-1 instrument. Monomer samples were prepared by grinding and then pressing with dry potassium bromide into pellets. Polymer samples were prepared by solution casting films or pressed potassium bromide pellets.

3. Mass Spectroscopy (MS)

Mass spectroscopic spectra of monomers were obtained using a VG Analytical 7070E-HF high resolution magnetic sector, double focusing mass spectrometer. MS measurements were run in an electron impact ionization mode of 70 eV, accelerating voltage of 6000V, scan rate of 5 sec/decay, range of 50-500 m/e and source temperature of 200°C.

4. Elemental Analysis

Chemical compositions of the synthesized monomers were determined by elemental analysis obtained from Atlantic Microlab, Inc. (Norcross, Georgia).

3.5.2 Molecular Weight Determination (Titration, Intrinsic Viscosity and GPC)

1. Potentiometric Titration

The number average molecular weight of a dicarboxyl terminated poly(arylene ether sulfone) was determined by end group analysis using a titration method. The acid-base titrations were carried out by using a MCI GT-05 automatic titrator. During the titration, the change in potential of an indicator electrode is observed as a function of the volume of a titrant added. Dry NMP was used as the solvent for the oligomers. A methanol solution of tetramethylammonium hydroxide was standardized over KHP and used as a standard titrant solution. The end point of a titration was detected automatically by the instrument and the number average molecular weight of the sample was calculated by the computer. The average of three trials was taken as the value for <Mn> of PES-COOH oligomers. The number average molecular weight, <Mn> was calculated using a formula shown below,

$$\langle Mn \rangle = \frac{n}{C \times (V - V_b)}$$

Where W is the weight of sample in grams, N is the number of end-group per molecular, C is the concentration of the titrant in mole/ml, V and V_b are the volume of titrant used for the sample and the blank solvent.

2. Intrinsic Viscosity

Intrinsic viscosity (IV) of the oligomers and polymers were measured by using a Cannon-Ubbelohde glass capillary viscometer in a temperature controlled water bath at

25°C. NMP, chloroform and m-cresol were common solvents for IV measurements. Generally, three or four concentrations of the polymer were used for the measurements. The time, t_o, was determined by averaging three measurements of pure solvent. The time, t, was the average of three measurements of each concentration. The three or four different concentrations were made by diluting with 5 ml of pure solvent after the measurement. The specific viscosity, η_{sp} , was determined by $(t-to)/to \approx (\eta-\eta_o)/\eta_o$. The intercept of η_{sp}/C versus concentration plot is defined as the intrinsic viscosity at zero concentration.

3. Gel Permeation Chromatography(GPC)

Gel permeation chromatography was utilized to estimate the molecular weight and molecular weight distributions. PAE samples were dissolved into NMP or chloroform and the polyamide samples were first derivatized to N-trifluoroacetylated deritivatives [142, 143] and then dissolved in a common GPC solvent such as tetrahydrofuran, chloroform or methylenechloride. The procedure for N-trifluoroacetylation of polyamides was as follows. Polyamide(0.1g) was added into a 50 ml flask along with dry methylene chloride(3 ml) and trifluoroacetic anhydride(0.2 g). The reaction mixture became homogenous within a period of a few minutes to several hours depending on the size of the sample and was judged to be complete after 15 hours.

3.5.3 Solvent Extraction of Segmented PES/Nylon 6 Copolymers

The unreacted monomer and cyclic oligomers of PES/nylon 6 copolymers were extracted by hot water in a soxhlet extractor for three days. The water extracted samples were then dried and subsequently extracted by chloroform to obtain an estimated value for the PES homepolymer.

3.5.4 Stress-Strain Behavior

Instron model 1123 was used to determine the stress-strain mechanical behavior of dogbone shaped specimens cut by number 5 die. The well dried sample was compression molded at 272°C(520°F) to produce a film of thickness ranging from 10 to 20 mil. The ASTM standard method D 638(89) at 0.5 inch/minute crosshead extension rate was utilized. The reported results were an average of 5 specimens. An extensiometer was employed to determine a more accurate elastic moduli.

3.5.6 Wide Angle X-ray Scattering (WAXS)

WAXS measurements were conducted by using a Scintag XDS 2000 x-ray diffractometer of Cu Kα radiation with 0.154 nm wavelength. The scanned angle, two theta(2θ), was from 10° to 35°at 0.5°/min scan rate. The samples were either in powder or film form.

3.5.6 Thermal Analysis (TGA and DSC)

1. Thermogravimetric Analysis (TGA)

TGA was performed on either a Perkin Elmer 7 series instrument or a DuPont Instruments 951 Thermogravimetric Analyzer. The analysis was conducted using 5-15 mg of sample and heating from 30°C to 750°C at a heating rate of 10°C/ minute under air or nitrogen.

2. Differential Scanning Calorimetry (DSC)

DSC measurements were conducted by using a Du Pont Instrument 912 DSC or a Perkin-Elmer 7 series DSC. In general, two scans were performed at a scan rate of 10°C/minute.

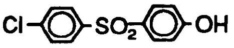
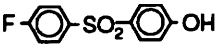
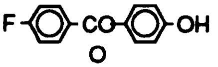
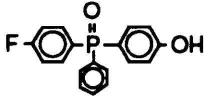
4. RESULTS AND DISCUSSION

4.1 Synthesis and Characterization of Monomers

4.1.1 Halogenophenols

The four halogenophenols, CHDPS, FHDPS, FHBP and FHPPO were obtained by partial hydrolysis of the corresponding dihalide in aqueous DMSO (Scheme 3.1). It has been reported that the order of halogen reactivities is F>Cl~Br for this type of reaction [154]. The reaction conditions for the four halogenophenols described in Section 3.2.1(Scheme 3.1) were based on the type of the halogens and the electron withdrawing groups. The electron withdrawing ability and the monomer reactivity can be judged from ^{13}C and ^{19}F chemical shift data. For example, ingeneral the more down field shift of a site with a halogen attached, the greater as the tendency of the site to undergo nucleophilic attack[42, 43]. The three electron withdrawing groups considered in this thesis have the order $-SO_2- > -CO- > -P(Ph)(O)-$.

Table 4.1 Synthesis of halogenophenols

Halogenophenols	Reaction		Concentration		
	T(°C)	t(hrs.)	M(mole)/DMSO(l)	yield(%)	mp(°C)
 (CHDPS)	105	24	3.13	82	149-150
 (FHDPS)	60	24	4.1	85	152-153
 (FHBP)	95	24	4.6	76	166-167
 (FHPPO)	70	24	1.73	68	220-222

Temperature is a critical factor for the partial hydrolysis reaction and this also can influence the purity of the product. Thus, if the reaction temperature is too high (eg. 75°C for the 4,4'-difluorodiphenyl sulfone), both halogens of the dihalide monomers can be hydrolyzed. Once this happens, the di-hydrolyzed species (biphenols) is very difficult to separate from the mono-hydrolyzed product (halogenophenols). In general, the yields of the halogenophenols are controlled by the concentration of the monomer in the dimethyl sulfoxide(DMSO)/water mixture. A large quantity of DMSO may allow the monomer, the hydrolyzed product, and the potassium hydroxide to dissolve well in the solution mixture and afford a better yield. Only very little amount of water is needed for this type of reaction to disolve the potassium hydroxide initially (eg. 50~70 wt% of KOH in water). Use of too much water for the reaction will result in low solubility of the dihalide monomers in the mixture solvents and will provide a relatively low yield. However, if relatively large quantity of DMSO (e.g. 1 mole dihalide/1 liter DMSO)for the partial hydrolysis reaction are employed, the unreacted dihalide may cause difficulties to the separation of the unreacted dihalide from the product upon filtration, in the case where conversion is less than 100%. In this research the quantity of DMSO used for the partial hydrolysis reaction was 1/4~1/5 of the reported value for the sulfone [54] and ketone monomers and was about 1/2 for the arylphosphine oxide monomers. The advantages are as follows: Firstly, the resulting product can be easily separated from the unreacted monomer by filtration (the crude products usually have monomer grade purity except FHDPS). Secondly, less DMSO was used in the reaction and any unreacted monomer can be easily recovered. The yields of the products are just a little lower than the reported value for the FHDPS preparation [54]. The yields and the melting points of the halogenophenols are listed in Table 4.1.

The yields of the halogenophenols can be increased if the DMSO quantity used for the hydrolysis reaction is increased as discussed earlier. Figures 4.1 through 4.4 show the ^{1}H-NMR spectra of the 4-halogenophenols. The impurity in the FHDPS spectra was the bisphenol, which is very easily formed even at 60°C(Figure 4.2). This is because the DFDPS has a strong electron withdrawing group and a good leaving group. The biphenol(ate) is not easily separated from the target product in this case.

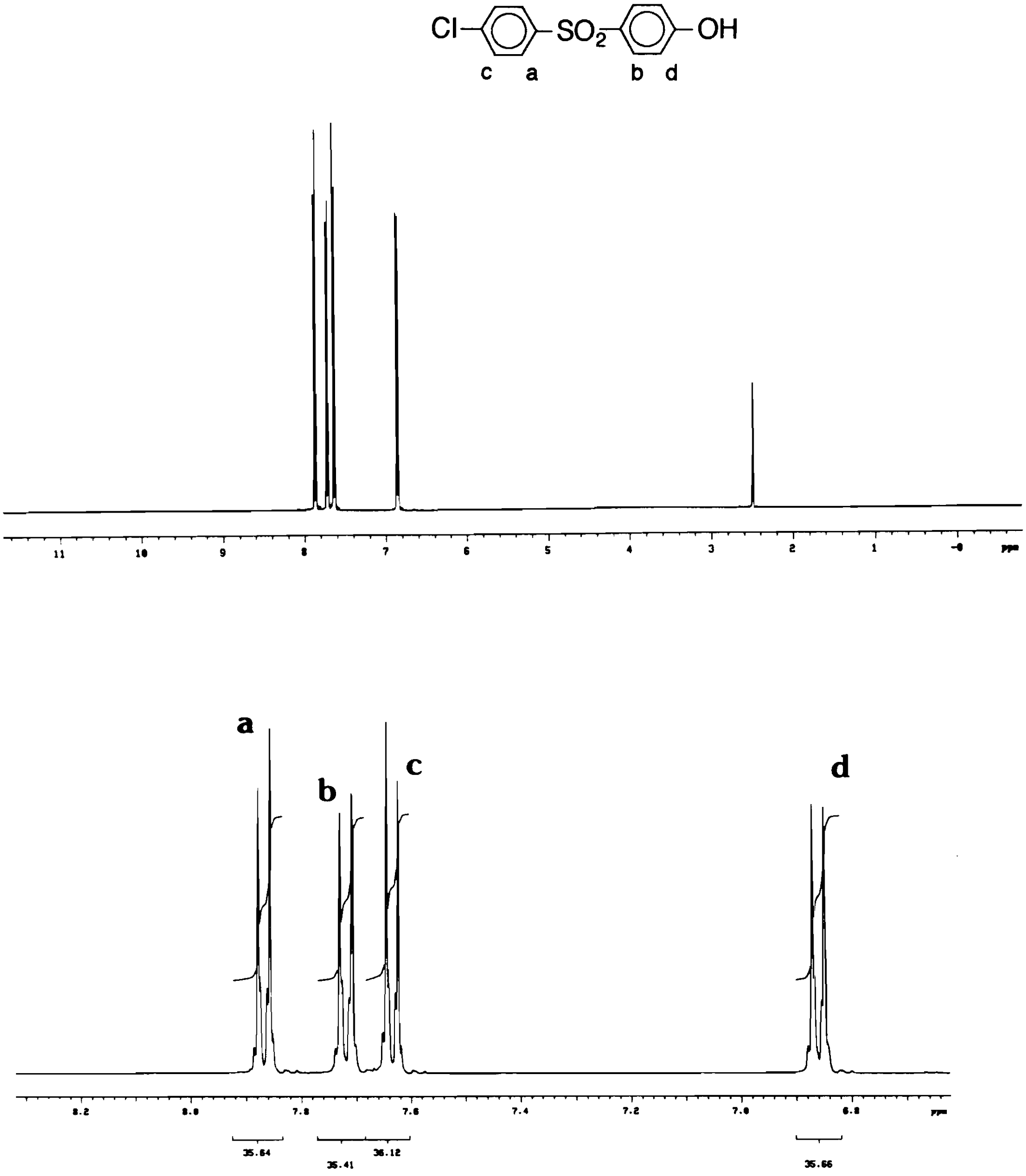


Figure 4.1 ^{1}H-NMR of 4-Chloro-4'-Hydroxydiphenyl Sulfone in DMSO-d_6

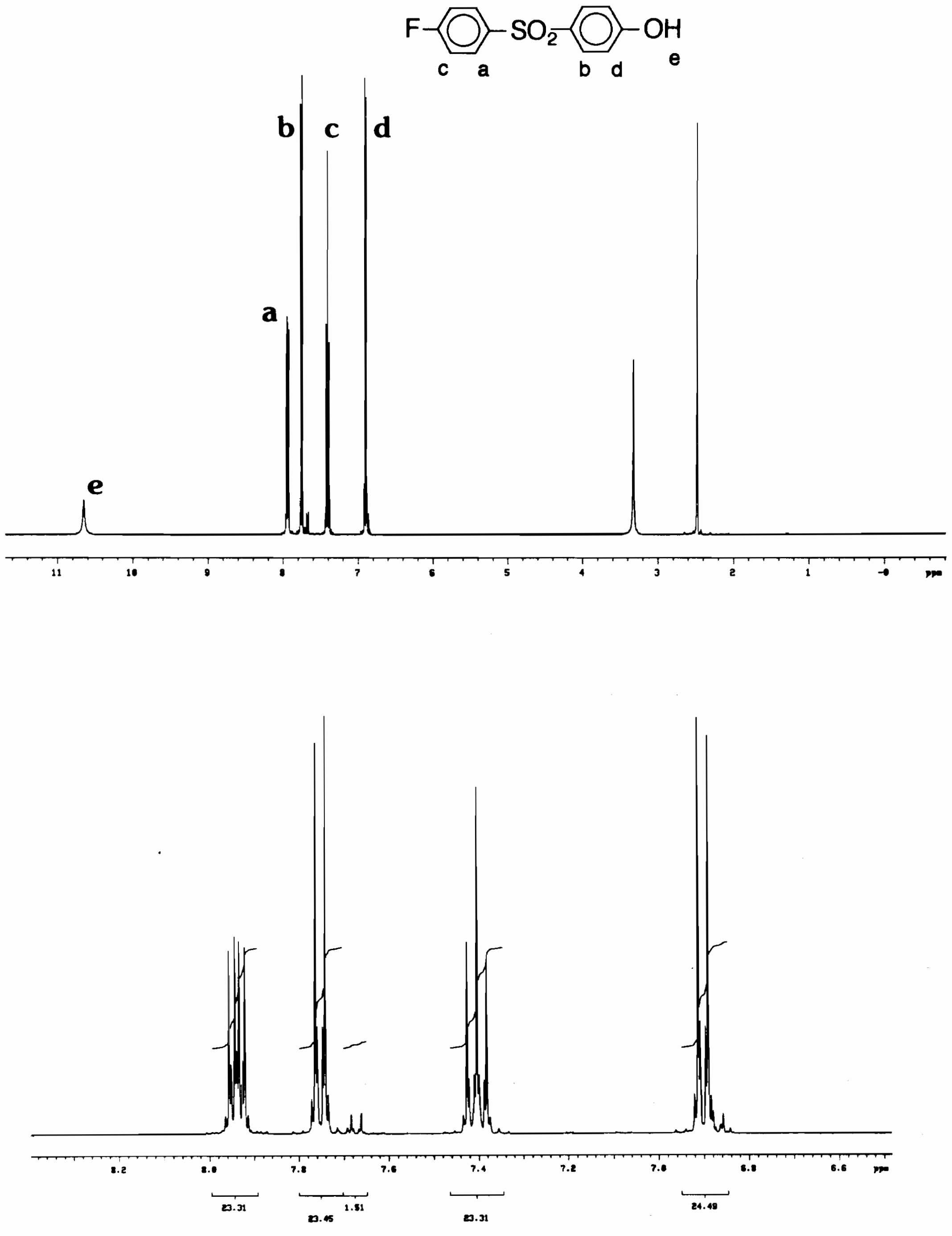


Figure 4.2 ^{1}H-NMR of 4-Fluoro-4'-Hydroxydiphenyl Sulfone in DMSO-d_6

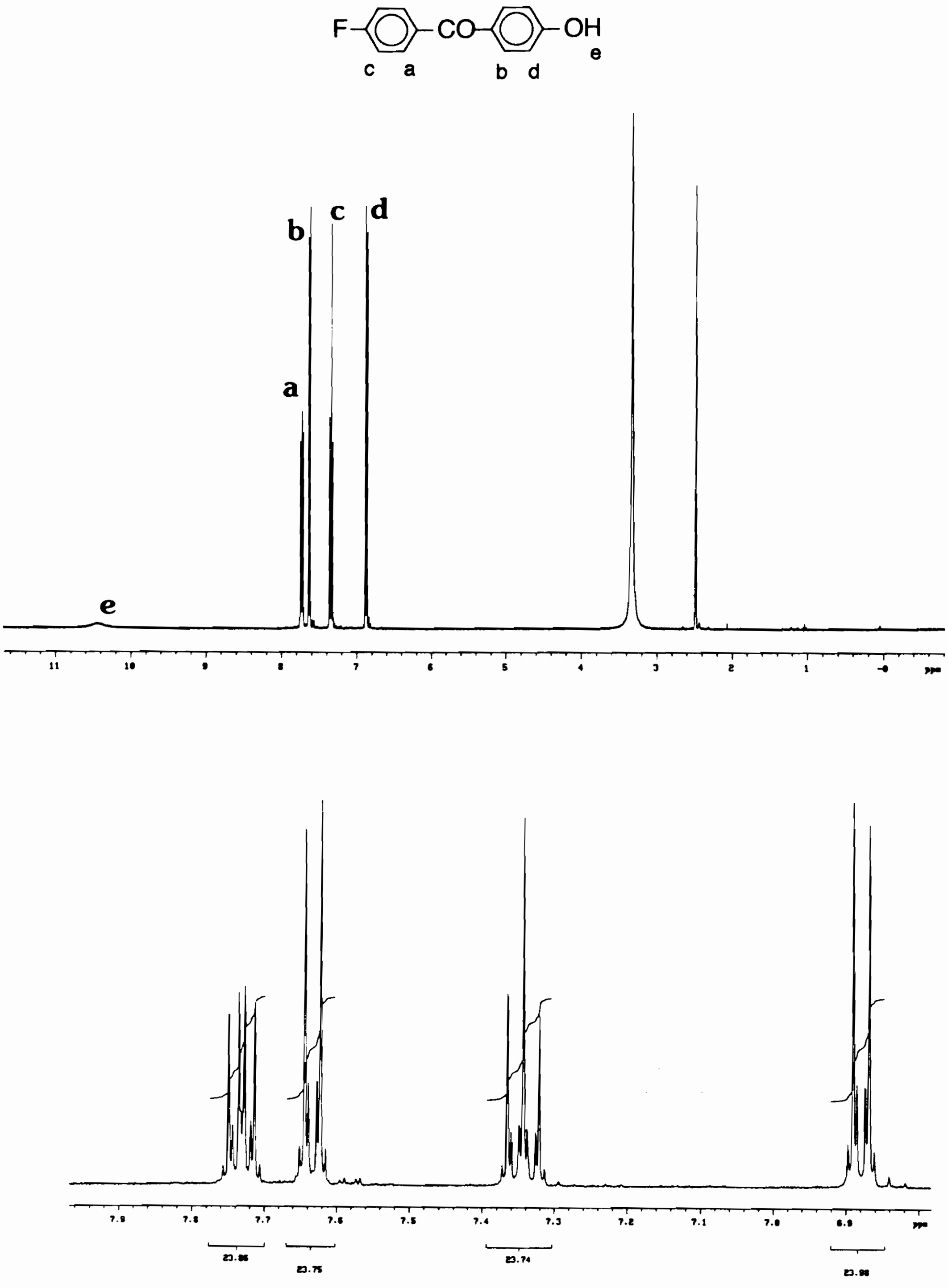


Figure 4.3 ^{1}H-NMR of 4-Fluoro-4'-Hydroxybenzophenone in DMSO-d_6

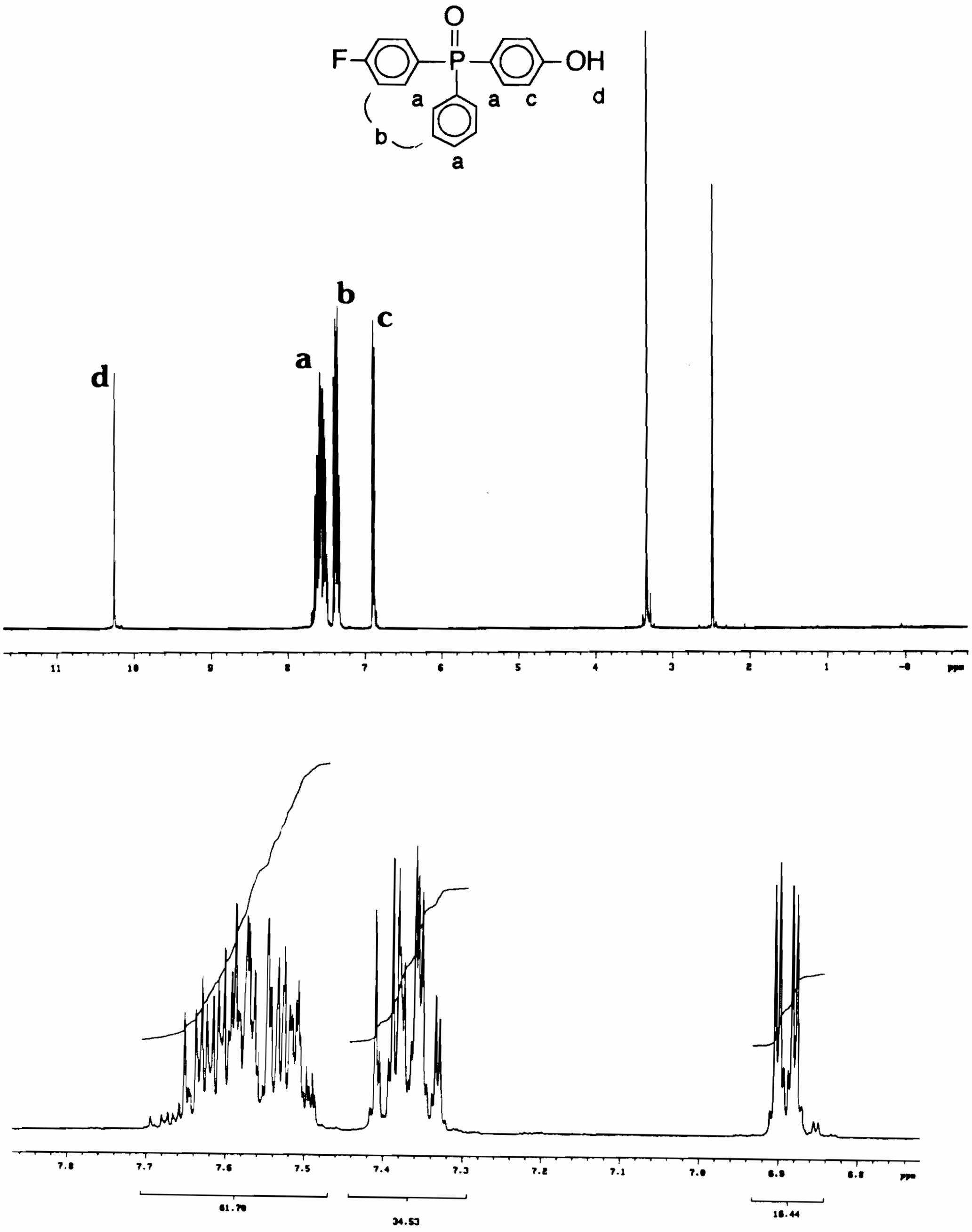


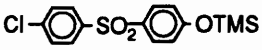
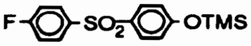
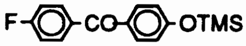
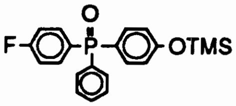
Figure 4.4 ^{1}H-NMR of 4-Fluoro-4'-Hydroxydiphenyl Phenyl Phosphine Oxide in DMSO-d$_6$

The reaction temperatures listed in Table 4.1 were actually the oil bath temperatures. Therefore, the real temperatures for the hydrolysis reactions are considered to be about 5~10°C lower. From this data, it can be concluded that the activated dihalides are very easily hydrolyzed by the hydroxide anion. Several reaction temperatures such as 95°C, 85°C and 70°C were investigated. Virtually all of these reactions afforded similar yields under similar reaction conditions. This suggested that temperature was not an influence on the yield as long as it was not too high. In fact, the temperature mainly influences the purity of the halogenophenols.

4.1.2 Silylated Halogenophenols

Silylation of halogenophenols is a relatively simple reaction and vacuum distillation is the best way to purify the product. Halogenophenols are solid materials, but the silylated halogenophenols are liquid at room temperature(Table 4.2).

Table 4.2 Silylated halogenophenols

Silyted Halogenophenol	Reaction			
	T(°C)	t(hrs.)	yield(%)	mp(°C)
 (Si-CHDPS)	110	24	99	*
 (Si-FHDPS)	110	24	95	*
 (Si-FHBP)	110	24	93	*
 (Si-FHPPO)	110	24	99	*

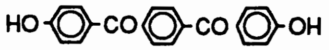
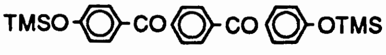
* Viscous fluid at room temperature

As described in Section 3.22, the silyl derivatized monomers such as the Si-FHDPS and Si-FHBP were purified by vacuum distillation at high temperatures. However, it was found that sometimes these two AB monomers might self-initiate the polymerization during the purification process. If these two silylated monomers were purified once by vacuum distillation, the self-initiated polymerization reaction did not take place at elevated temperatures without the catalyst present. The purified monomers were colorless. (Si-FHBP develops a light yellow color about one day later). If they were exposed to the air for about two hours or more, the liquid monomers slowly changed to solid forms, which were corresponding to the hydrolyzed phenolic derivatives. The other two silylated compounds, Si-FHPPO and Si-CHDPS, were not able to be purified by vacuum distillation due to their high boiling points. Therefore, they were used without further purification. When the Si-FHPPO was exposed to air, it changed to a white solid within a short time (5-10min). Figures 4.5 through 4.8 are the ^{1}H-NMR spectra of these four silylated monomers.

4.1.3 1,3 & 1,4-Bis(4-hydroxybenzoyl) Benzene (BHBB) and 1,3 &1,4-Bis(4-trimethyl siloxy benzoyl) Benzene (Si-BHBB)

The bis(4-hydroxybenzoyl)benzene (BHBB) was mainly generated via hydrolysis of bis(4-fluorobenzoyl)benzene (BFBB). Since the fluorines of BFBB are separated by two ketone groups, upon hydrolysis, each site has no influence on the other site. Therefore, the major products were BHBB (Table 4.3). The relatively low yield of BHBB is due to a large quantity of water was used for the reactions (ie. Large water present limits the reaction temperatures and the solubility of BFBB in DMSO). As discussed in the section

Table 4.3 Bis(4-hydroxybenzoyl) benzene and bis(4-trimethyl siloxy benzoyl) benzene

Monomer	Reaction			
	T(°C)	t(hrs.)	yield(%)	mp(°C)
 (1,4-BHBB)	110	30	75	>260
 (1,3-BHBB)	110	30	60	213-214
 (Si-1,4-BHBB)	110	24	85	126-127
 (Si-1,3-BHBB)	110	24	81	*

* Viscous fluid at room temperature

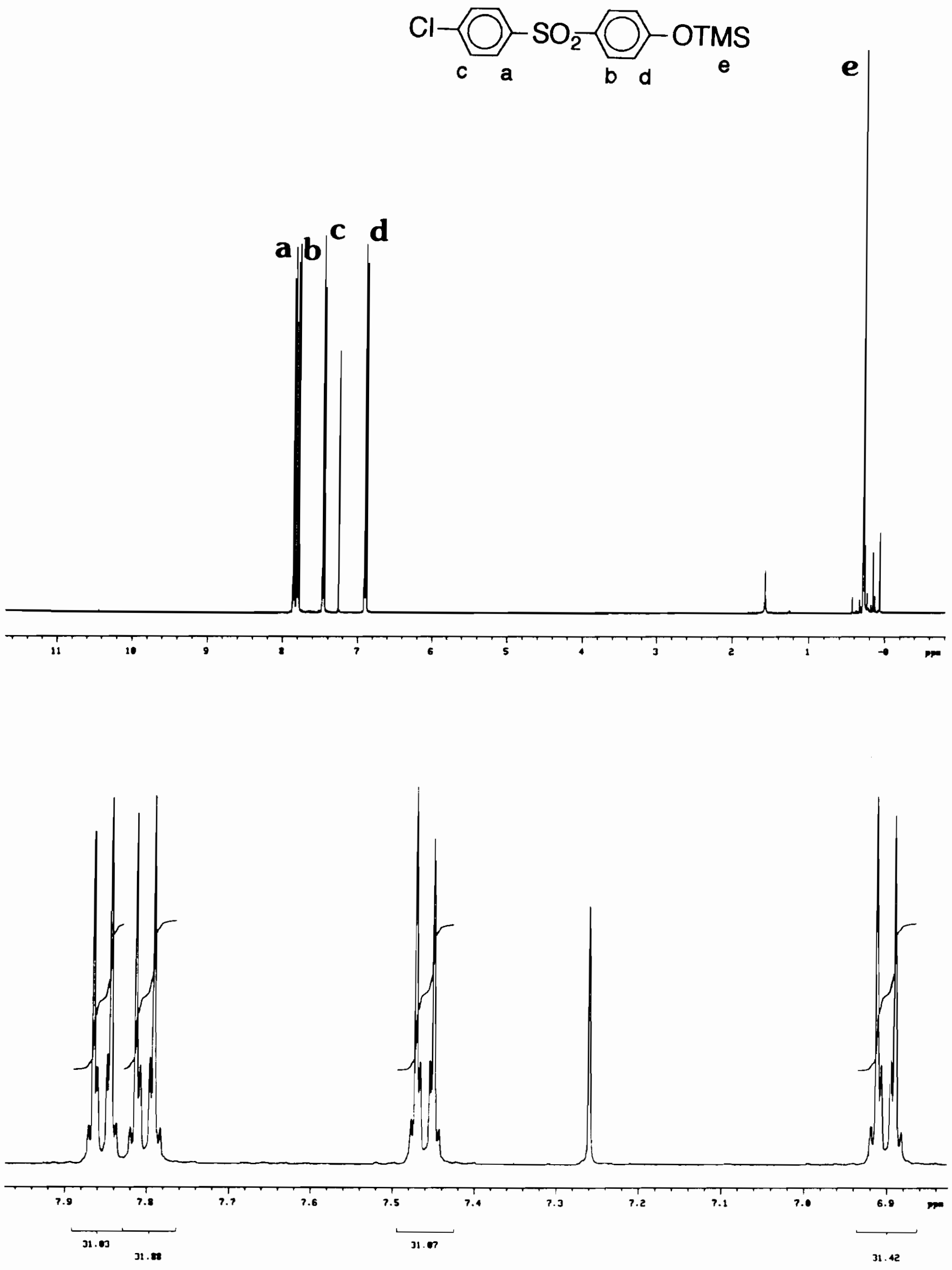


Figure 4.5 ^{1}H-NMR of 4-Chloro-4'-Trimethylsiloxydiphenyl Sulfone in $CDCl_3$

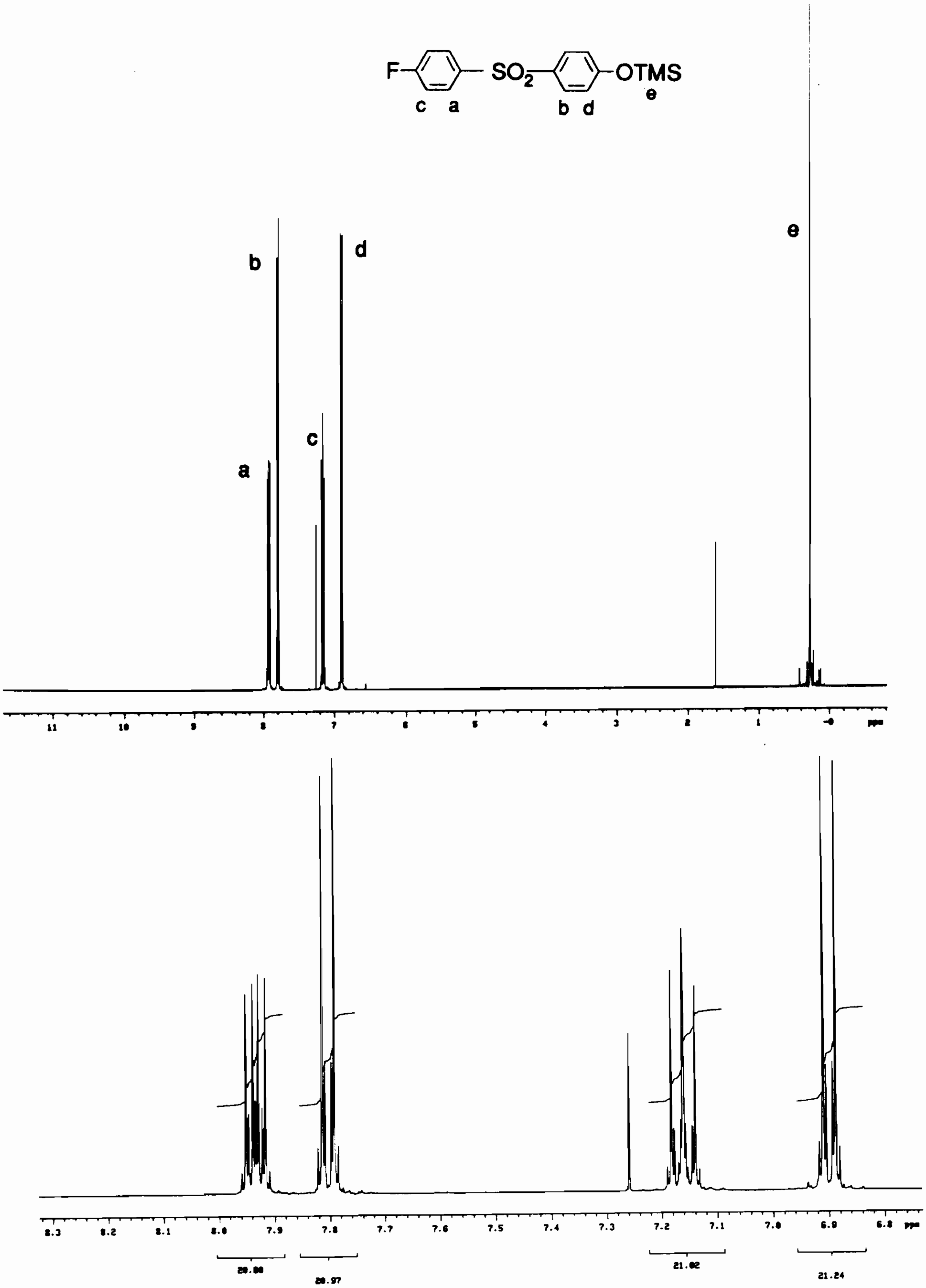


Figure 4.6 ^{1}H-NMR of 4-Fluoro-4'-Trimethylsiloxydiphenyl Sulfone in $CDCl_3$

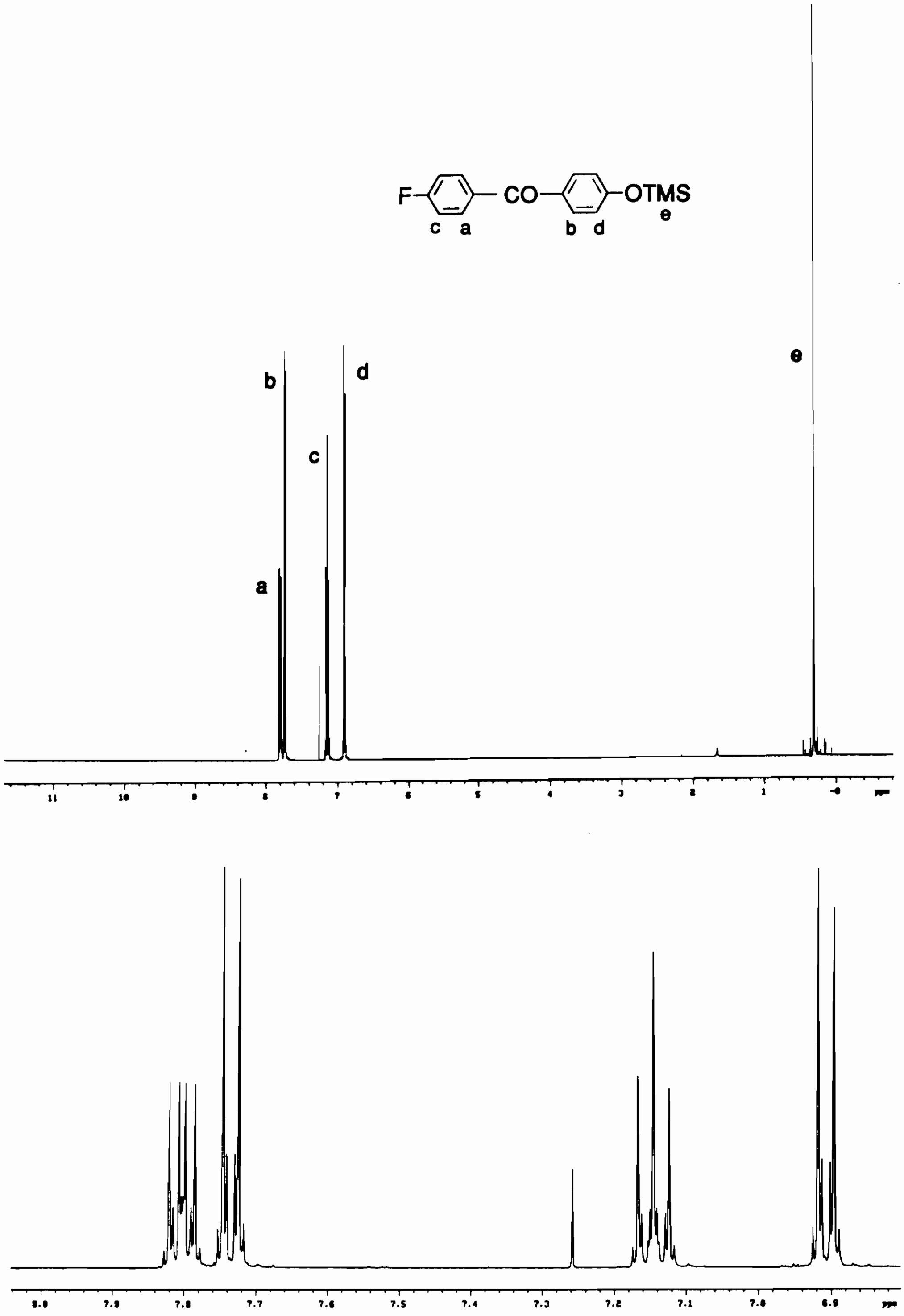


Figure 4.7 ^{1}H-NMR of 4-Fluoro-4'-Trimethylsiloxybenzophenone in $CDCl_3$

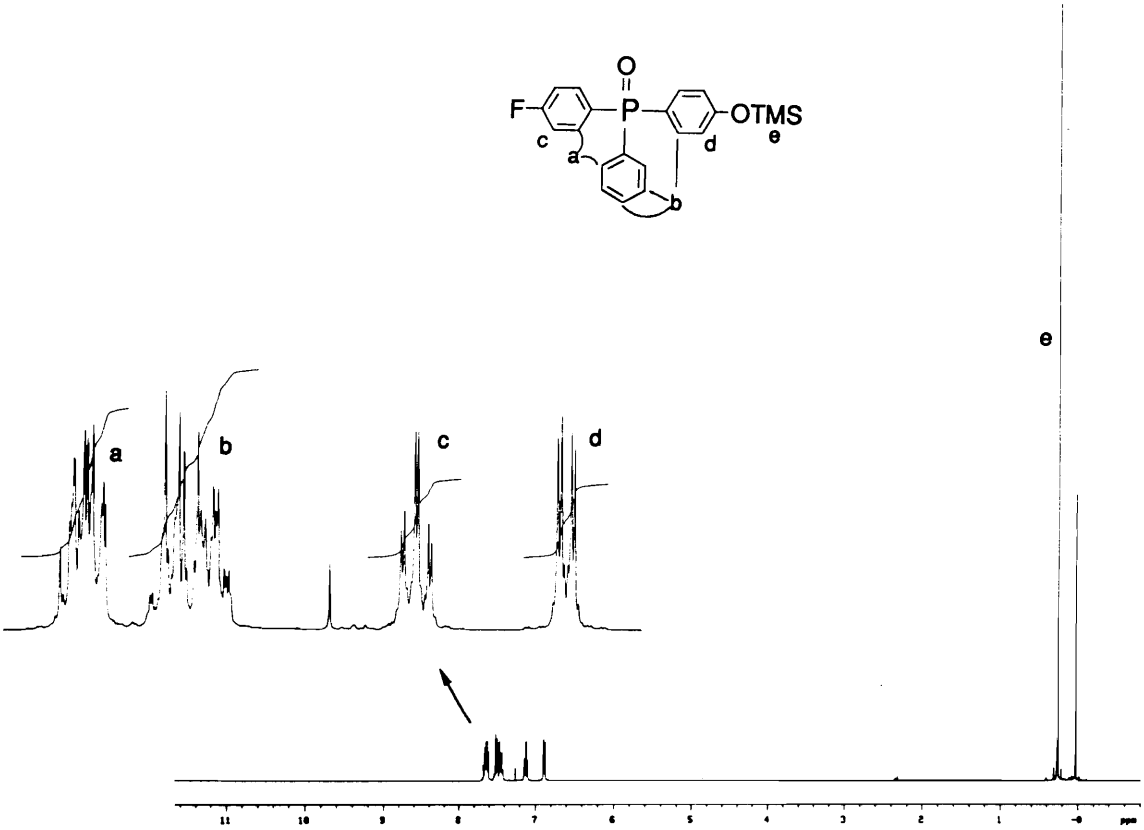


Figure 4.8 ^{1}H-NMR of 4-Fluoro-4'-Trimethylsiloxydiphenyl Phenyl Phosphine Oxide in CDCl$_3$

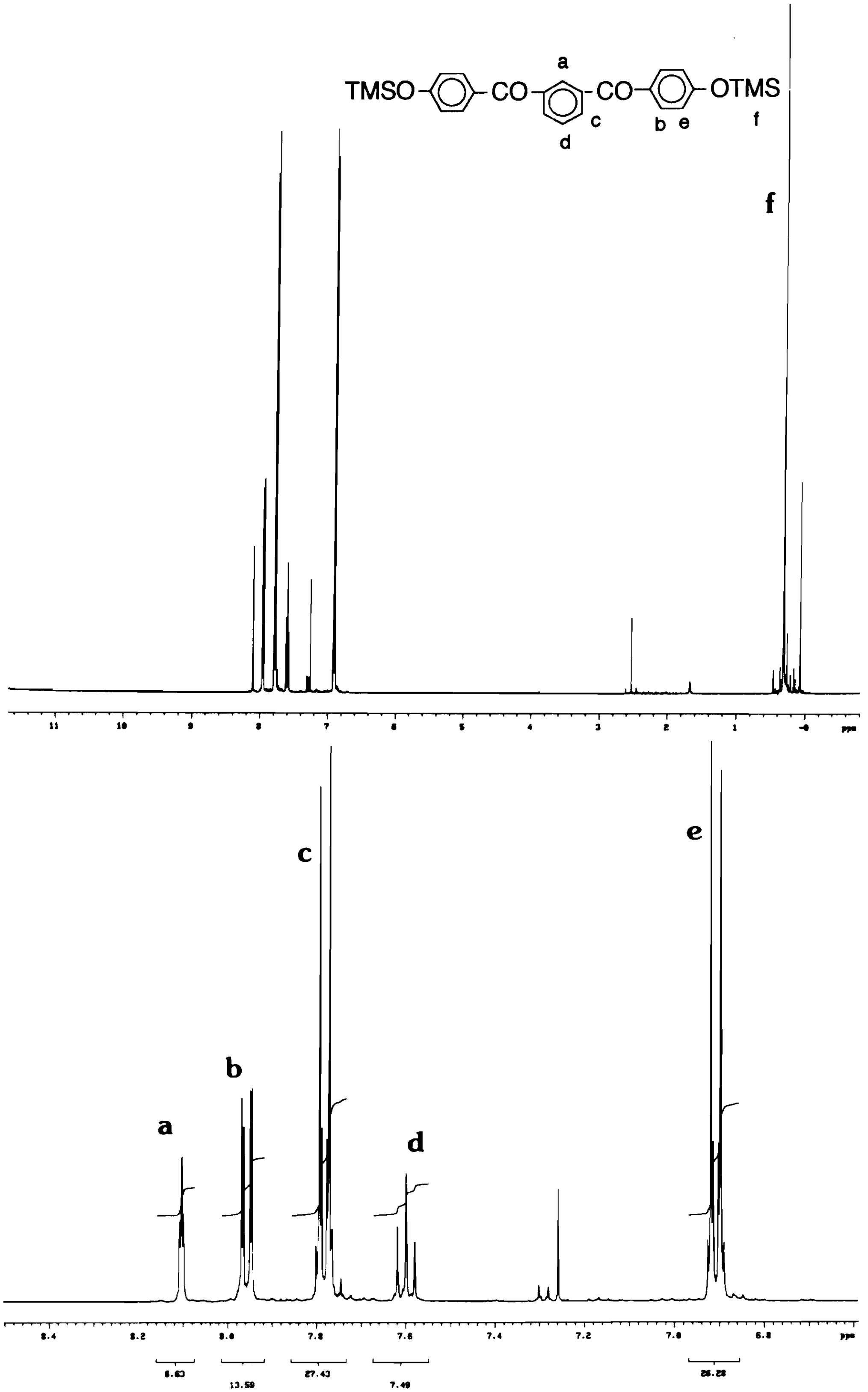


Figure 4.9 ^{1}H-NMR of 1,3-Bis(4-trimethylsiloxybenzoyl)Benzene in $CDCl_3$

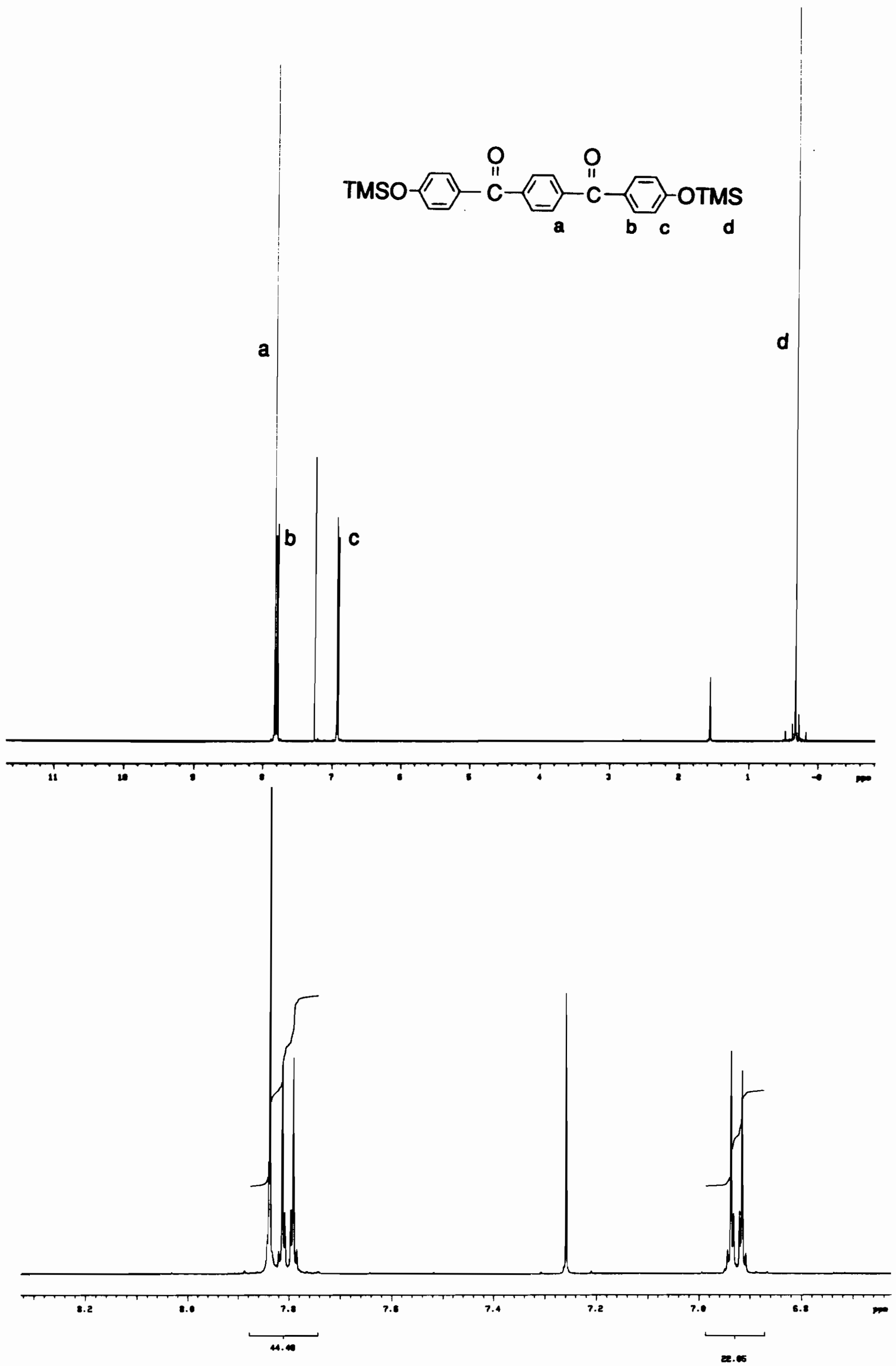


Figure 4.10 ^{1}H-NMR of 1,4-Bis(4-trimethylsiloxybenzoyl)Benzene in $CDCl_3$

4.11, the yields of BHBB can be improved by increasing the DMSO quantity and reducing the water content. The silylated forms of BHBB have high boiling points, which limit the purification by normal vacuum distillation. However, Kugelrohr distillation or sublimation can be used to obtain pure products as shown in Fig. 4.9 and 4.10 At room temperature, the silylated 1,3-Si-BHBB is a very viscous fluid and 1,4-Si-BHBB is a solid.

4.1.4 Tris(4-fluorophenyl) Phosphine Oxide (TFPPO)

TFPPO was synthesized via a Grignard reagent route. Both the TFPPO and its intermediate, tris(4-fluorophenyl)phosphine, produced needle-like crystals. The ^{1}H-NMR spectra of TFPPO had two groups of peaks (Figure 4.11).

4.1.5 Tris(4-hydroxyphenyl)Phosphine Oxide (THPPO)

THPPO was also synthesized via a Grignard reagent route. The cleavage of the methyl group of the tris(4-methoxyphenyl)phosphine oxide was conducted in HBr/AcOH Mixture(Scheme 3.6). The overall yield was relatively low(53%). The ^{1}H-NMR spectra of THPPO is shown in Figure 4.12.

4.1.6 2,2',4,4'-Tetra(trimethylsiloxy) Benzophenone

The tetra silylated product is a light colored liquid and its stability in air was similar to or better than the Si-FHBP.

4.1.7 Bis(4-carboxyphenyl) Phenyl Phosphine Oxide (BCPPO)

The synthesis of BCPPO via three reaction steps is shown in Scheme 3.9. The overall yield of the diacid from dichloro phenyl phosphine sulfide was about 60% as discussed in Section 3.2.8. The ^{1}H-NMR spectra of BCPPO is shown in Figure 4.13

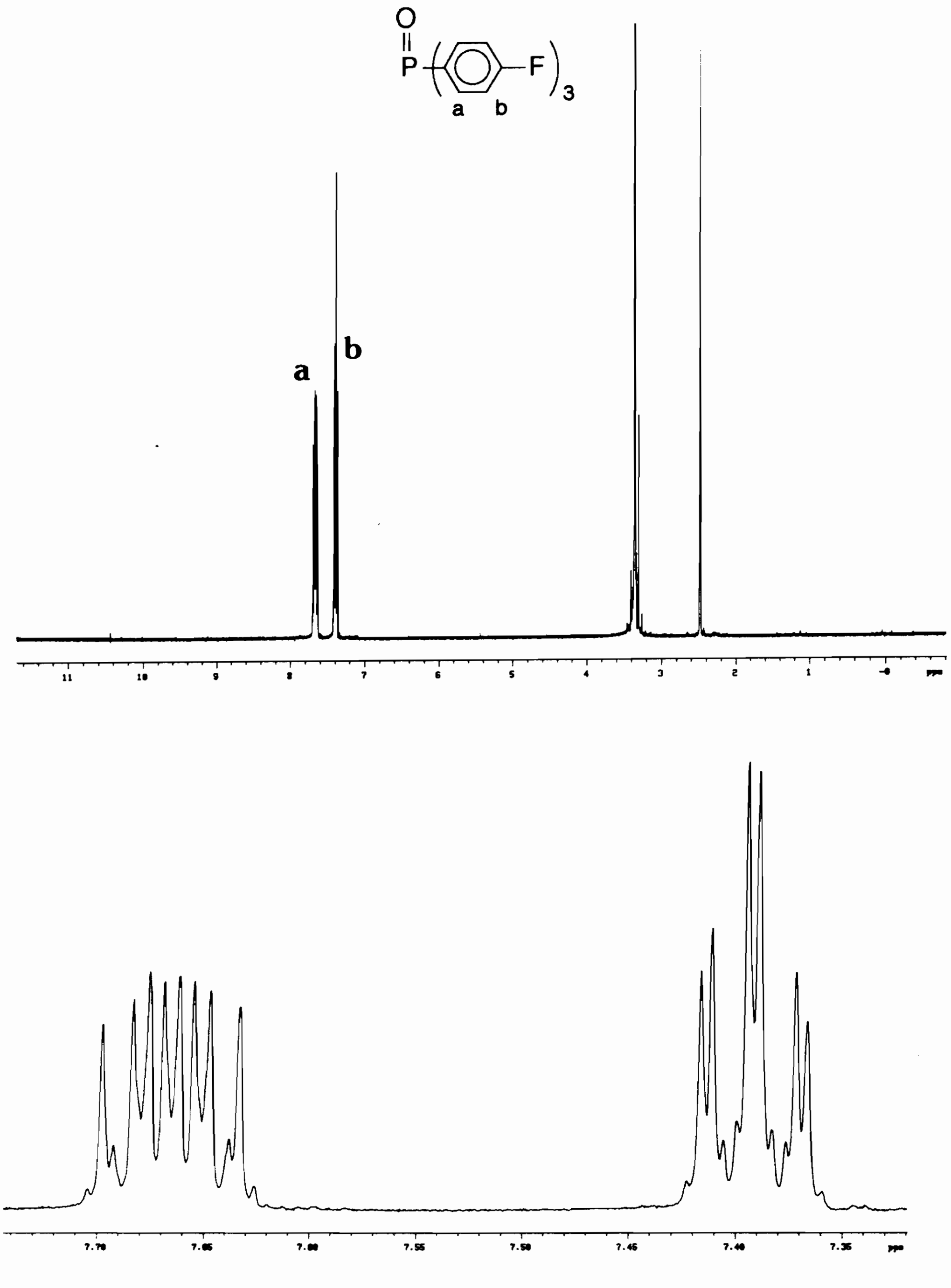


Figure 4.11 ^{1}H-NMR of Tris(4-fluorophenyl)Phosphine Oxide in DMSO-d6

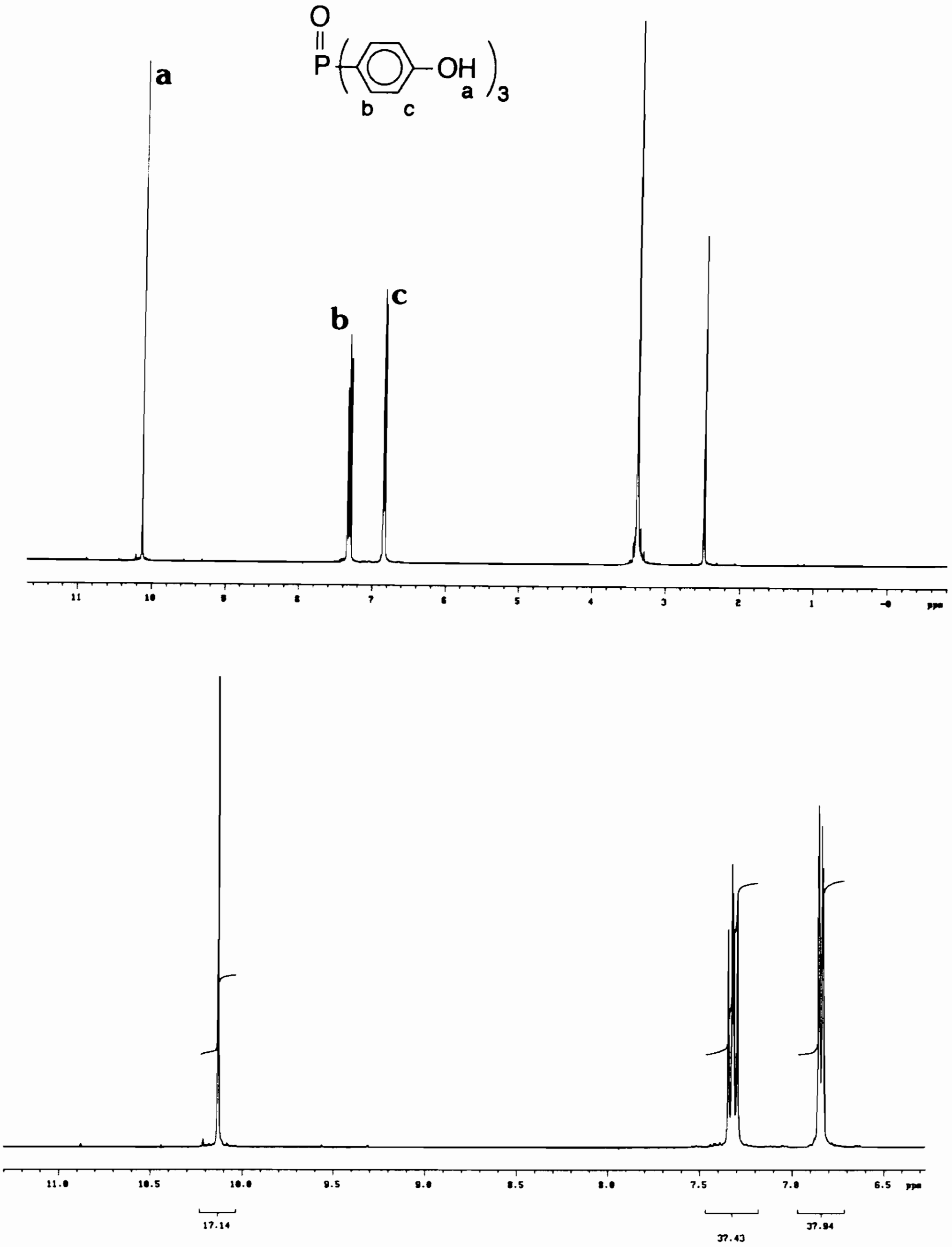


Figure 4.12 ^{1}H-NMR of Tris(4-hydroxyphenyl)Phosphine Oxide in DMSO-d6

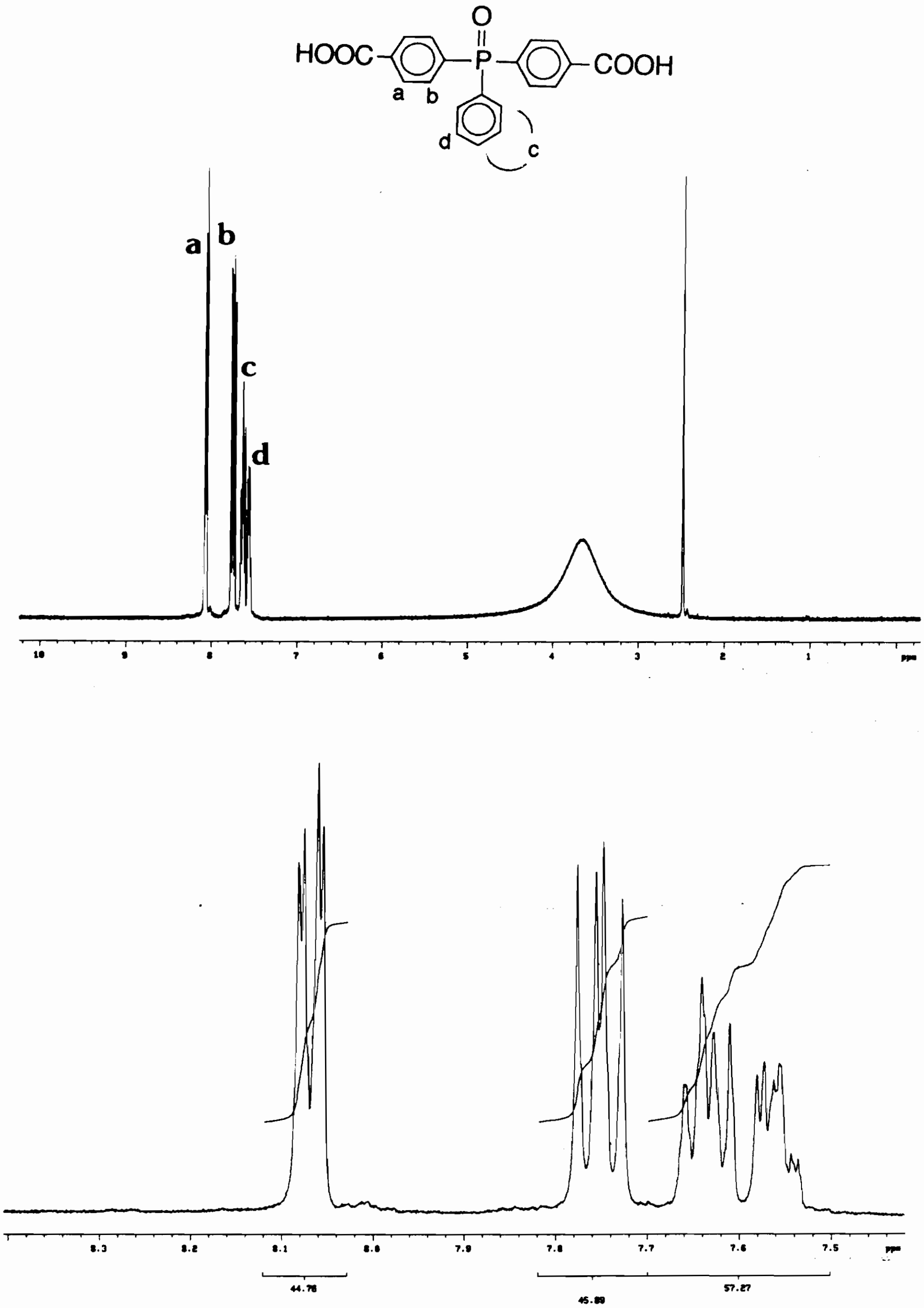


Figure 4.13 ^{1}H-NMR of Bis(4-carboxyphenyl)Phenyl Phosphine Oxide in DMSO-d6

4.2.1 Synthesis and Characterization of Homo-Poly(arylene ether)s via AB Type Silylated Monomers

The silylated monomer Si-FHPPO is very easily hydrolyzed back to halogenophenol when exposed to air. During the polymerization reaction and under Ar or N_2 flow, it was noticed that sometimes a small portion of the Si-FHPPO changed from fluid to white solid. The solid was the hydrolyzed product (halogenophenol) as indicated by NMR. This limited the polymerization to low molecular weight. The TGA & DSC traces of PEPO are shown in Figures 4.14 and 4.15. The char yield in air at 800°C was 22 wt%, and its 5% weight loss temperature was 571°C. The PEPO homopolymer is an amorphous material with a Tg at 233°C and it can be dissolved in many solvents such as chloroform, NMP and DMSO.

Table 4.4 Characterization of poly(arylene ethers) synthesized from AB silylated monomers

Monomer	IV[1]	Tg[2](°C)	Tm[2](°C)	TGA[3](°C)	Polymer
Si-FHDPS	0.58	230	no	532	PES
Si-FHBP	–	155	360		PEK
Si-FHPPO	0.28	233	no	571	PEPO

1. in NMP at 25°C 2. 2nd heat of DSC 10°C/min 3. 5 wt% loss in air 10°C/min

For the PEK synthesis, the resulting polymer produced a powder like material at 340°C. This semi-crystalline powder has a Tg of 155°C, a Tm at 360°C and does not dissolve in common solvents. The Si-CHDPS was found to be non-reactive since the reaction product basically was still the starting monomer. On the other hand, the fluorinated monomer was quite reactive. It was noticed that the fluorotrimethylsilane was evolved when the reaction temperature reached 220~230°C for the polymerization of Si-

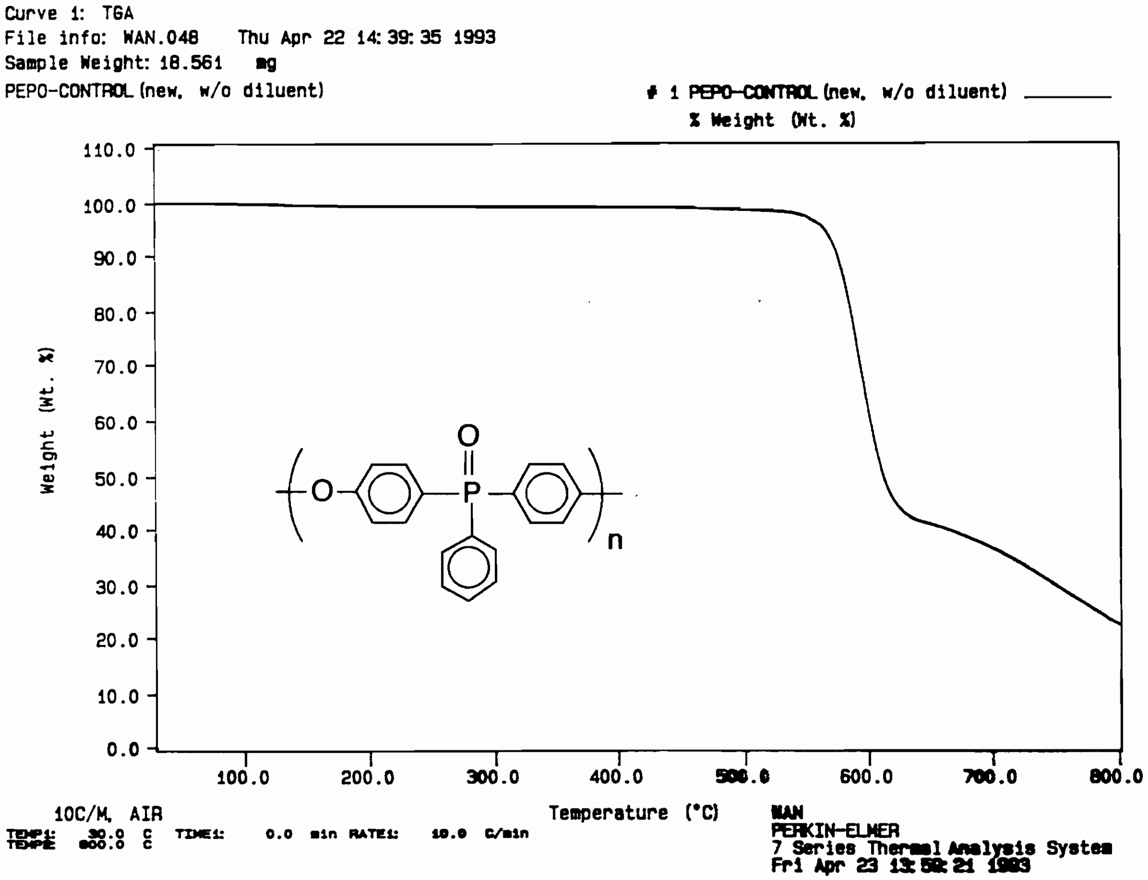
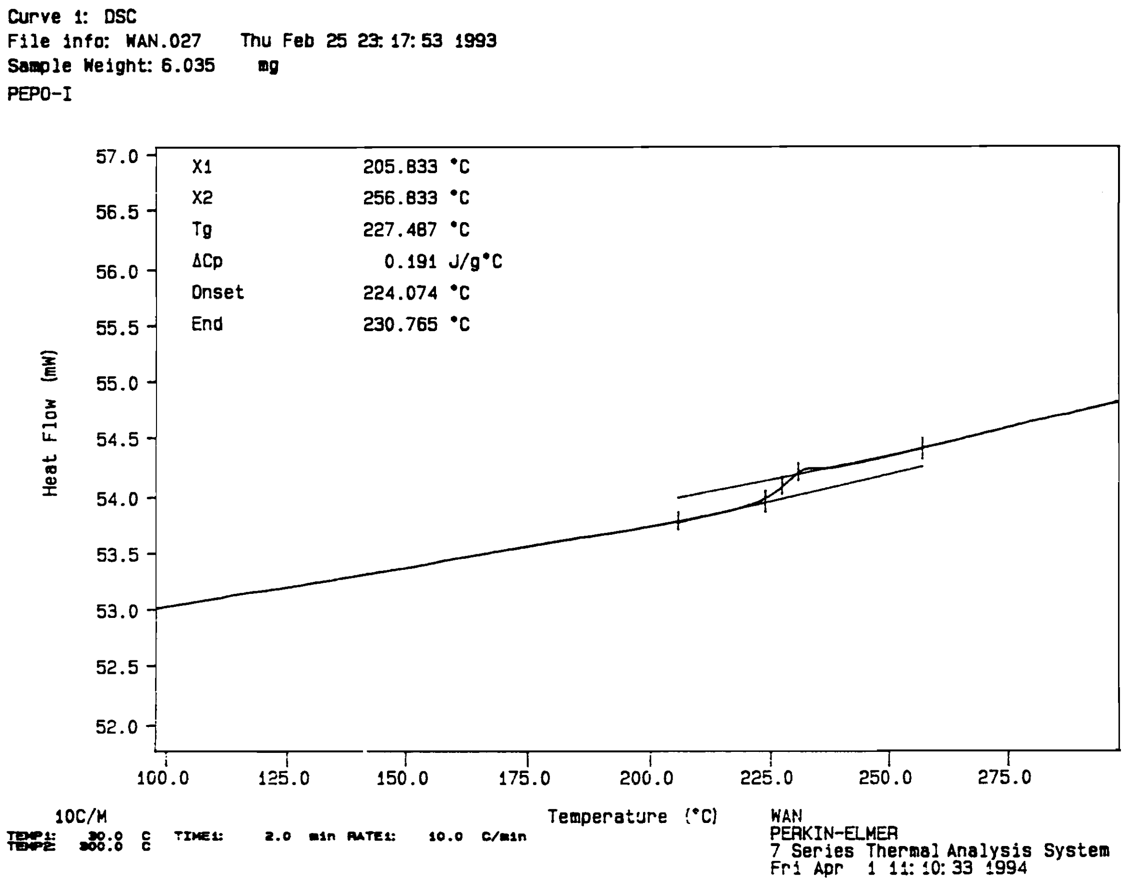


Figure 4.14 Dynamic TGA thermograms in air of PEPO homopolymer



```
Curve 1: DSC
File info: WAN.027    Thu Feb 25 23:17:53 1993
Sample Weight: 6.035    mg
PEPO-I

X1          205.833 °C
X2          256.833 °C
Tg          227.487 °C
ΔCp           0.191 J/g°C
Onset       224.074 °C
End         230.765 °C

10C/M
TEMP1:   30.0  C  TIME1:    2.0  min RATE1:   10.0  C/min
TEMP2:  300.0  C

WAN
PERKIN-ELMER
7 Series Thermal Analysis System
Fri Apr  1 11:10:33 1994
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Figure 4.15 DSC trace of PEPO homopolymer

FHDPS. The recovered PES polymers had a fraction that was not soluble in boiling chloroform. It ihas been reported that crosslinking can take place if the reaction time is long at high temperatures [24]. This crosslinking mechanism has been proposed by Attwood et.al. for PES synthesized via the nucleophilic route [26, 60] (Scheme 2.5). The insoluble gel fraction of PES from the silyl ether displacement reaction might be generated via the same mechanism as proposed in the literature[60]. Characterization data of poly(arylene ethers) prepared via AB silylated monomers are shown in Table 4.4.

4.2.2 Synthesis and Characterization of Star-Branched Poly(arylene ether)s via AB type Silylated Monomers

Star-branched PAEs were synthesized by either a one step or two step process. For the one step process, the branching reagent was added at the beginning of the polymerization and the resulting polymers were randomly star-branched. In the two step process, a certain length of PEPO was controlled by using a monofunctional monomer, then the branching agent was used to obtain (ideally) a 4-arm PEPO. (Scheme 3.10)

Characterization data for the branched PAEs are shown in Table 4.5. The 3-arm PES and PEPO were prepared via the one step process and the 4-arm PEPO was synthesized by the two step reaction. The 2-arm(linear) PEPO was the product of the first step of the two step reaction. The 3-Arm PES has a very high intrinsic viscosity. When it was worked up after the polymerization reaction (i.e., dissolved in boiling chloroform), a very large portion(35~40%) of the polymer was not soluble in chloroform. This insoluble part appeared to be swelling in the chloroform. The recovered soluble fraction has an intrinsic viscosity of about 0.61 in NMP. The Tg of this branched PES specimen was 236°C. Figure 4.16 and 4.17 show the TGA and DSC traces of the branched PES, with a calculated number average molecular weight 23,000g/mole.

Table 4.5 Star-branched poly(arylene ether)s via AB type silylated monomers

Polymer	arm	<Mn>$_{theor.}$	IV[1]	TGA[2]	Tg	GPC	
						<Mn>	<Mw>
PEPO	2	control	0.28	571	233		
PEPO	2	5K	0.18	563	211	7.2K	14.0K
PEPO	2	7.5K	0.16	551	212		
PES*	3	23K	0.61	537	236		
PEPO	3	30K		564	227		
PEPO	4	20K	0.22	566	221	10.1K	21.4K
PEPO	4	30K	0.21	564	220		

1. in NMP at 25°C   2. 5% weight loss in air

* soluble fraction only; partially gelled

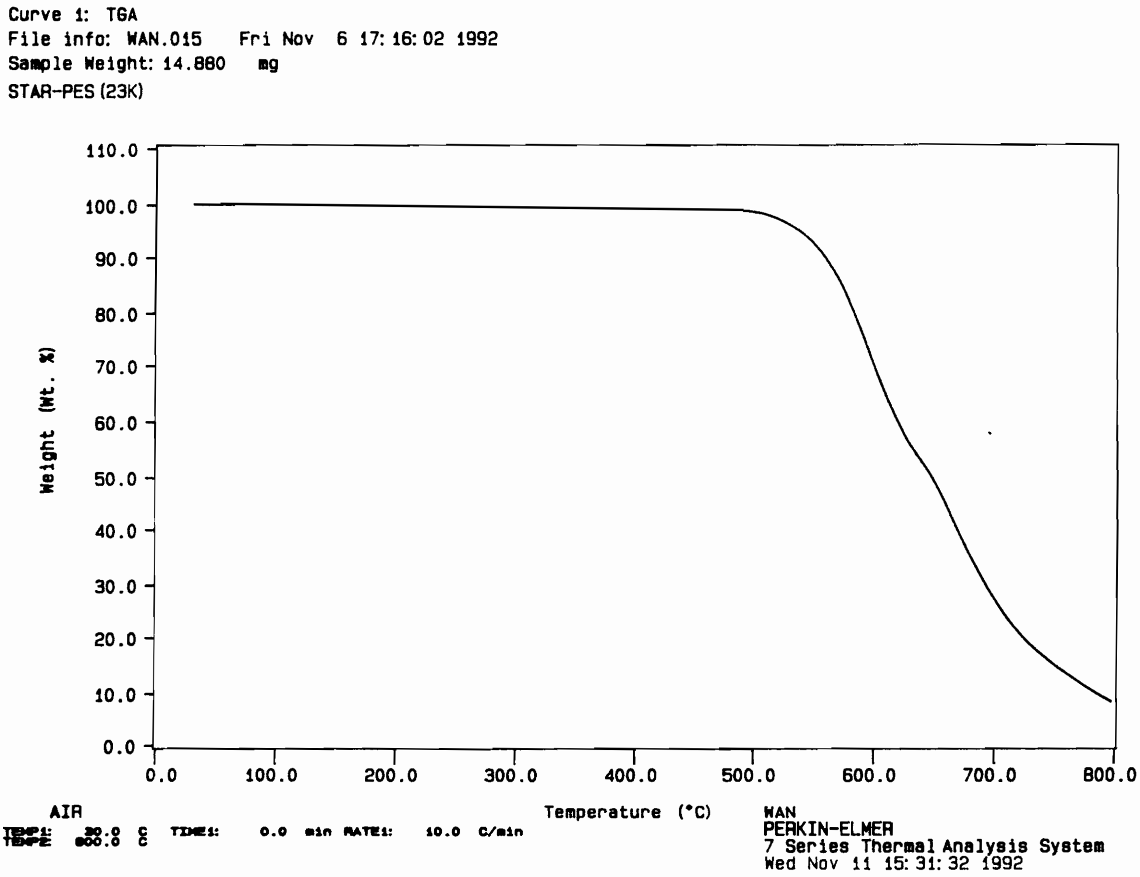
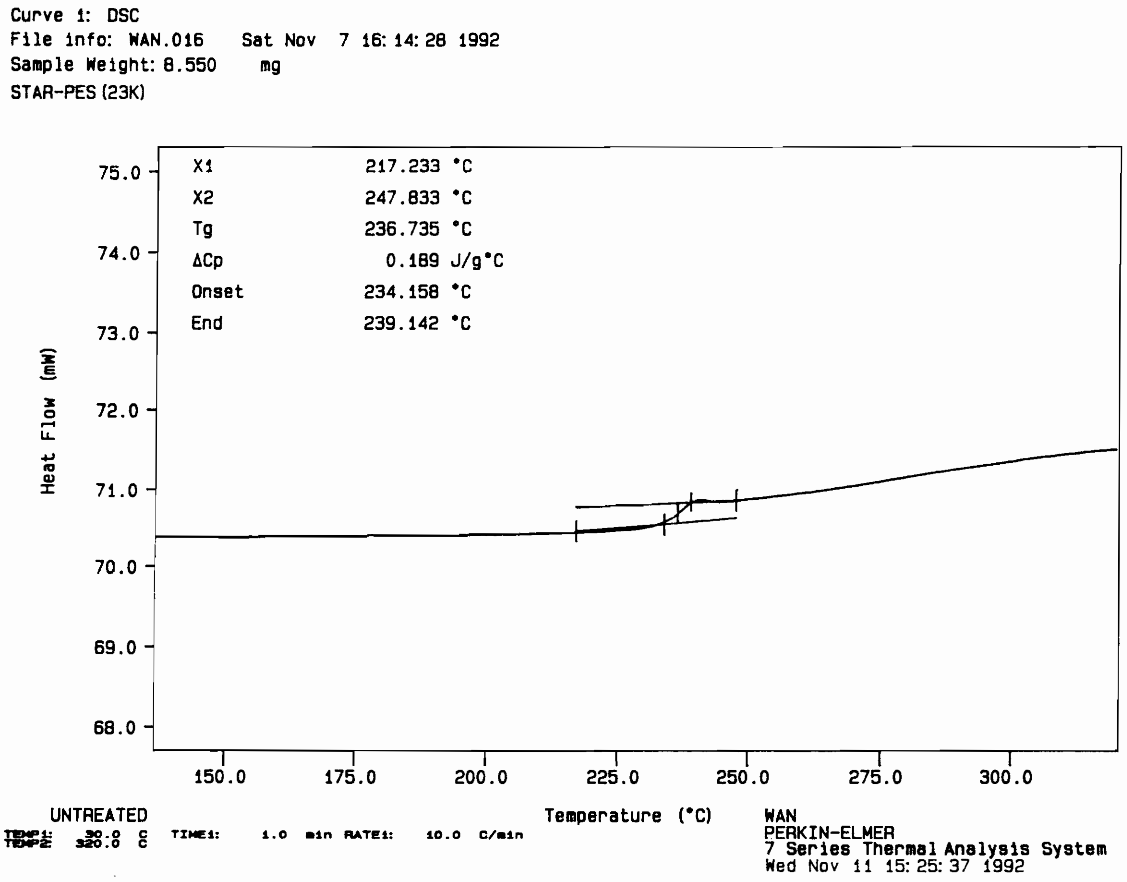


Figure 4.16 Dynamic TGA thermogram in air of the 3-arm branched PES



Curve 1: DSC
File info: WAN.016 Sat Nov 7 16:14:28 1992
Sample Weight: 8.550 mg
STAR-PES (23K)

X1	217.233 °C
X2	247.833 °C
Tg	236.735 °C
ΔCp	0.189 J/g°C
Onset	234.158 °C
End	239.142 °C

UNTREATED
TEMP1: 30.0 C TIME1: 1.0 min RATE1: 10.0 C/min
TEMP2: 320.0 C

WAN
PERKIN-ELMER
7 Series Thermal Analysis System
Wed Nov 11 15:25:37 1992

Figure 4.17 DSC trace of the 3-arm branched PES

The intrinsic viscosity of the 4-arm PEPO was just slightly higher than the first step product, 2-arm PEPO. This result may be due to incomplete reaction, decomposed branching agent or again decomposed starting material(AB monomer). In addition, the topology of the polymers may also have some influence on the intrinsic viscosity (i.e. hydrodynamic volume relative to the linear counterpart)

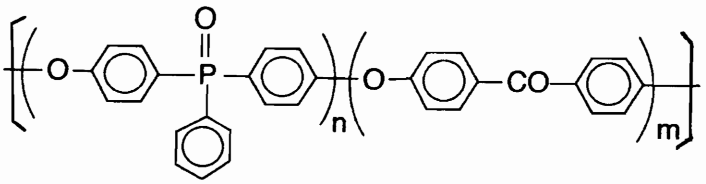
4.2.3 Random and Block PEK/PEPO Copolymers via AB Type Silylated Monomers

A random (or statistical) copolymer and a tri-block copolymer were synthesized by using Si-FHBP and Si-FHPPO monomers in a 50/50 molar ratio. Since both monomers are AB type monomers, the stoichiometry for both reactions are not so crucial. The intrinsic viscosity of the random PEK/PEPO copolymer was 0.67 dl/gm in NMP at 25°C. The DSC trace showed that the random copolymer was an amorphous material (Fig 4.18a). From the TGA traces (Fig 4.19), the copolymers appear have good thermal stability and show high char yields even in air.

Table 4.6 Random and tri-block copolymer of PEK–PEPO (50:50 mole%)

Polymer	IV[1]	Tg[2]	Tm[2]	TGA[3]	Char%
Random (PEK/PEPO)	0.67	204	no	557	33
Tri-block (PEK-PEPO-PEK)	—	222(1st) 200(2nd)	353(1st) no (2nd)	564	22

1. in NMP(25°C) 2. DSC (10°C/min) 3. 5 wt% loss in air(10°C/min)



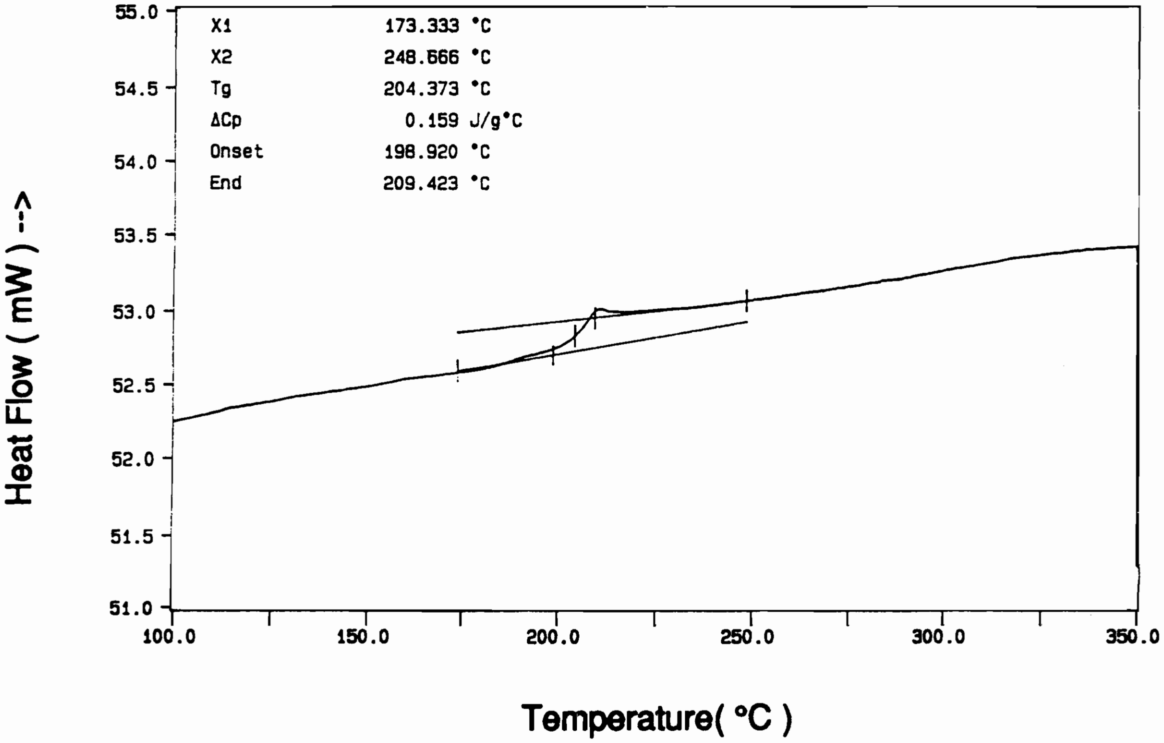


Figure 4.18 a) DSC trace of PEPO/PEK(50/50) random copolymer

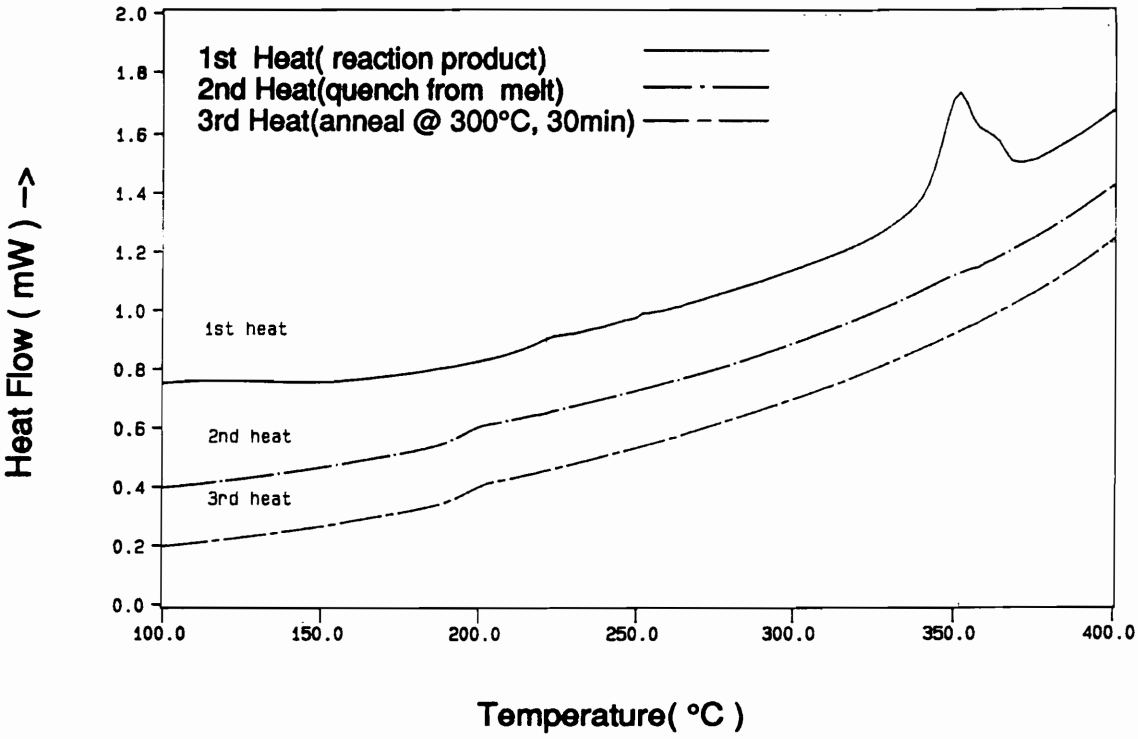


Figure 4.18 b) DSC traces of PEK/PEPO/PEK tri-block copolymers (50 mole% of PEK)

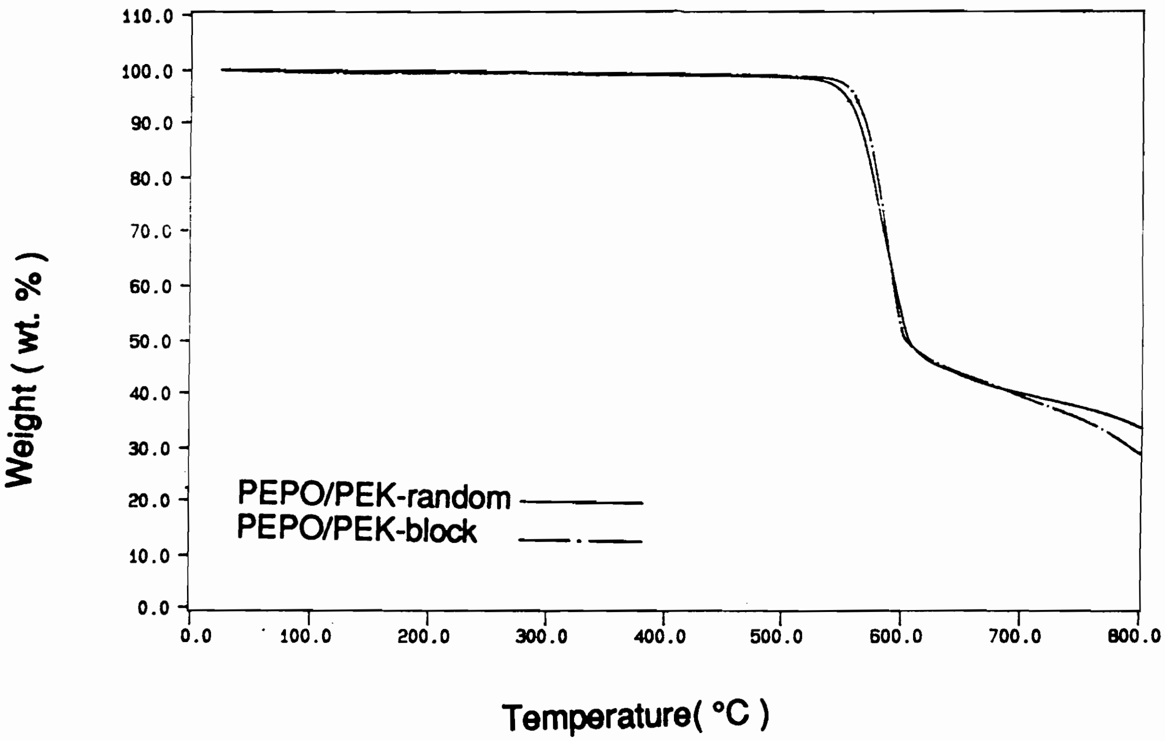


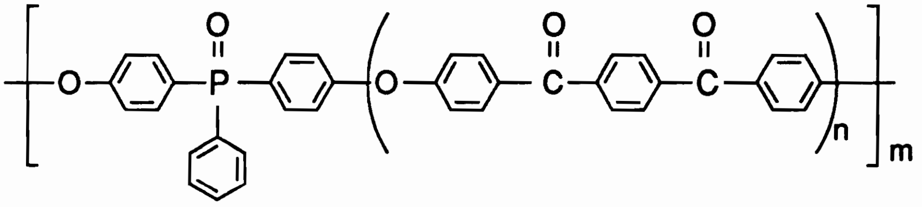
Figure 4.19 TGA traces in air for PEPO/PEK random and tri-block copolymers (50 mole% of PEK)

The tri-block PEK-PEPO-PEK was synthesized in a one pot, two step reaction. The central block was an amorphous PEPO, with a theoretical molecular weight of 15,000g/mole. The two outer PEK blocks have the same total moles as the central block. By the end of the reaction, a solid copolymer was produced in the reactor at 330°C. The TGA trace was also shown in Fig. 4.19. Fig. 4.18b displays the DSC traces of the tri-block copolymer. The first heat of the tri-block copolymer shows a Tg at 222°C and a Tm at 353°C but the 2nd heat(after quench cooling to room temperature) and 3rd heat (after annealing at 300°C for 30 min) only show a Tg at 200°C(Table 4.6). The reason for this observation is that the Tm of homopolymer of PEK is 360~367°C (Table 2.1 and 4.6). The polymerization temperature used for the second step was 330°C, which was lower than the Tm of the PEK segment. Therefore, the outer block (ie. PEK) solidified (or crystallized) during the polymerization. This was the reason why the DSC detected a Tm peak of the tri-block copolymer of the first heat. The Tg at 220°C of the DSC first heat is due to the central PEPO block. Once the temperature is raised above the Tm of the outer block (ie. PEK block), the PEPO and PEK blocks may have phase mixed. This miscible copolymer showed only one Tg at 200°C which is between the Tg of homo-PEK (154°C) and homo PEPO (220~230°C). The crystallinity of the crude product provided solvent resistance to common organic solvents.

4.2.4 Poly(ether phosphine oxide ether ketone ketone) Copolymers(PEPO/EKK)

These PEPO/EKK copolymers were made from AA and BB type monomers; therefore, proper stoichiometry is essential to obtain high molecular weight. The reaction is shown in Scheme 3.12 (Section 3.3.5). Table 4.7 presents the characterization data of the copolymers. As shown in the table, the copolymers with 50 mole% of phosphine oxide incorporation is an amorphous material, which is soluble in NMP but not in

Table 4.7 Solution and thermal characterization of PEPO/EEK copolymers



EPO/EKK	IV[1]	Tg[2](°C)	Tm[2](°C)	TGA[3](5%)	Char% 750°C(air)
50/50	0.41	201	no	550	56
40/60	0.42	200	*	548	63
30/70	—	198	346	542	23
20/80	—	198	377	534	22

* Shows a Tm peak after annealing

1. in NMP(25°C)

2. DSC 1st heat(10°C/min)

3. in air(10°C/min)

DMSO, DMF, DMAc and chlorinated solvents. The copolymers with phosphine oxide content from 20 to 40 mole% incorporation are crystallizable polymers on heating.

The copolymers show good thermal stability and high char yields in air at 750°C (TGA traces shown in Fig 4.20). For example, the 50/50 and 40/60 molar ratio of PEPO/EKK copolymers have char yields values about 56% and 63% respectively. The high char yields suggested that these copolymers may be used as flame-resistant polymeric materials. The DSC traces of the PEPO/EKK copolymers are shown in Figure 4.21. The Tg of the copolymers are around 200°C. The reported Tm was from the lst heat of DSC measurement. A crystalline melting transition of the copolymer at 40/60 composition was detected when the copolymer was annealed.

The silylated monomer used for the reactions shown in Scheme 3.13 was para Si-BHBB. The iso Si-BHBB has also been copolymerized with bis(4-fluorophenyl) phenyl phosphine oxide (BFPPO) at a 50/50 molar ratio. The resulting copolymer has a Tg at 175°C and it undergoes 5% weight loss at 544°C. The char yield was about 39% at 750°C in air and its intrinsic viscosity was 0.24 in NMP at 25°C. This low intrinsic viscosity was likely due to imbalanced stoichiometry. Unlike the para-form of Si-BHBB which is a solid at room temperature, the meta-form of Si-BHBB is a viscous fluid. Therefore, it is more difficult to precisely define the reaction. The DSC trace of the PEPO/iso-EKK with a molar ratio of 50/50 is shown in Fig 4.22.

4.2.5 Perfectly Alternating 1,3 &1,4-Poly(arylene ther ketone ketone) (PEKK)

The all para PEKK has a very high Tm at 391°C (Table 1.1). The corresponding all iso PEKK has a relatively low Tm below 300°C. PEKK is generally synthesized commercially via the electrophilic route. However, in this research, a perfectly alternating para/iso PEKK was synthesized via the silylated bisphenol nucleophlic route.

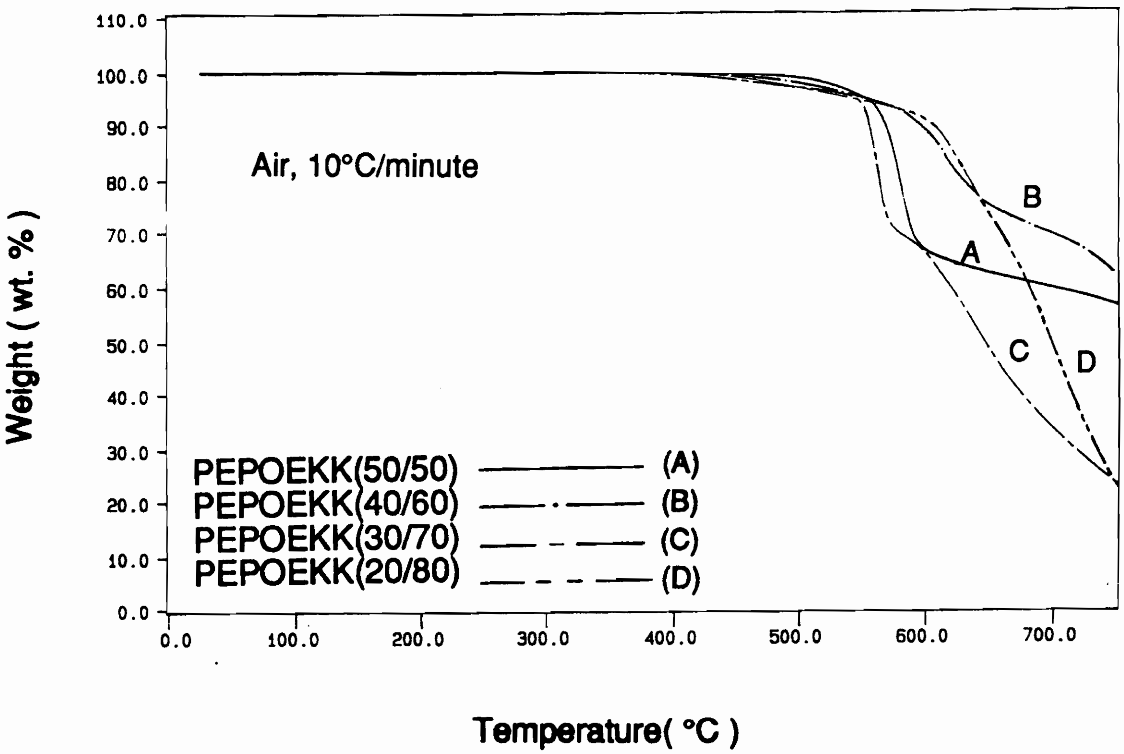


Figure 4.20 Dynamic TGA traces of PEPO/EKK random copolymers in air

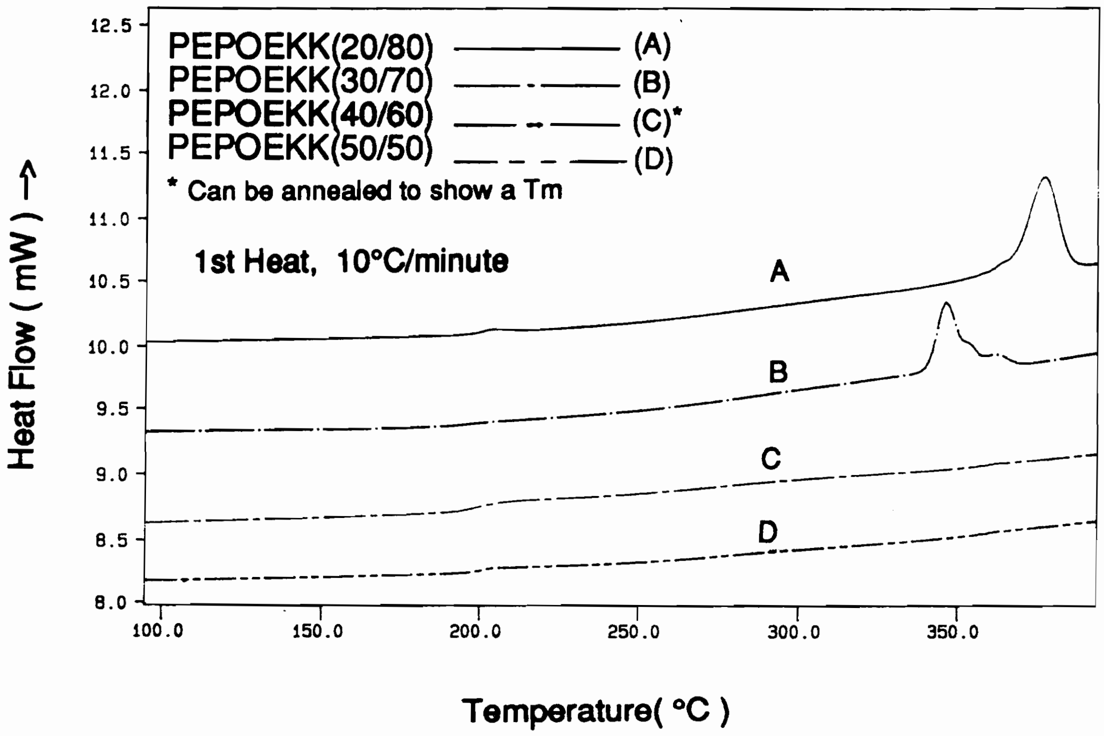


Figure 4.21 DSC traces of PEPO/EKK copolymers

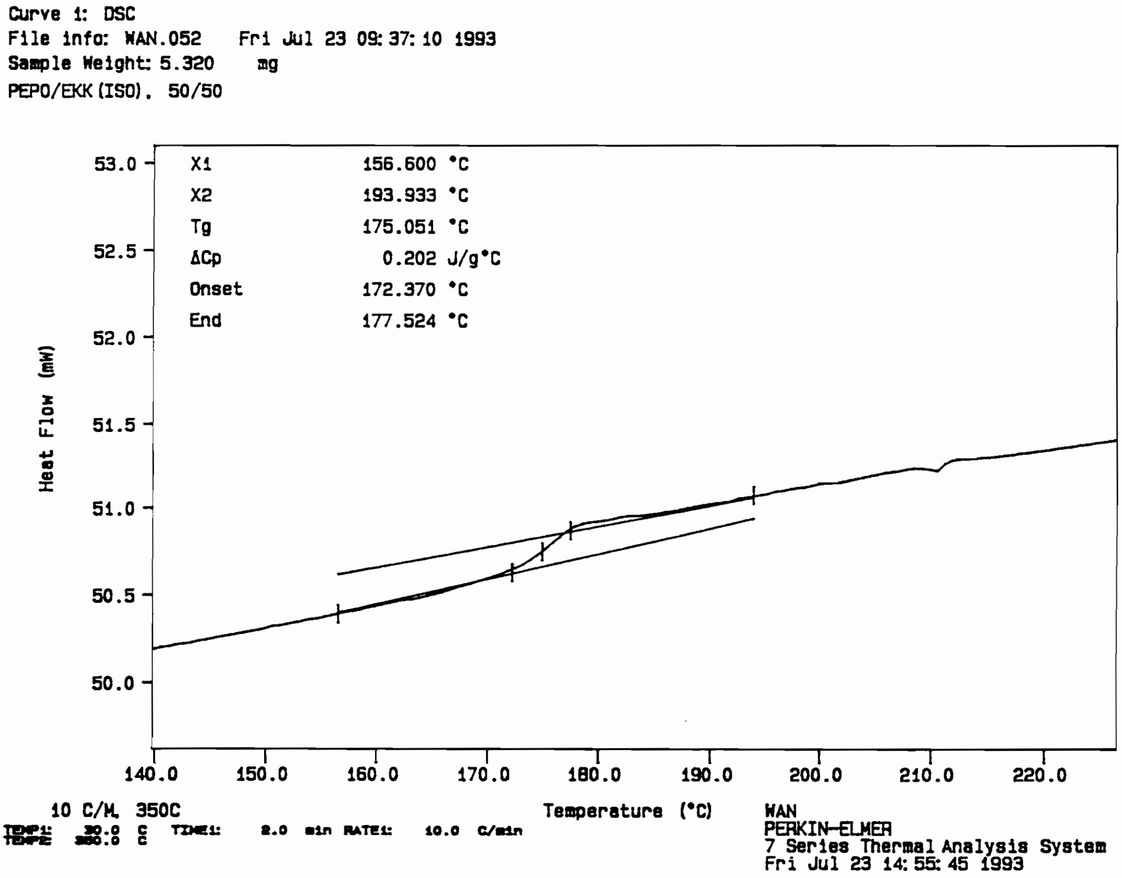


Figure 4.22 DSC trace of PEPO/iso-EKK (50/50) copolymer

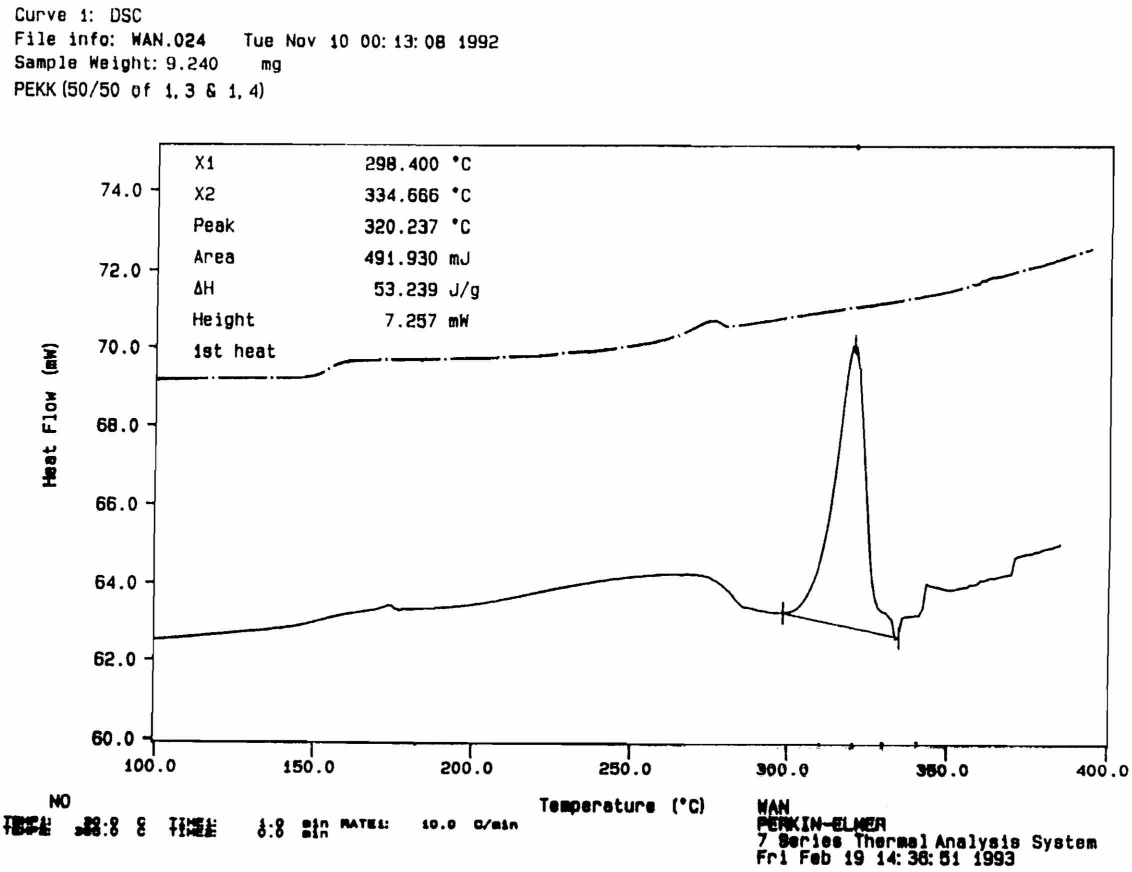


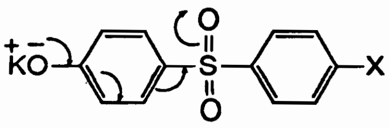
Figure 4.23 DSC trace of perfectly alternating 1,3 & 1,4-PEKK

The resulting polymer has a Tg at 154°C and a Tm at 320°C. (Fig. 4.23) In contrast to the triaryl phosphine oxide containing PEPO/EKK, perfectly alternating PEKK has no char yield in air at 750°C

4.2.6 Homo and Co-Poly(arylene ether)s Directly Synthesized from AB Type Halogenophenols

Halogenophenols are important A-B monomers which can be polymerized under suitable conditions. For example, ICI's Victrex® may be polymerized from 4-halo-4'-hydroxy diphenyl sulfone. The corresponding ketone monomer, 4-fluoro-4'-hydroxy benzophenone, has also been used to obtain PEK. Since four types of halogenophenols have been prepared, attempts were made to polymerize the halogenophenol monomers directly by using diphenyl sulfone as a diluent and K_2CO_3 as a base. Two homo polymers and three copolymers were synthesized by this method.(Scheme 3.15)

The self-reactivity of the halogenophenols is much lower than the corresponding reactivity of dihalides with diphenols. This is attributed to the so called "bridge effect" of the AB halogenophenol [38, 154]. The halogen and the phenoxide anion deactivate each other in halogenophenoxide and therefore have lowered self-polyetherification rates. In order to obtain high molecular weight polymers from these halogenophenols, a high temperature was used in the polymerization. The polymerization usually couducted in two or three stages. In the first stage, the potassium carbonate was used to convert the phenol group to phenoxide and the generated water was removed by dry nitrogen. Table 4.8 summarize the polymers synthesized via this direct route.



deactivated halogenophenoxide

The PES had a IV of 0.34 for the reaction conducted at 130°C for 3 hours and 240°C for 5 hours. This IV would likely be improved if the reaction temperature were higher. The homo PEPO showed a very low IV value. It was obtained by the precipitation of the reaction mixture and NMP into a methanol/water mixture (pure methanol can not be used to obtain PEPO powder).

Table 4.8 Poly(arylene ether)s synthesized from halogenophenols

Monomer	IV[1]	Tg[2]	Tm[2]	TGA[3]	Polymer
CHDPS	0.34	220	no	530	PES
FHPPO	0.19		no		PEPO
CHDPS/FHPPO	0.68	231	no	527	PES/PEPO
CHDPS/FHBP	–	180	no	533	PES/PEK
FHPPO/FHBP	–	200	no	558	PEPO/PEK

1. in NMP at 25°C 2. 2nd heat of DSC 10°C/min 3. In air 10°C/min; 5% wt. loss

In contrast to the homopolymerizations, copolymerizations of the halogenophenols were more successful (Table 4.8). These three copolymers basically were produced by the same reaction conditions at an equimolar ratio. All these copolymers are amorphous in nature. From the results of the silyl ether displacement route and the direct reaction route, it was noticed that the copolymerization of phosphine oxide containing monomers with other comonomers can generate higher molecular weight polymeric materials than homopolymerization of phosphine oxide monomer. Figure 24 a & b show the DSC and TGA traces of PES/PEPO copolymers prepared via direct polymerization route.

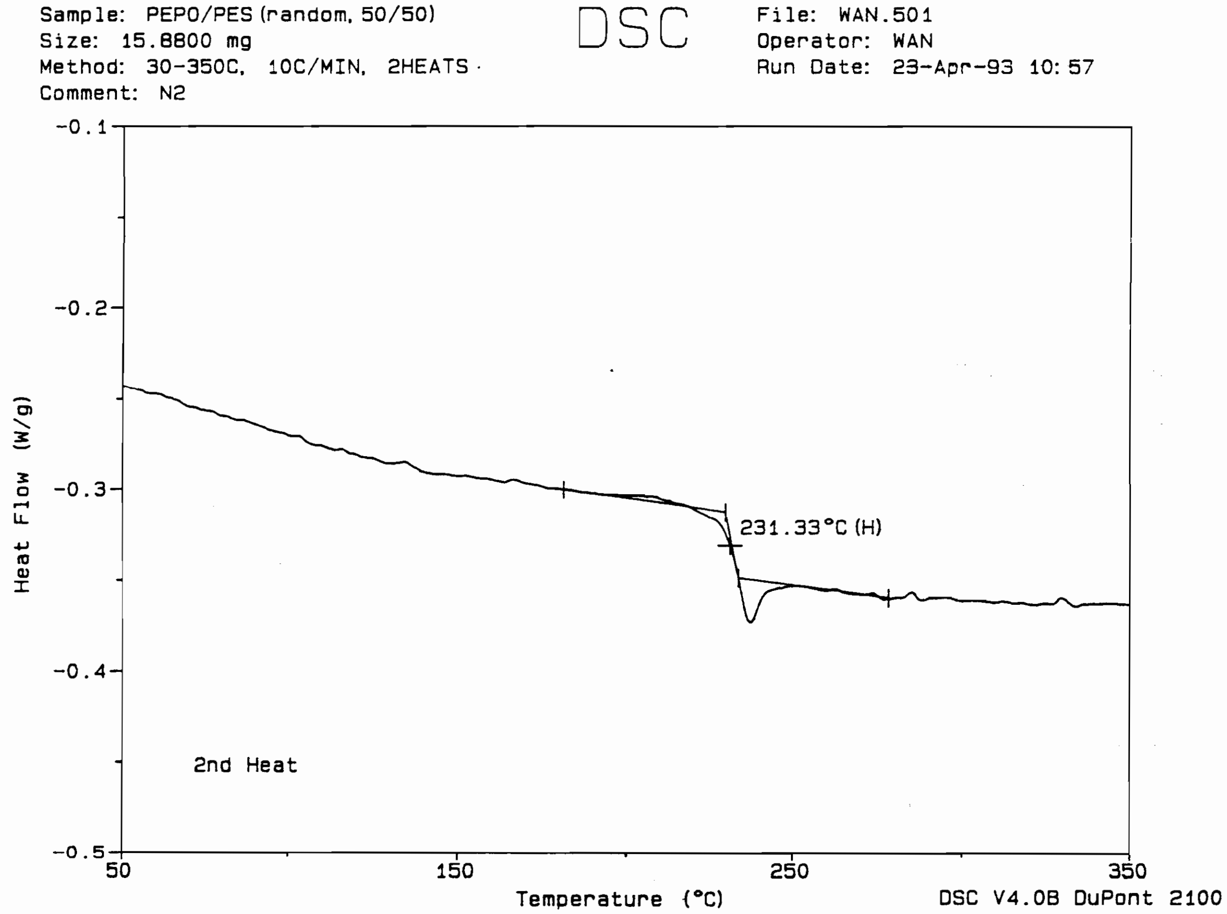


Figure 24 a) DSC trace of PES/PEPO copolymer

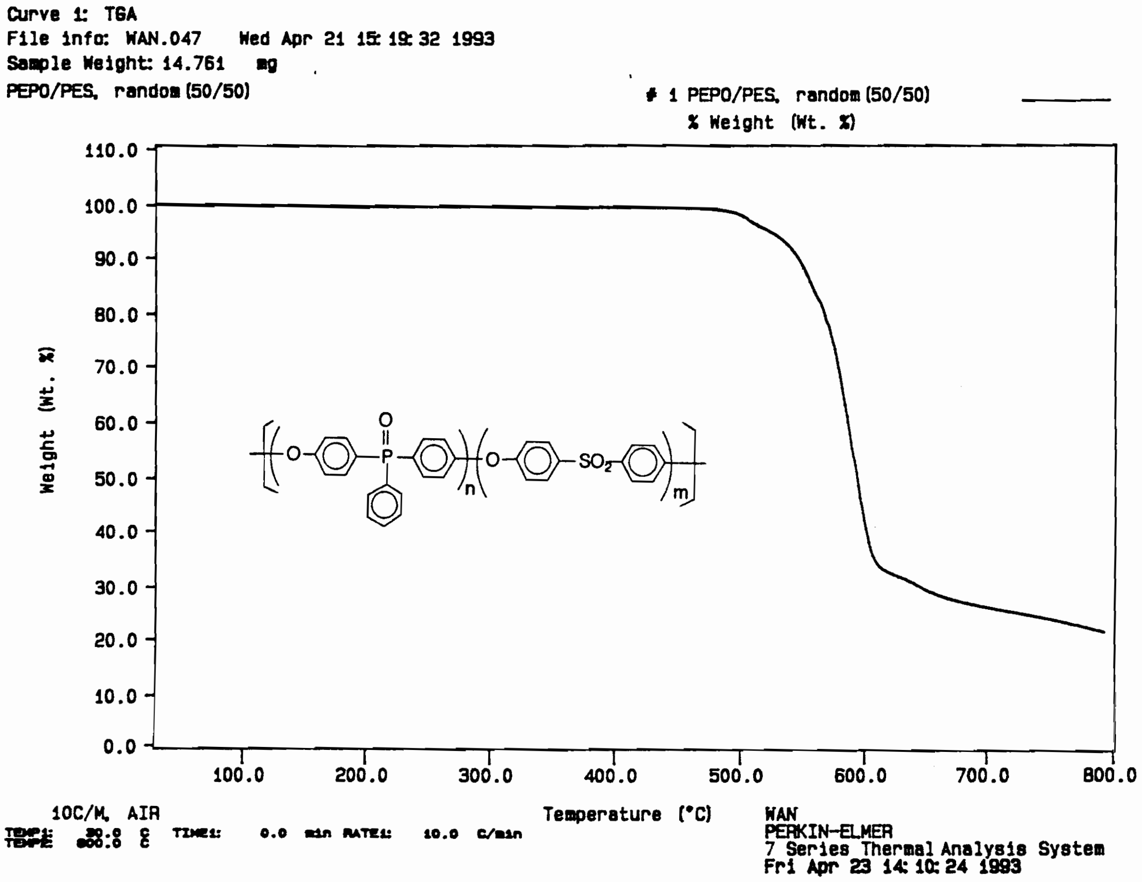


Figure 24 b) TGA traces of PES/PEPO (50/50 mole%) copolymers

4.2.7 Solution Polymerization of AB Type Halogenophenols

The AB type halogenophenols have a relatively low self-polymerization reactivity. Under the investigated conditions FHDPS and FHPPO failed to form high MW polymers. The recovered products after the reaction were oligomers and even monomers. One may conclude that for the deactivated AB monomers, the low temperature solution route is not feasible.

4.2.8 Carboxyl Terminated Poly(arylene ether sulfone) Oligomers

The purpose of synthesizing carboxy terminated PES oligomers was to incorporate this engineering polymer into a segmented nylon 6 copolymer to improve the properties of the nylon 6. PES has several outstanding properties such as a high Tg, good thermal stability, ductility and resistance to aqueous acids and bases. The carboxy functionalized PES were synthesized by an aromatic nucleophilic substitution reaction as illustrated in Scheme 3.16. The monofunctional end-cap, 3-hydroxybenzoic acid, was used to control the molecular weight as well as to functionalize the oligomers[115, 116-b]. The meta form was chosen because of its enhanced solubility relative to the para isomer. The carboxyl group was found not to interfere with this polymerization. DMSO was chosen as the solvent for the nucleophilic reaction since it has been reported that DMSO can provide better solubility for the potassium salt of hydroxybenzoic acid [116]. A summary of the polysulfone oligomers prepared is shown in table 4.9. As can be seen from the table, the theoretical molecular weight and titrated molecular weights are very close. However, it was found that in the attempts to synthesize higher molecular weight PES-COOH oligomers, those two values deviated. For example, the theoretical 15K, 18K, and 20K PES-COOH oligomers have only 14.1K, 15.5K and 17K <Mn> value as determined by potentiometric titration. This problem may be associated with the polymer prematurely precipitating during the reaction, or with the potassium salt of hydroxybenzoic acid in DMSO reaching saturation. Therefore, a co-solvent system such as DMSO/DMAc[116c] or a less concentrated solution may possibly solve the problem.

Table 4.9 Characterization of Carboxyl terminated poly(arylene ether) sulfone oligomers

Expt Mn(g/mole)	Tit. Mn(g/mole)*	IV$_{NMP}$	Tg(°C)
3000	3300	0.122	152
6000	6030	0.176	170
10000	10300	0.249	176
13000	12400	0.294	181

* By potentiometric titration

4.3 Modification of Polyamides

4.3.1 Nylon 6 / Poly(arylene ether sulfone) Segmented Copolymers

Both nylon 6 and poly(arylene ether sulfone) are considered to be engineering thermoplastics. The carboxyl functionalized PES has been successfully incorporated into polyarylates to toughen the LCP[116]. Attempts here were to improve the solvent resistance of the PES and the mechanical properties of the nylon 6 by incorporation of carboxyl functionalized PES into the nylon 6 matrix. Such semi-crystalline block copolymers have a variety of attractive properties[155]. For example, this copolymer may have applications as interleaf materials for composites or adhesive materials between two components.

Two series of copolymers were synthesized and these included the incorporation of different weight ratios of PES oligomers with the same segment length and different segment lengths of PES at the same weight ratio. The characterization results are summarized in Table 4.10 and Table 4.11.

Nylon 6/PES copolymers were synthesized according to Scheme 3.17. The initial argon pressure was used to exclude oxygen, to prevent vigorous boiling of water and chlorobenzene in the early stage and to minimize the monomers loss from the reaction vessel followed by polymerization on the heat transfer surface. The small amount of water added acts as a catalyst for ε-caprolactam polymerization by opening the ring to generate aminocapropic acid.

Table 4.10 displays the results of the nylon 6/PES copolymers with different wt% incorporation of PES oligomer at a <Mn> value of 10,300 g/mole. Table 4.11 presents data on copolymers of 30 wt% incorporation of PES with different segment lengths. The water extraction values afforded reasonable results for the residual monomer and cyclic oligomer after the equilibrium polymerization of ε-caprolactam. The chloroform extraction results showed that at higher wt% PES incorporation, or longer PES segments, more copolymer was extracted out. ^{1}H-NMR was used to analyze the extracted components, which were largely composed of PES (more than 80%). This indicated that the copolymers of higher wt% PES incorporation, or longer PES segments showed decreased solvent resistant. The system is a phase separated copolymer. From Table 4.10, the lower Tg of nylon 6 did not change when the PES content increased. The upper Tg of PES segments were not detected until the incorporation of PES reached 40wt%. For the second series of copolymers (Table 4.11), the lower Tg of the 3K-PES/nylon 6 copolymer was increased to 50°C. This is possibly due to some low molecular weight PES homopolymer being physically occluded or dissolved in the nylon 6 phase. The lower Tg of the rest of the copolymers basically did not change. The crystal melting transition temperatures were depressed when PES wt% was increased. There is no clear trend of Tm for the 30 wt% PES (with different segment length)segmented copolymers.

The mechanical behavior of the compression molded samples showed interesting results. Figures 4.25 and 4.26 are the stress-strain profiles of these two series of

Table 4.10 Poly(arylene ether sulfone)(Mn=10,300 g/mole) /nylon 6 segmented copolymers; Influence of chemical composition

N6/PES[a]	Tg (°C)	Tm (°C)	TGA[b] (°C)	[η][c] (dl/gm)	H_2O Ext.[d] (wt%)	$CHCl_3$[d] (wt%)	Elongation%[e]	E(ksi)[e]
100/0	44,—	221	399	1.71	10.3	~0	220	365
90/10	44,—	220	404	1.11	7.1	~0	385	403
80/20	43,—	217	411	1.06	8.3	~0	31	444
70/30	43,—	216	412	0.66	4.6	8.4	23	458
60/40	43,171	213	400	0.67	5.2	22.0	18	462
50/50	43,170	210	400	0.58	3.6	47.5	15	403

a. PES segment is 10,300 g/mole

b. 5% Weight loss temperatures, in air, 10°C/minute

c. m-cresol at 25°C (after H_2O extraction)

d. $CHCl_3$ sol fraction (after H_2O extraction)

e. ASTM standard D 638-89 (test at 0.5 inch/min)

Table 11 Influence of poly(arylene ether sulfone) segment length (30 weight percent) on nylon 6 segmented copolymer behavior

<Mn> of PES[a] (x 10^{-3})	Tg (°C)	Tm (°C)	TGA[b] (°C)	[η][c] (dl/gm)	H_2O Ext.[d] (wt%)	$CHCl_3$[d] (wt%)	Elongation%[e]	E(ksi)[e]
3	50	214	407	0.72	10.6	~0	291	409
6	46	216	406	0.81	9.8	~0	34	468
10	43	216	412	0.66	4.6	8.4	23	458
13	44	217	393	0.71	5.7	11.3	23	451

a. 30 wt% incorporation

b. 5% Weight loss temperatures, in air, 10°C/minute

c. Test in m-cresol at 25°C (after H_2O extraction)

d. $CHCl_3$ sol fraction (after H_2O extraction)

e. ASTM standard D 638-89(test at 0.5 inch/min) copolymers. From both the Figures(4.25, 4.26) and the Tables(4.10, 4.11), it is clear that the copolymers containing 10 wt% 10.3K PES and 30wt% of 3.3K PES have improved both in elongation and modulus compared to homopolymer nylon 6. Other copolymers in both series improved in moduli, but showed greatly decreased elongation.

Wide angle x-ray scattering (WAXS) has been utilized to further analyze these copolymers. Figures 4.27 and 4.28 present the WAXS patterns of the copolymers after water extraction and oven drying at 120~130°C for two days. The two peaks of the WAXS traces indicated that all annealed copolymers showed virtually α-form crystals, which is the most stable crystal form of nylon 6. A small diffraction peak of the γ-form crystals appeared in the copolymers with 3K-PES (Figure 4.28) and it decreased as the PES segmental length increases. It was reported that the α form crystals have a (200) plane at 2θ 20.2~20.6° and (002)+(202) planes at 2θ 22.6~24° [148-151]. The α form crystal is favored if the polymer is annealed [149-153]. From these two figures, it is clear that the PES segments in the copolymer backbone generally did not affect the nylon 6 crytal structure if the copolymer samples were dried at elevated temperatures(e.g. 120~130°C). However, a decrease in crystallinity in the copolymers was observed for the copolymers with higher PES weight% incorporation (Figure 4.27).

Figures 4.29 and 4.30 show the WAXS patterns of the quenched copolymers. For the quenched nylon 6, the γ form crystal is reportedly preferred [152]. The γ form crystal has a (001) plane at 2θ~21.3° and (200)+(201) planes at 2θ~22.5° with only 1/6 the intensity of the (001) plane [151]. From Figure 4.29, only 10 wt% PES incorporated copolymer showed similar crystal diffraction peaks (α and γ form) as the homo polymer. The rest of the copolymers exhibited γ form crystal diffraction peaks and their crystallinity decreased with increase in PES concentration. From Figure 4.30, the 3K PES incorporated copolymer (30wt%) showed only an amorphous halo, while other copolymers exhibited γ form peaks. Combining the results of Figures 4.29 and 4.30 with the mechanical test data

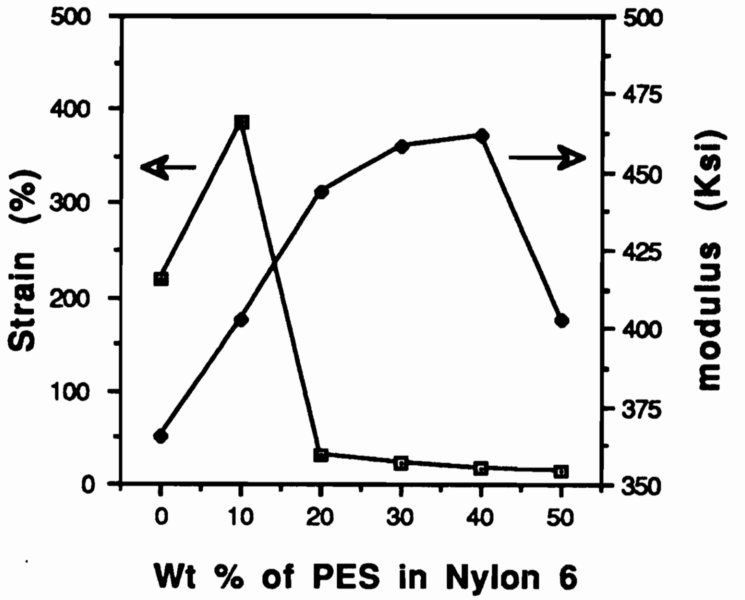


Figure 4.25 Mechanical behavior of the nylon 6/PES copolymers as a fraction of the weight% incorporation of poly(arylene ether sulfone) (10K) oligomers

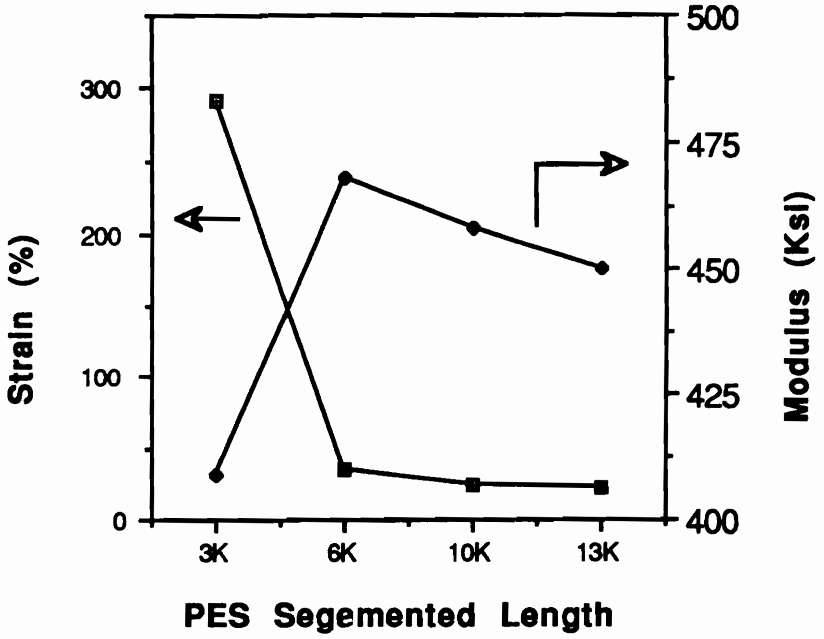


Figure 4.26 Mechanical behavior of the nylon 6-poly(arylene ether sulfone) segmented copolymers as a function of segment (30% PES)

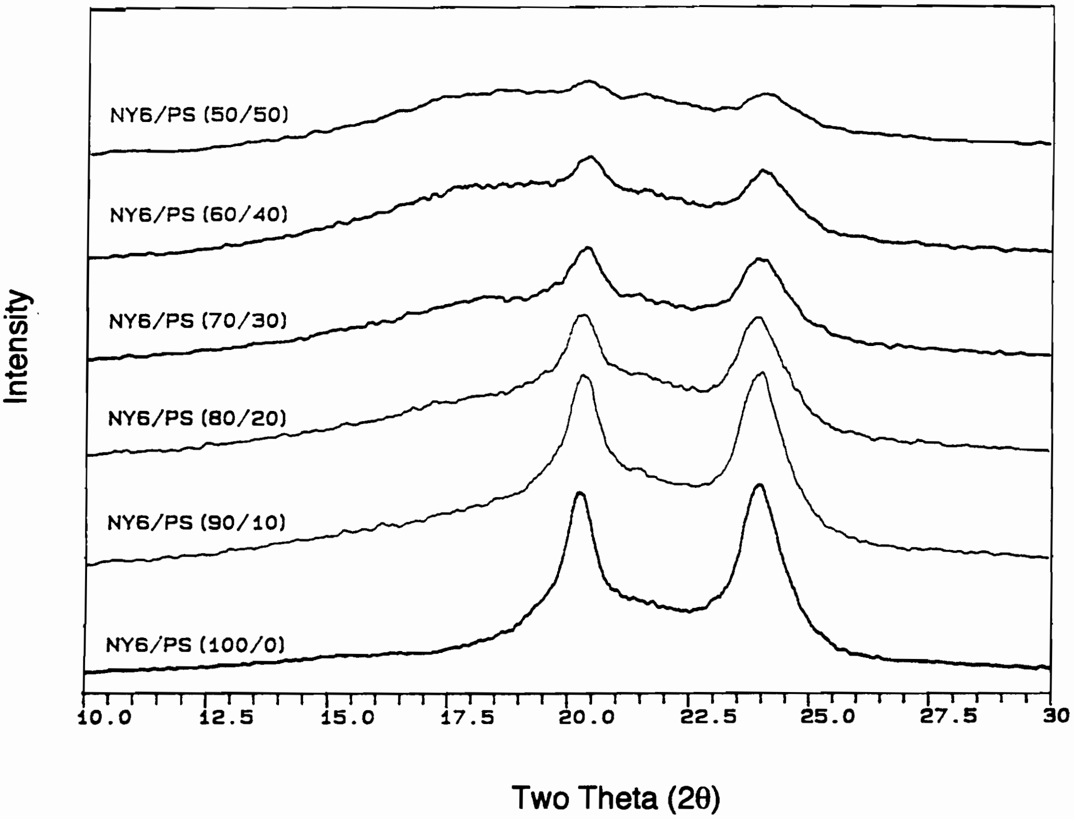


Figure 4.27 WAXS of the nylon 6/PES segmented copolymers as a function of wt% incorporation of PES (10K) oligomers

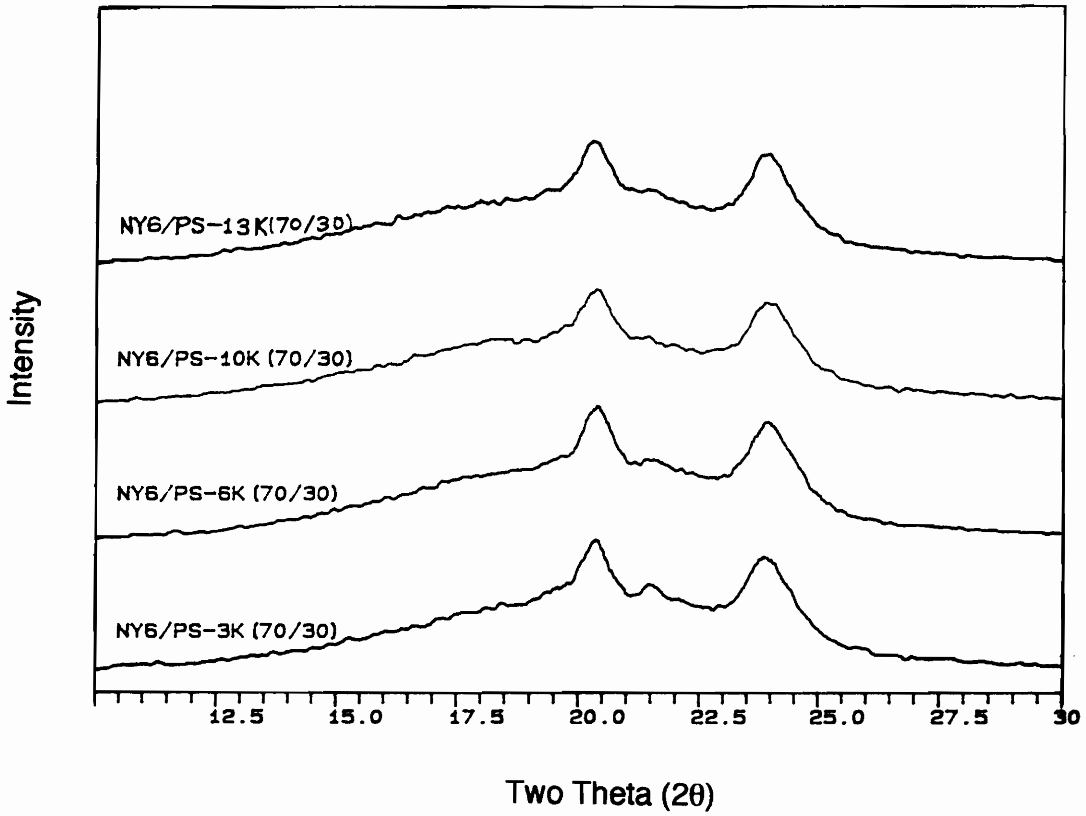


Figure 4.28 WAXS of the nylon 6/PES segmented copolymers as a function of segment length of the PES at 30 wt% incorporation

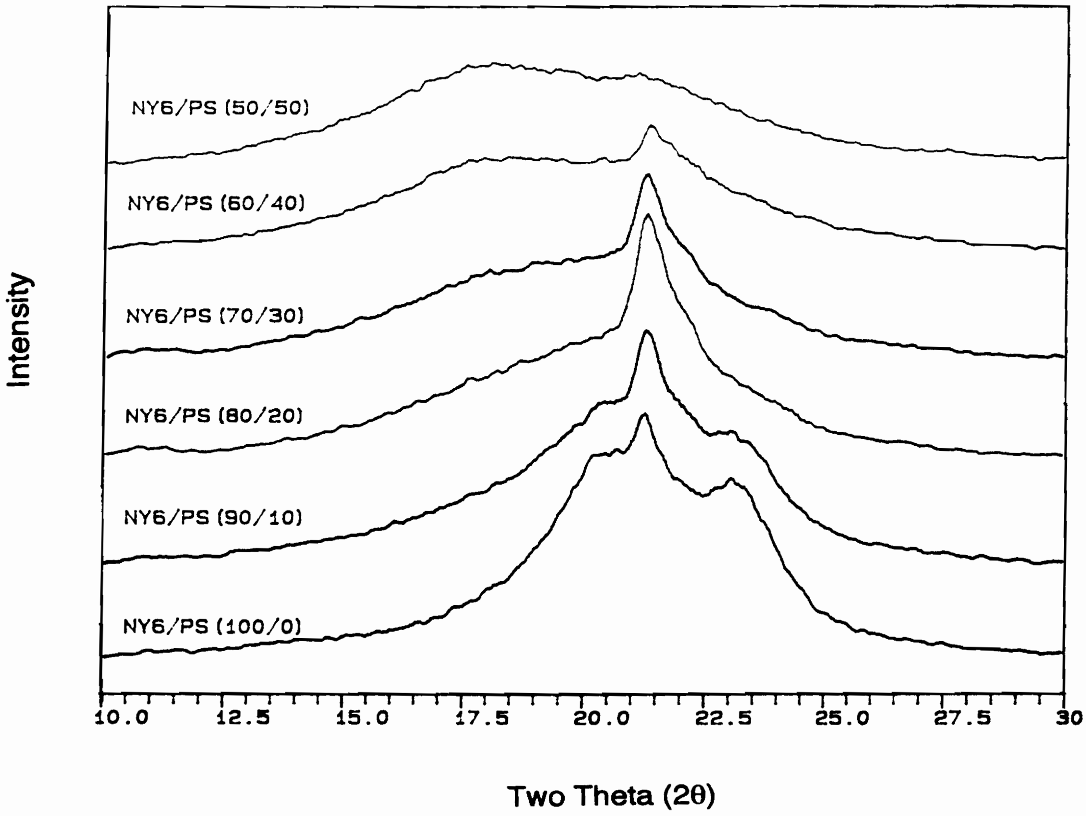


Figure 4.29 WAXS of the nylon 6/PES segmented copolymers as a function of wt% incorporation of PES(10K) oligomers(quenched sample)

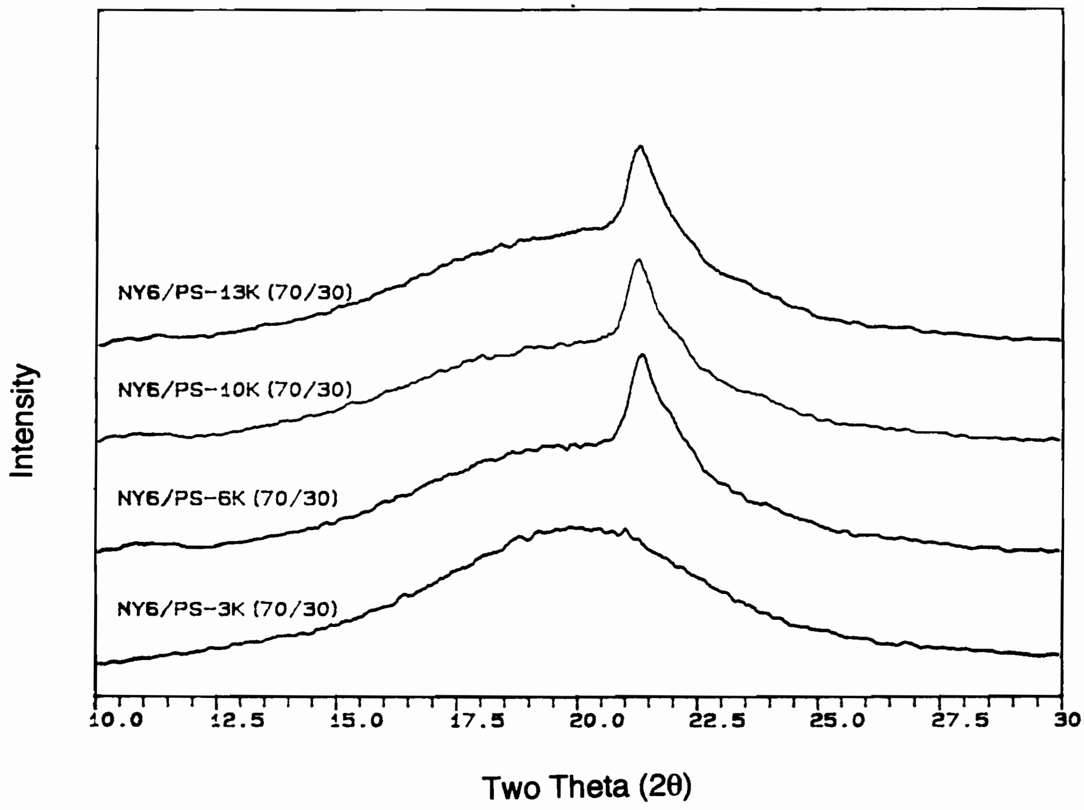


Figure 4.30 WAXS of the nylon 6/PES segmented copolymers as a function of segment length of the PES at 30 wt% incorporation(quenched samples)

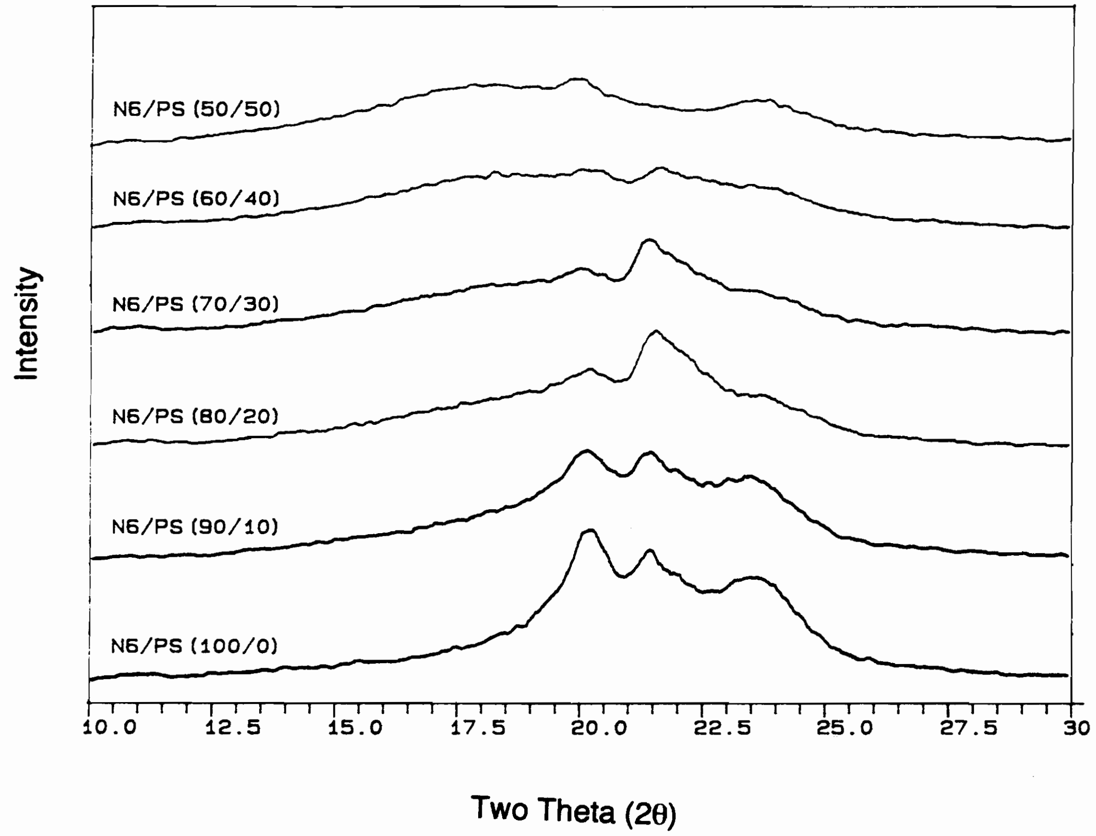


Figure 4.31 WAXS of the nylon 6/PES segmentyed copolymers as a function of wt% incorporation of PES (10K) oligomers(annealed in boiling water 1 hr.)

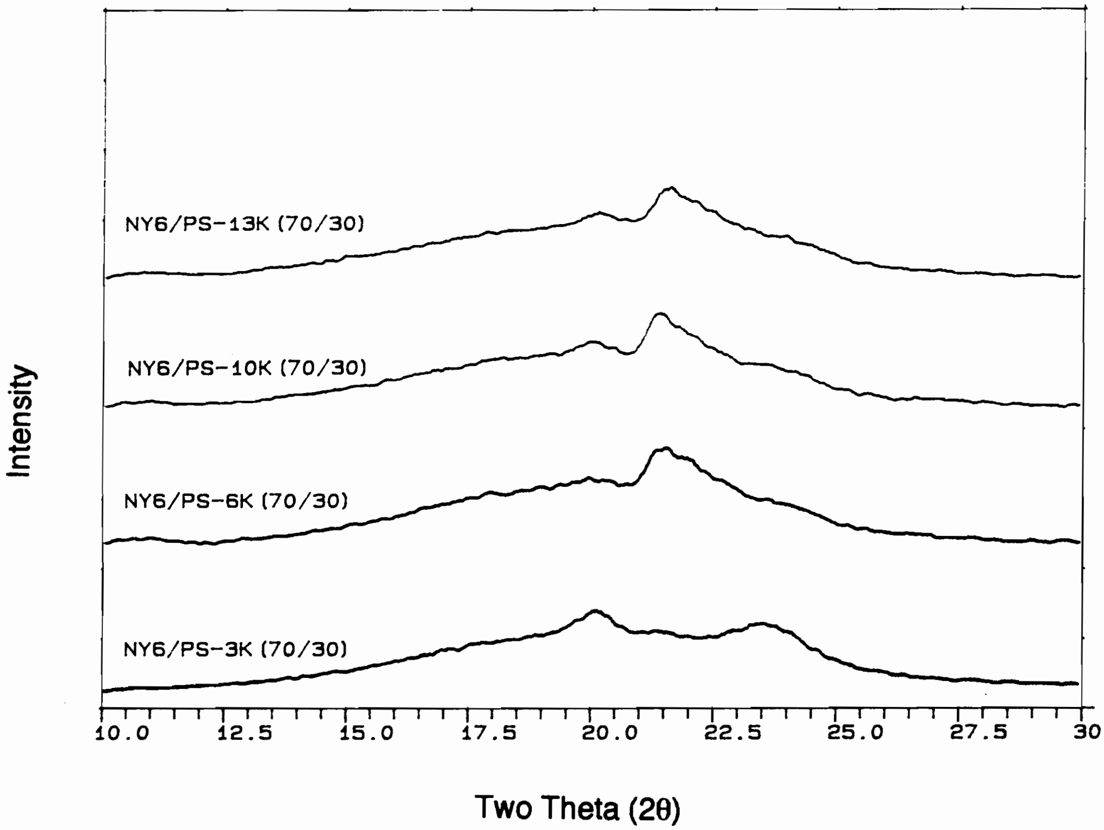


Figure 4.32 WAXS of the nylon 6/PES segmented copolymers as a function of segment length of the PES at 30 wt% incorporation (annealed in boling water 1 hr)

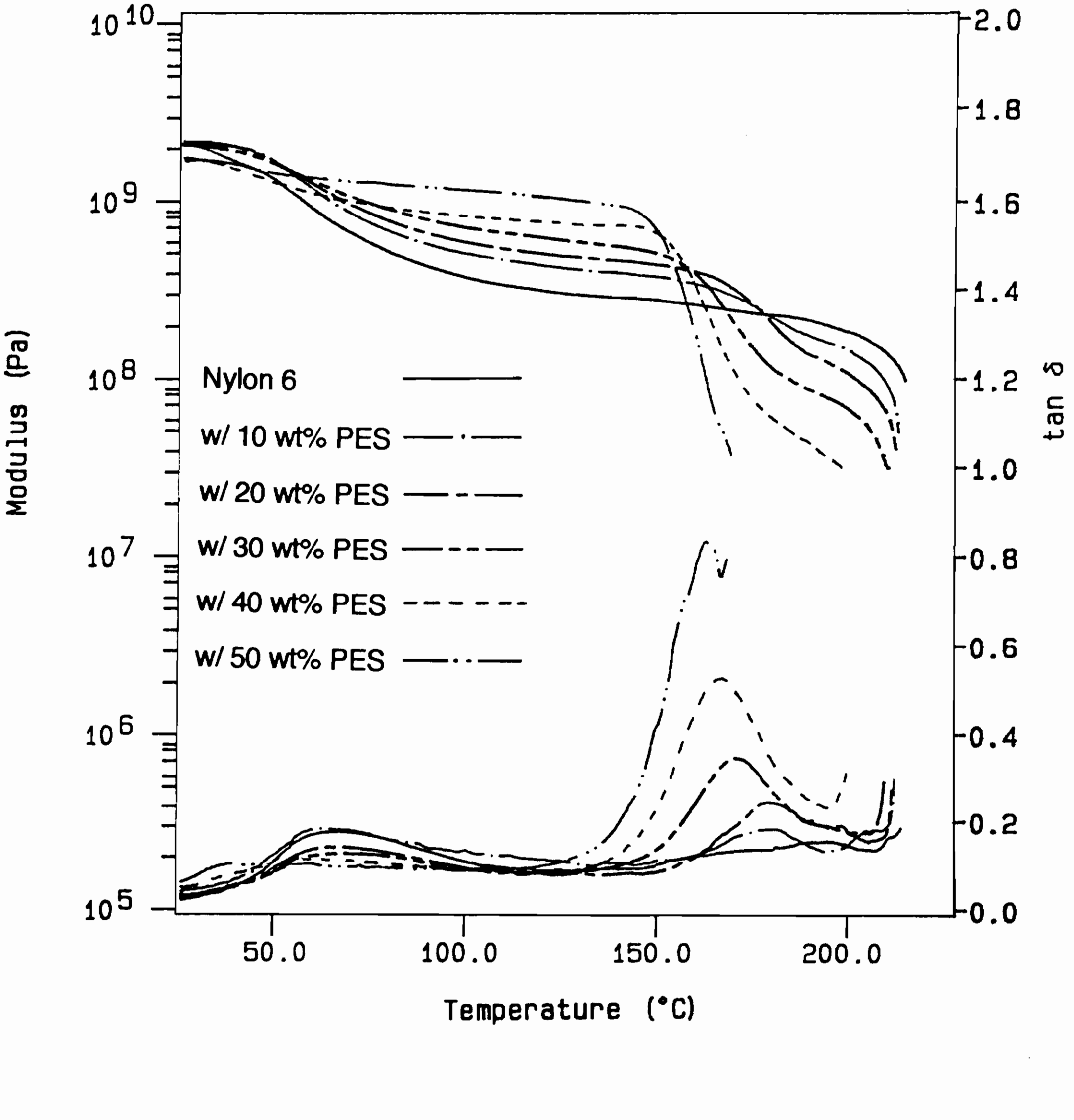


Figure 4.33 DMA trace of nylon 6/PES segmented copolymers as a function of wt% incorporation of PES (10K) oligomers(3 point bending)

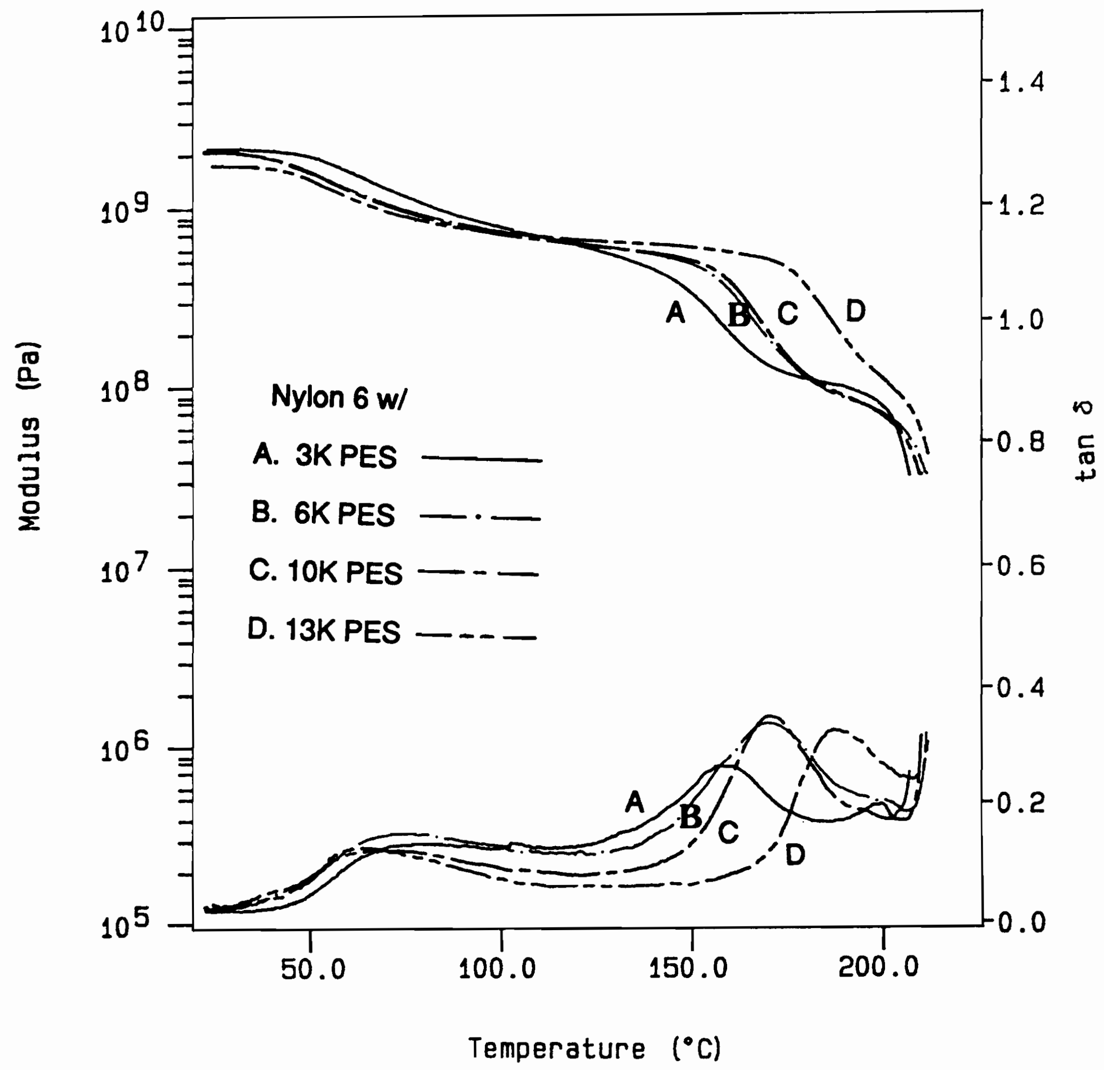


Figure 4.34 DMA traces of nylon 6/PES segmented copolymers as a function of segment length of the PES at 30 wt% incorporation(3 point bending)

in Tables 4.10 and 4.11, one may speculate that the formation of the γ form crystalline structure in the quenched samples was the reason for the low elongation values for those coolymers which only γ form crystals. For the 50 wt% incorporated copolymer, the low elongation value might be due to either the low nylon 6 content or the relatively low molecular weight.

In order to check whether the quenched copolymers were able to transform their crystalline structure from the γ-form to the α-form, an annealing experiment was conducted for the copolymers in boiling water for 1 hour. Figures 4.31 and 4.32 show the WAXS diffraction patterns of these samples annealed in boiling water. Comparing these two figures with the previous two WAXS figures(4.29 & 4.30), it is clear that the α-form crystal was increased after annealing in boiling water. The α-form can be further increased by annealing at higher temperature, or just by increasing the annealing time.

Dynamic mechanical analysis (DMA) results of these two series of copolymers are shown in Figures 4.33 and 4.34. As shown in Fig. 4.33, the storage modulus is influenced by both of the composition and the Tm of the copolymers. Higher incorporation of PES produces a higher residual storage modulus at temperatures above the Tg of the nylon 6. When the temperatures were in the range of the Tg of the PES segments, the storage modulus decreased again. The retained high temperature modulus is due to the crystallinity of the copolymers and it drops fast as the crystallinity decreased or disappeared. The final steep decrease in modulus occurs when the temperatures approach the Tm of the copolymers. Tan δ curves of the copolymers clearly suggest that the materials are phase separated copolymers. The lower peak is the Tg of nylon 6 phase and the upper peak is due to the Tg of the PES phase and the areas under the peaks were influenced by the composition of the copolymers. Fig 4.34 presents DMA traces of the copolymers with different lengths of PES and one may note the storage moduli were moduli were influenced by the PES segment length. Longer PES segments produce a higher storage modulus at high temperatures. The content of the nylon 6 in this series of copolymers was equal and the lower Tg was virtually the same. The upper Tg was determined by the PES segments and the longer segment of PES shows a higher upper Tg value.

4.3.2 Synthesis and Characterization of Triaryl Phosphine Oxide Containing Nylon 6,6 Copolymers

The utilization of the triaryl phosphine oxide monomers in high performance copolymer systems such as poly(arylene ether)s and polyimides is a relatively recent development. The phosphine oxide moiety contributes thermal and oxidative stability coupled with high glass transition temperatures. The high char yield properties of these polymers suggested that these materials could be used as flame-resistant materials and this development has been extended to synthesize crystallizable nylon 6.6 copolymers. The phosphine oxide copolymers were prepared with bis(4-carboxyphenyl)phenyl

Table 4.12 Characterization of triarylphosphine oxide containing nylon 6,6 copolymers

P(O)% in N66	$[\eta]^1$	Tg^2 (°C)	Tm^2 (°C)	TGA^3 (°C)	Char % (750°C)	Tg^4 (°C)
0	1.32	58	253	410	0	64
10	2.40	59	214	405	3.8	80
20	2.68	75	208	403	7	86
30	1.59	89	no	402	8.5	—

Note: 1. In m-cresol at 25°C

2. Second heat of the quench cooled samples (10°C/min)

3. 5 wt% loss in air

4. By DMA at heating rate 5°C/min and 1Hz

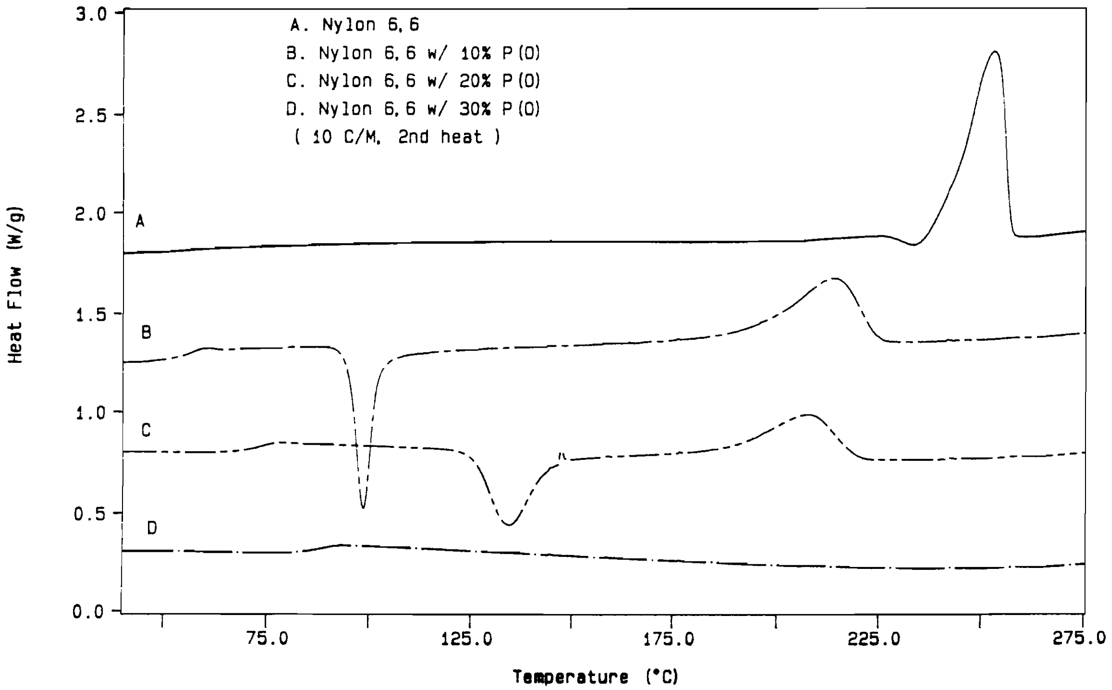


Figure 4.35 DSC traces of triarylphosphine oxide containing nylon 6,6 copolymers (heating curves)

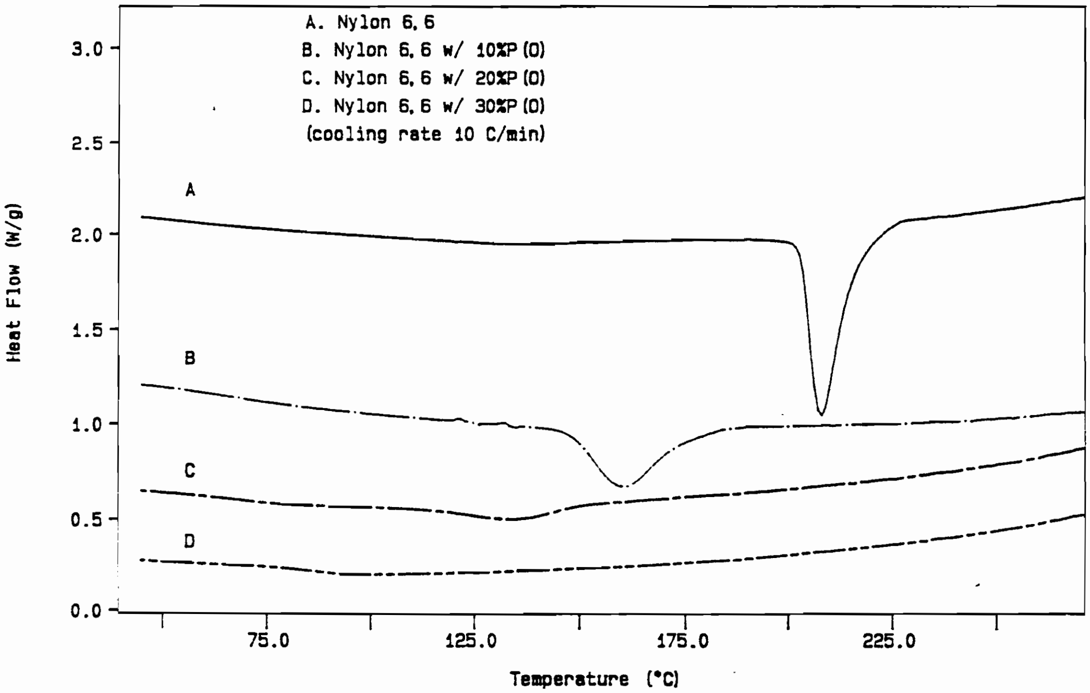


Figure 4.35 b) DSC of triarylphosphine oxide containing nylon 6,6 copolymers (cooling curves)

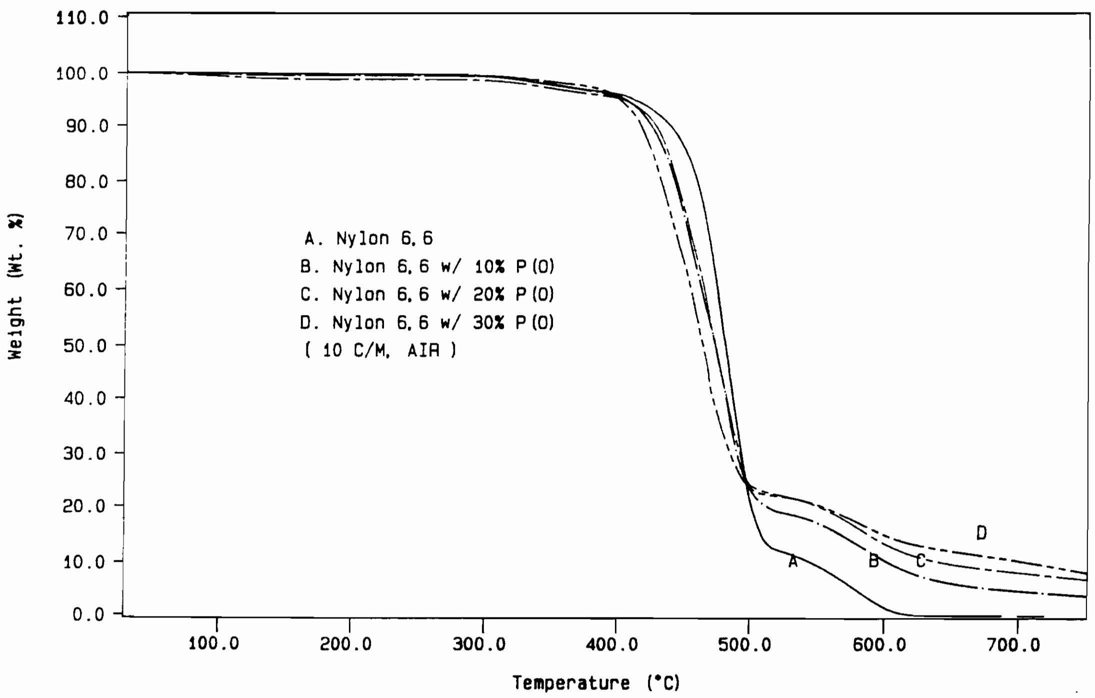


Figure 4.36 Dynamic TGA of triarylphosphine oxide containing nylon 6,6 copolymers in air

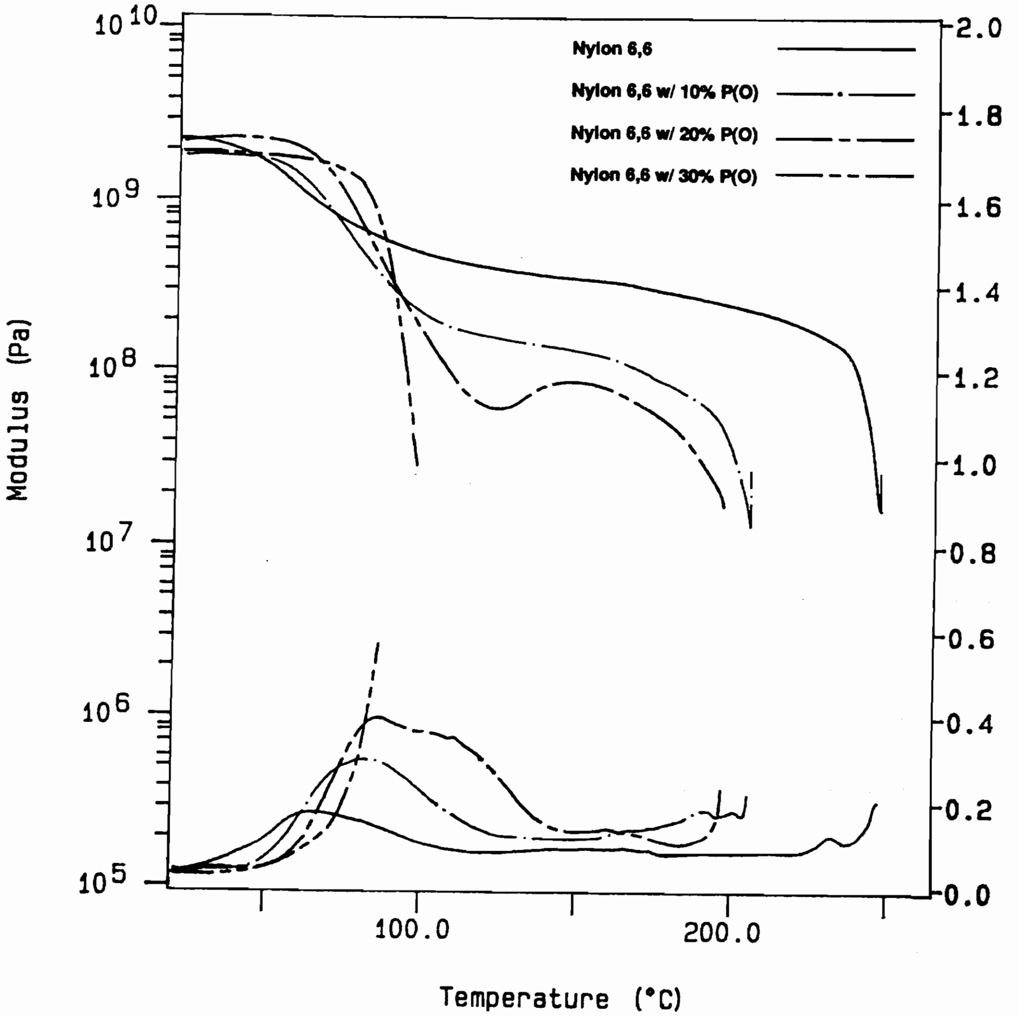


Figure 4.37 Dynamic mechanical behavior of compression molded triaryl phosphine oxide containing nylon 6,6 copolymers (3 point bending)

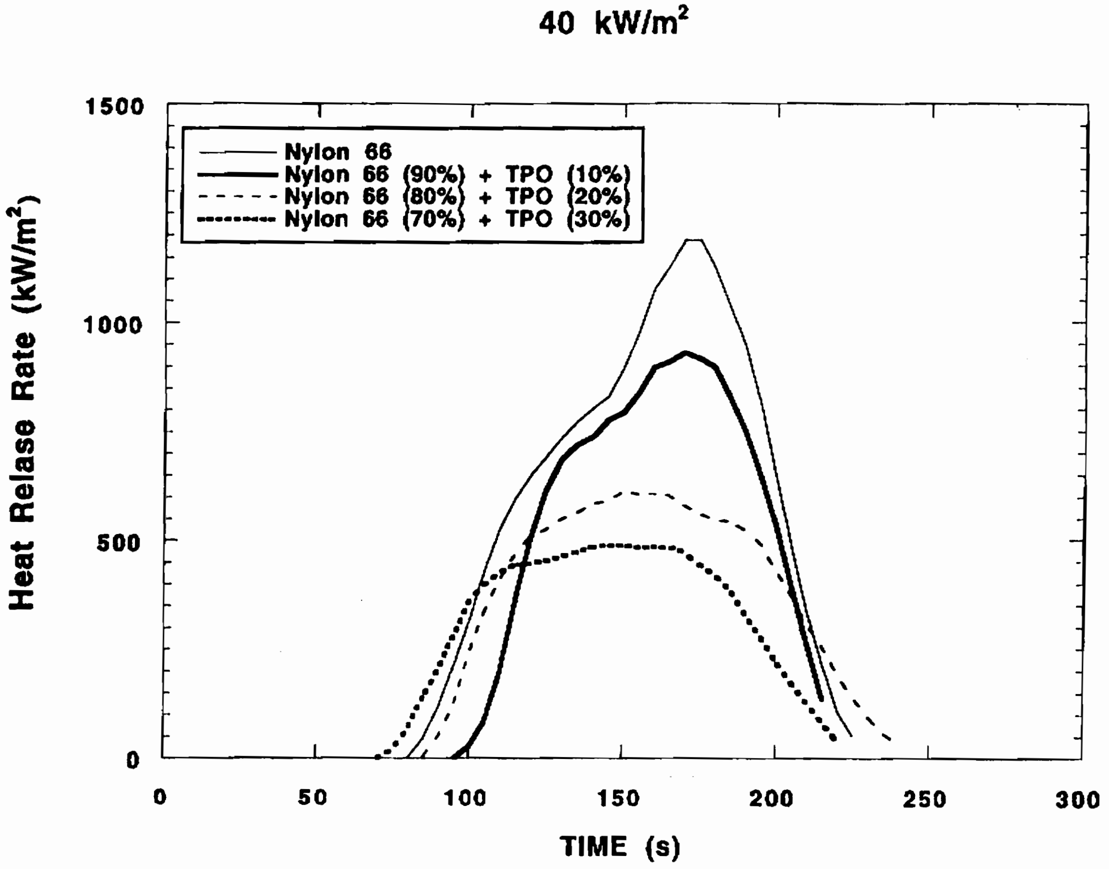


Figure 4.38 Heat release rate of triarylphosphine oxide containing nylon 6,6 copolymers [156]

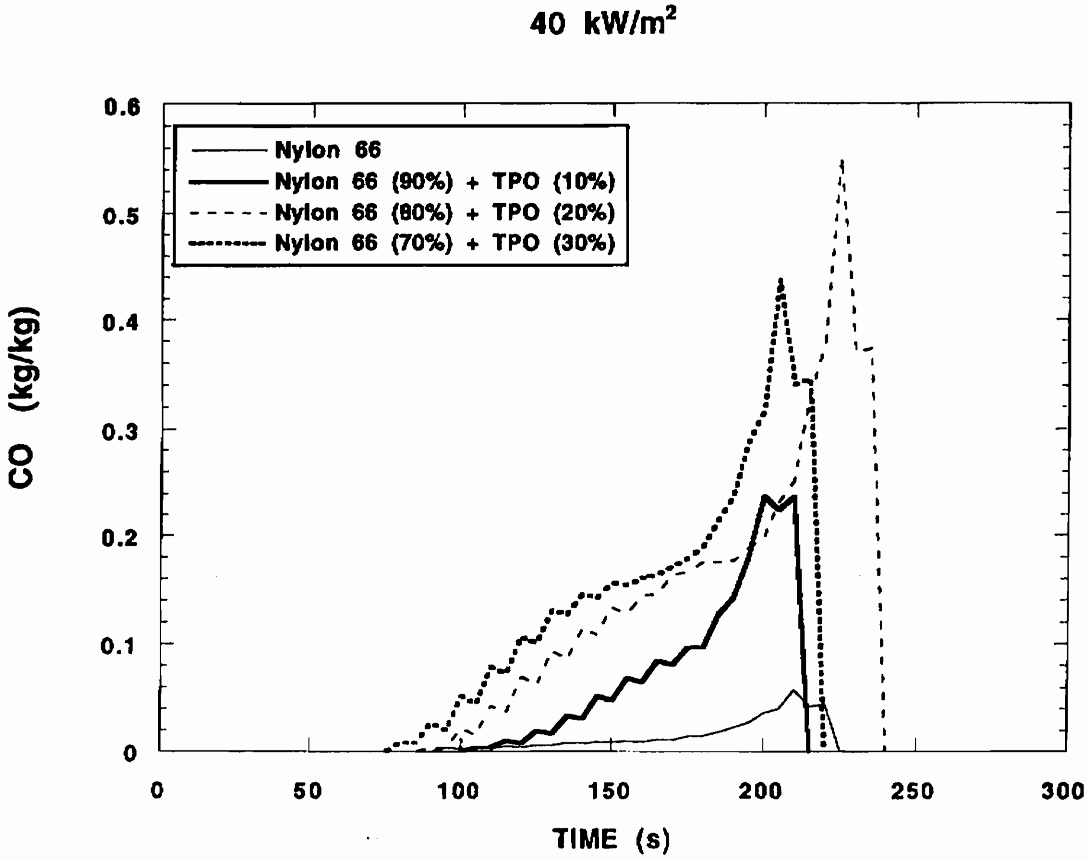


Figure 4.39 Carbon monoxide generation from the incomplete combustion of phosphine oxide containing nylon 6,6 copolymers[156]

phosphine oxide, as shown in reaction Scheme 3.2. The incorporation of the triarylphosphine oxide was controlled from 0-30 mole%, since higher levels were not expected to be crystallizable. Characterization of the triarylphosphine oxide containing copolymers is summarized in Table 12. As shown in Table 4.12 and Figure 4.35(a, b), the copolymers exhibit a crystalline transition if the incorporation of the phosphine oxide comonomer is lower than 30 mole% but even at 30 mol%, the copolymer is virtually amorphous. The nylon 6,6 homopolymer has a very fast crystallization rate. However, once the triarylphosphine oxide comonomer was incorporated into the copolymer backbone, the crystallization rate decreased and the Tm is depressed, as expected.

The glass transition temperatures of the copolymers along with the char yields increased as the phosphine oxide content increased. The increased char yield of the copolymers can also be seen in Figure 4.36. The char yield usually strongly correlates with the flame retardancy of the material. High char yields suggest better flame resistance and vice versa. From the DMA traces(Figure 4.37), the storage modulus decreases as the temperature increases and the final drop in the curve occurs as the temperature approachs the Tm of the polymers. The DMA trace of 30% P(O) copolymer shows that it is amorphous.

Cone calorimetry[156] results show that the heat release rate is significantly reduced for 20 & 30 mol% incorporation of phosphine oxide comonomer (Figure 4.38)[157]. The preliminary results suggested that the copolymers may have improved flame resistance. However, the soot and carbon monoxide also increased significantly under the test condition(40kW/m^2, ~540°C)(Figure 4.39)

5. CONCLUSIONS

5.1 Poly(arylene ether)s

Several activated dihalides have been partially or fully hydrolyzed by potassium hydroxide in aqueous dimethyl sulfoxide in reasonably high yields. These hydrolysis reactions were basically affected by several factors, the concentration of DMSO, and the reaction temperature. The quantity of the DMSO influences the yields of the hydrolysis products and the temperatures of the hydrolysis reactions can influence the purity of the halogenophenols. For the "isolated" fluorines in the activated dihalide such as bis(fluorobenzoyl)benzene, no "bridge effect" is possible and both fluorines were readily hydrolyzed to phenoxide anions. The halogenophenols and bisphenols were easily converted to the corresponding silylated monomers by refluxing with hexamethyldisilazane. Vacuum distillation or sublimation was employed to purify the most of the silylated monomers.

Numerous PAEs were synthesized via the silyl ether displacement route. The AB types monomers were used to generate linear as well as star-branched PAEs. The AA, BB type of monomers were used to synthesize PEPO/EKK copolymers and perfectly alternating 1,3 & 1,4-PEKK copolymers. The silyl ether displacement route has been shown to be versatile, as illustrated by the fact that both the statistical copolymer as well as the block copolymer can be prepared via this route.

The char yields of the triaryl phosphine oxide containing homo-and co-PAEs were high in air at 750-800°C, as shown by dynamic TGA measurements. This result suggested that the triaryl phosphine oxide containing polymers were good flame-resistant materials.

Although the halogenophenols have relatively lower reactivity, they can still be polymerized by using the appropriate reaction conditions (i.e. at elevated temperatures)

5.2 Segmented PES/Nylon 6 Copolymers

Carboxyl terminated PES oligomers of controlled molecular weights have been successfully synthesized via nucleophilic route, using m-hydroxybenzoic acid as the end capper. The expected number average molecular weight <Mn> of PES-COOH oligomers and the experimental <Mn> obtained by titration were in good agreement. However, it was found that for higher molecular weight PES-COOH oligomer synthesis, these two <Mn> values diverged. The PES-COOH oligomers have been successfully co-polymerized with ε-caprolactam to produce segmented copolymers. The copolymers were phase separated systems as shown from the DSC data and the DMA traces. It was found that the copolymers at low weight percent of PES incorporation or short PES segments greatly improved the mechanical properties of the compression molded samples. Wide angle X-ray diffraction patterns of the copolymers which were dried at elevated temperature showed the dominant α form, while for the quenched samples, the γ form was the preferred crystalline structure.

5.3 Triaryl Phosphine Oxide Containing Nylon 6,6 Copolymers

Crystallizable triaryl phosphine oxide containing nylon 6,6 copolymers have been synthesized in relatively high molecular weights. The content of triaryl phosphine oxide comonomer in the melt synthesized copolymers was controlled from 0~30 mole%. The copolymers were melt crystallizable at 10 and 20 mole% incorporation, although the melting point is reduced as expected. Crystallinity was totally disrupted at 30 mole% incorporation, but the Tg values are systematically increased.

Cone calorimetric tests conducted on the copolymers in a constant heat environment (40 kW/m^2) exhibit significantly depressed heat release rates for the copolymers, as a function of higher triaryl phosphine oxide content, which is very desirable. Dynamic TGA results in air also showed that the char yield increases with an increase in phosphine oxide content. On the other hand, initial results suggested that "soot" and carbon monoxide generated may be higher, possibly as a consequence of the incomplete combustion of the copolymers.

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PART II

Polyarylates, Liquid Crystalline Foams and Triaryl Phosphine Oxide Containing Poly(ethylene terephthalate) Copolymers

I. INTRODUCTION

Liquid crystalline polyesters(LCPs) are known to be high performance thermotropic materials. These polymers possess many interesting properties such as high thermoxidative stability, excellent solvent resistance, low melt viscosity, low coefficient of thermal expansion and excellent mechanical properties. One particular interest in the thermotropic liquid crystalline polymers is that the LCPs can be oriented in the thermotropic state to produce highly anisotropic materials which exhibit higher strength and higher modulus than other engineering thermoplastics.

Commercial examples to date include Vectra® which is a poly(oxybenzoate/oxynaphthoate) based system, Xydar® which is a poly(oxybenzoate/biphenol terephthalate) based system and other materials which are analogous or a variation on the above two systems. Although many outstanding characteristics have been identified, the ability of these materials to generate structural foams has been limited. However, by introducing a modest amount of branching via the use of muti-functional reagents into the LCPs, interesting liquid crystalline morphological foam-like materials can be generated via a gas supersaturation technique. The liquid crystalline foams are a new class of low density materials which may possess the high stiffness characteristic of conventional liquid crystalline polymers combined with isotropic physical properties in the bulk phase.

Several objectives of this research are described in this section of the thesis. In order to disrupt the crystallinity of the LCPs, several multi-functional branching reagents were prepared. Then, the branching reagent along with the AB types of monomers were polymerized in a melt acidolysis reaction. The resulting polymers showed for the first time that the interesting liquid crystalline foam structures could be generated. The modest disordering due to the branching agent is apparently responsible for this successful development.

As illustrated in Part I, the triaryl phosphine oxide moiety acts as flame retardant in the phosphine oxide containing polymers. In order to obtain flame resistant specialty and high volume polyesters, attempts have been extended to synthesize phosphine oxide containing wholly aromatic polyarylates as well as poly(ethylene terephthalates).

From the literature, the wholly aromatic polyarylates containing phosphine oxide were basically synthesized via a solution acid chloride route. No satisfactory high molecular weight phosphine oxide containing polyarylates have ever been reported. Therefore, the approach here was to incorporate the phosphine oxide moiety via the melt acidolysis reaction into the polyarylate matrix.

Poly(ethylene terephthalate) (PET) has major applications in textile fiber, film and beverage bottles. The incorporation of the triarylphosphine oxide comonomer into PET may enhance the flame resistance of the copolymers. However, unlike nylon 6,6 which has a very fast crystallization rate, PET has a very slow crystallization rate. Once the phosphine oxide comonomer was incorporated, the crystallization rate was further depressed. The level of crystallinity and the Tm were also reduced. The synthesis and characterization of the triarylphosphine oxide containing PET is discussed herein.

2. LITERATURE REVIEW

2.1 INTRODUCTION

Polyesters are an important class of engineering thermoplastic polymers. They offer diverse applications in a variety of areas. Aliphatic polyesters have not found great commercial interest due to their low melting points. In contrast, aromatic polyesters such as polyarylates[1,2], liquid crystalline aromatic polyesters (LCPs) [3-10], and, particularly poly(ethylene terephthalate) (PET) [11-13] are widely used for resins, fibers and films. In recent years, high molecular weight PET has been made through improvements in technology and they are suitable for blow-molded beverage bottles.

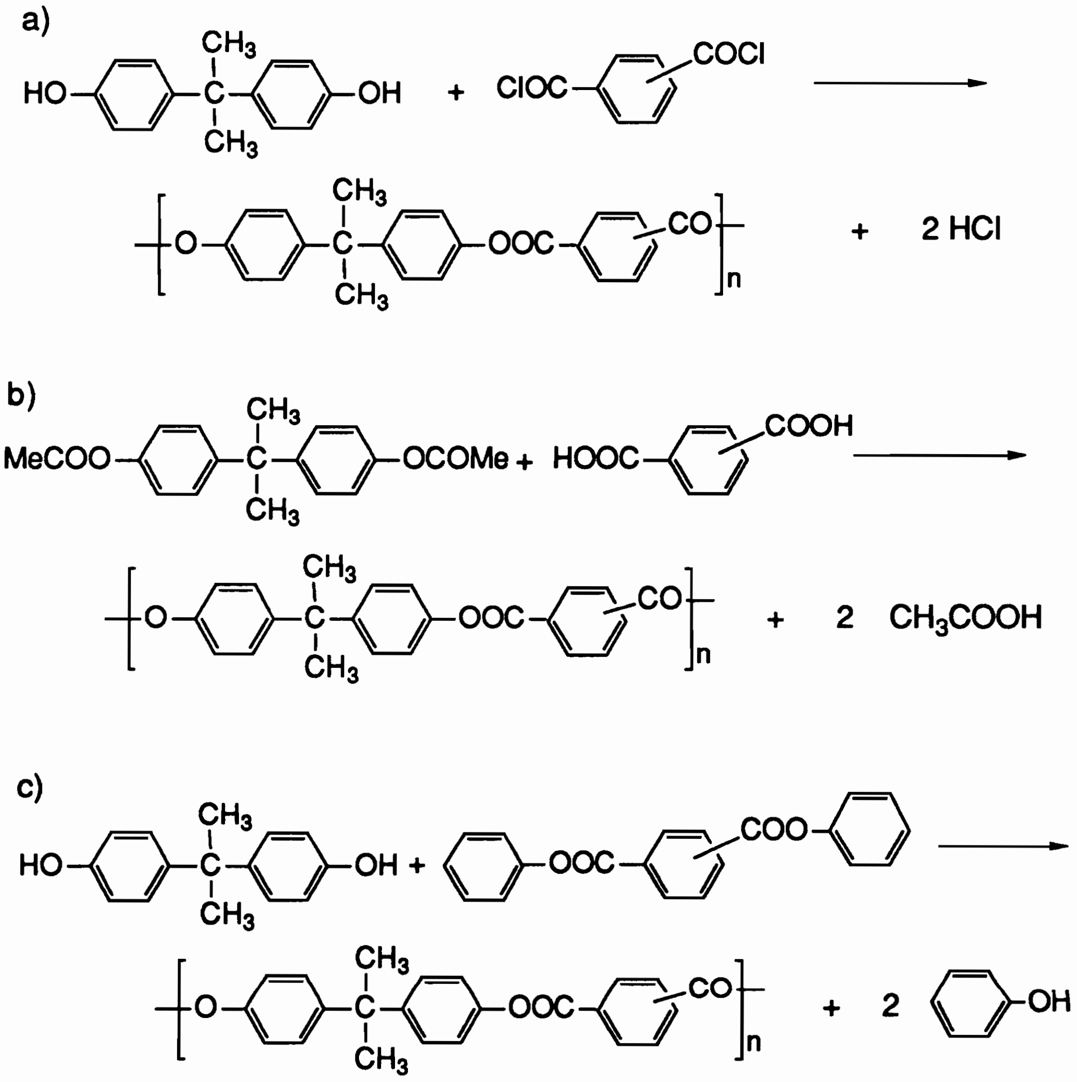
Polyarylates and LCPs, which usually show high-softening temperatures, excellent mechanical properties, processability and weatherability, are advanced materials. They have potential in applications that require improved performance at elevated temperatures. Great attention has been paid to the synthesis of the melt processable aromatic LCPs. They can be prepared, in general, through the polymerization of co-monomers similar to the preparation of homo-polyesters. The following sections will discuss the general synthetic methods and the properties of polyarylates, LCPs and PET. These will be followed by discussion of solid state polymerization and foam formation.

2.2 Polyarylates

Commercial introduction of polyarylates as engineering polymers began in 1970. This class of polymers (polyarylates) includes the highly oriented liquid crystalline materials, the semi-crystalline polyarylates, and the transparent amorphous bisphenol A based polyesters [2]. Therefore, the liquid crystalline polyesters are synthesized by routes similar to other polyarylates. PET, however, is usually generated by different routes, which will be discussed later. A number of polyarylate compositions can be made from available AA/BB and AB monomers such as bisphenols, aromatic dicarboxylic acids and aromatic hydroxy-carboxylic acids. These polymers are usually prepared either in the high temperature melt (diacetate or diphenate routes) or low temperature processes (acid chloride route). The acid chloride route generally is a solution process, while the other two methods can be conducted in solution, in melt or as a slurry (Scheme 2.1).

2.2.1 Properties of polyarylates

Amorphous bisphenol A based (iso / terephthalates) are tough materials having excellent mechanical and thermal properties. The polymers at composition near 100% isophthalate or above 75% terephthalate units crystallize readily and exhibit crystalline melting points in excess of 280°C [2, 14]. Ardor® D-100 is a typical example of a commercially available amorphous polyarylate (Table 2.1). The mechanical properties of amorphous polyarylates are similar to their amorphous polycarbonate counterparts. For highly crystalline polyesters such as Xydar® SRT-300, a LCP in nature, the mechanical properties in terms of tensile modulus and tensile strength are much better than those of the amorphous polyarylates (Table 2.2). However, LCPs have much poorer mechanical properties in the transverse direction of flow than in the direction of flow. Polyarylates have excellent resilience, which gives these polymers excellent flexural recovery or elastic rebound. This unique property widens the potential applications of these materials[1].



Scheme 2.1 Major reaction routes to prepare polyarylates a) acid chloride b). diacetate c). diphenate[2]

Table 2.1 Properties of amorphous polyarylate(Ardor® D-100)[2]

Glass transition temperature(°C)	190
Heat distortion temperature, 0.25 inch(°C)	174
Density (gml^{-1})	1.21
Tensile modulus (psi)	295,000
Yield strength (psi)	9,500
Elongation at yield (%)	8.0
strain at break (%)	50.0
Flexural modulus (psi)	310,000
Flexural strength at 5% strain (psi)	11,000
Notched izod impact, 1/8 inch	4.2
Tensile impact strength	140
Refractive index	1.61
Dielectric constant (60Hz)	2.73

Table 2.2. Mechanical properties of Xydar® (SRT-300)[2]

Tensile modulus (psi)[a]	2,400,000
Tensile strength (psi)[a]	20,000
Elongation (%)[a]	4.9
Flexural modulus (psi)[b]	2,000,000
Flexural strength (psi)[b]	19,000
Impact strength[c]	355°C
notched	2.4
reverse	7.3

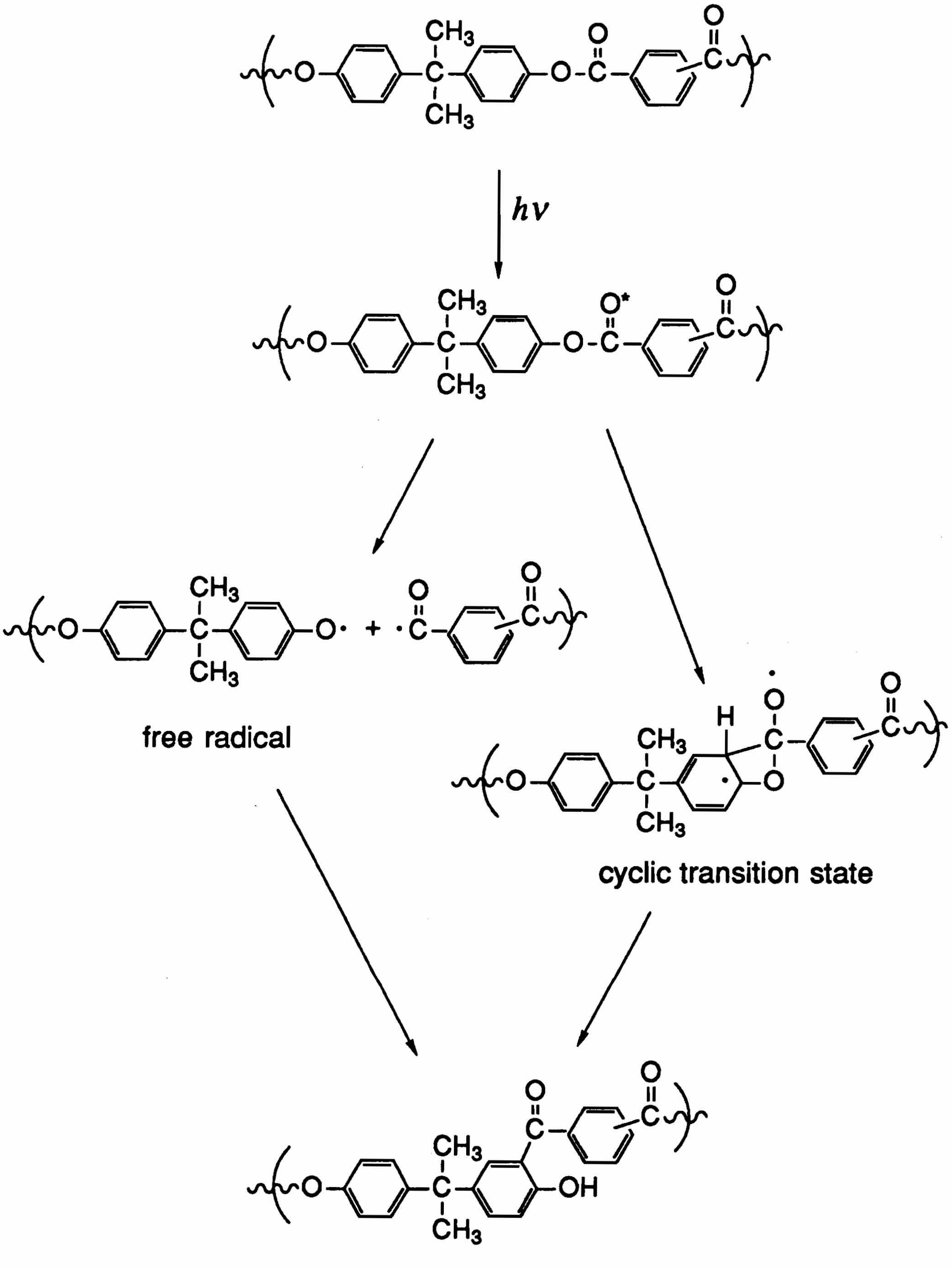
a. ASTM D-638 b. ASTM D-790 c. ASTM D-256

Polyarylates undergo Fries rearrangement upon irradiation with UV light. This solid state rearrangement occurs on the surface of the polyarylates. This rearrangement was reported and confirmed by several groups (15-17). The mechanisms of this rearrangement are believed to follow two paths: (i) via a cyclic transition state generating an o-hydroxybenzophone moiety or (ii) via free radical intermediates [2, 17] (Scheme 2.2). The o-hydroxybenzophone moieties undergo a tautomeric enol-keto equilibration by absorption of UV radiation and dissipation of the energy in a non-radiation manner[18]. As a result of the inherent UV resistance, polyarylates display excellent retention of mechanical properties under prolonged weathering conditions. As a coating or laminate materials, polyarylate provides a UV barrier for other performance plastics.

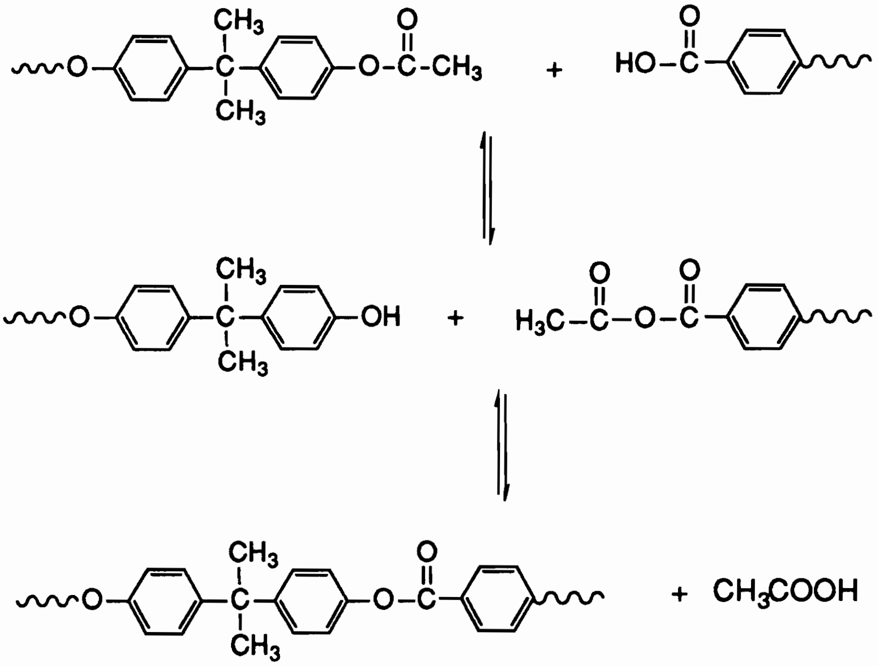
Polyarylate resins exhibit good combustion resistance in terms of low flame spread, a high oxygen index, and low smoke generation. Unmodified polyarylates exhibit sufficient fire-retarding characteristics for many applications.

2.2.2 Synthetic methods for polyarylates

As mentioned earlier, polyarylates generally were prepared in the melt (diacetate or diphenate route) [19, 20] or via the acid chloride route [2] (Scheme 2.1). Other synthetic methods, such as direct reactions of diacid with diphenol have no examples shown in commercial processes. The melt processes are favorable over the acid chloride route for economic and simplicity reasons [2]. The acid chloride processes need high cost acid chloride monomers relative to the corresponding acid. More solvents is involved in the acid chloride route than in the melt process, so extensive solvent recovery is required in this process. The diacetate route (melt acidolysis) is more attractive than the diphenate route, because the latter route requires more extreme reaction conditions and large phenol recycle streams.



Scheme 2.2 Fries rearrangement of polyarylates[2, 17]



Scheme 2.3. Simple mechanism of the diacetate route to synthesize polyarylates[24]

2.2.2.1 The diacetate route (melt acidolysis)

The diacetate processe was first described by Conix[21] and by Levine and Temin [22]. This process involves reaction of stoichiometric amounts of an aromatic dicarboxylic acid and the diacetate derivative of an aromatic diphenol at high temperature under an inert atmosphere(Scheme 2.1). Since melt acidolysis is a reversible melt process, the generated acetic acid must be continually removed from the equilibrium in order to drive the reaction forward and secure high molecular weight polymers. It was proposed that the mechanism of this reaction to generate the aromatic ester linkage is through a mixed anhydride intermediate followed by a free phenol end-group which reacts with the anhydride and subsequently eliminates a molecule of acetic acid (Scheme 2.3) [23] This mechanism of the acidolysis reaction was confirmed by Hall, et al.

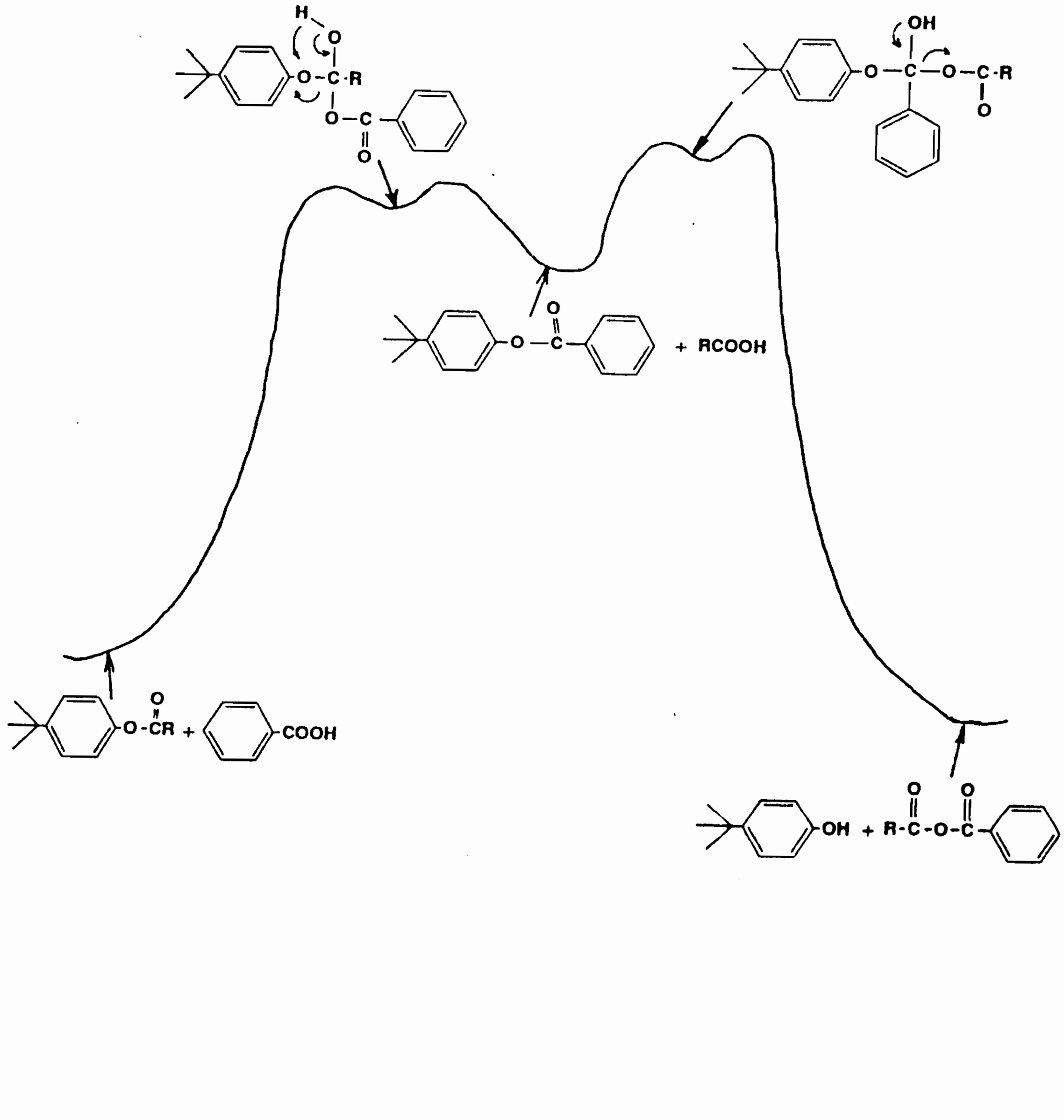
recently [24]. The proposed reaction coordinates of their model study are shown in Scheme 2.4. The byproduct, acetic acid, must be removed in order to get aromatic ester bond formation and to avoid the reversal of equilibrium to the starting materials or the mixed anhydride.

The acidolysis reaction can be conducted in a neat condition[25, 26], but as such it may suffer from the problems of stoichiometric imbalance due to the sublimation of the low melting diacetates and reduced reaction rates due to the build up of the viscosity. It was shown that the imbalance problem can be solved by the addition of a small amount of inert solvent such as chlorobenzene or dichlorobenzene to the reaction mixture at the initial stage of the reaction[27, 28]. The sublimed monomers can be rinsed back to the reaction vessel by the solvent. Once the monomers were converted to oligomers, no sublimation was found in the pre-polymerization stage. The acidolysis reaction also can be conducted in the presence of an inert diluent[29-31]. Typical diluents which have been reported in the literature are diphenyl ether, diphenyl ether-biphenyl eutectic mixture, chlorinated biphenyls, diphenyl sulfones and γ-lactones.

The diacetate process can be improved reportedly by using low levels (50-150 ppm) of esterification catalysts. The most common catalysts used for the reaction are based on antimony, titanium, magnesium, manganese, and zinc metal acetate salts [2]. However, the use of catalysts may result in deleterious effects on the color and hydrolytic stability of the products.

2.3 Liquid crystalline polymers

Although low molecular mass liquid crystalline compounds have been known for more than a century, their prominence is attained only during the past 30 years. The first liquid crystalline polymer, which is an aromatic polyamide called Kevlar®, was invented by DuPont in the early 1970s [32]. This work stimulated worldwide interest in the



Scheme 2.4. Proposed reaction coordinates for the reaction of p-tert-butylphenyl ester and benzoic acid.[24]

research on LCPs. The goal of the intense research activity has been focused on understanding molecular parameters and optimizing processing conditions in order to utilize the unique properties exhibited by this class of rigid, rodlike polymers.

The statistical theories of spontaneous ordering of rodlike polymer molecules in dilute solutions evolved for the first time in the late 1940s [33, 34]. Flory extended this theory to concentrated solutions by using a modified lattice theory[35]. His theory predicts that for polymer solutions above a certain critical concentration, rodlike molecules that possess an axial ratio (the ratio x of length to diameter) greater than approximately 6.4 will spontaneously form two phases. One of these phases is an isotropic solution, another phase is a lyotropic solution in which the rodlike molecules are highly correlated with respect to their long axis. A simple mathematical formula that fairly accurately describes the relationship between the axial ratio and the concentration is

$$\upsilon_p = (8/x)\,(1-2/x)$$

where x is the axial ratio and υ_p is the volume fraction. This theory also predicts that in a polydisperse system higher molecular weight species segregate into the lyotropic phase excluding the lower molecular weight species. This has been experimentally verified by qualitative analysis[36].

2.3.1 Types of liquid crystalline polymers

Liquid crystalline materials can be divided into two categories, thermotropic and lyotropic. The thermotropic materials exhibit an ordered melt on fusion while the lyotropic materials form ordered phases in an appropriate solution. For both thermotropic and lyotropic materials, the ordered phases (also called mesophases) are usually classified in four categories: nematic with order in one direction; smectic with a molecular arrangement in layers (two directions); cholesteric with a rotating order; and, discotic with piles of disclike molecules (Figure 2.1).

Since thermotropic polymers can be melt processed to get the mesophases or liquid crystalline phases, research on LCPs has mainly focussed on thermotropic materials during the last two decades. The next two sections will briefly discuss the properties and processing of thermotropic LCPs.

2.3.2 Engineering properties of LCPs

Most main chain liquid crystalline polymers exhibit nematic order(one dimensional) in their molten state and a crystalline order(three dimensional) in their solid state. A useful relationship for specifying the degree of order is the Hermans orientation function:

$$S \text{ (or } f) = 1/2\,(3\,\mathrm{Cos}^2\theta - 1)$$

Here the letters S or f are referred to the order parameter and the orientation factor, respectively. These values range from "0" for an un-oriented state to "1" for a perfect unidirectional orientation.

A simple picture of rigid rodlike molecules in molten state or in solution at rest and in a flow field is shown in Figure 2.2. At quiescent state, the rodlike molecules form some domains with high order, but the total S is zero. As a result, the lyotropic solution appears to be turbid and the thermotropic LCP melt is usually opaque. When the domains are sheared, the domain walls begin to merge and in the idealized case, all the rods are oriented along the direction of flow. The order parameter is 1.0 in this situation. Because perfect alignment cannot be achieved, the value of S is usually between 0.4 ~ 0.6 for nematic phases [28].

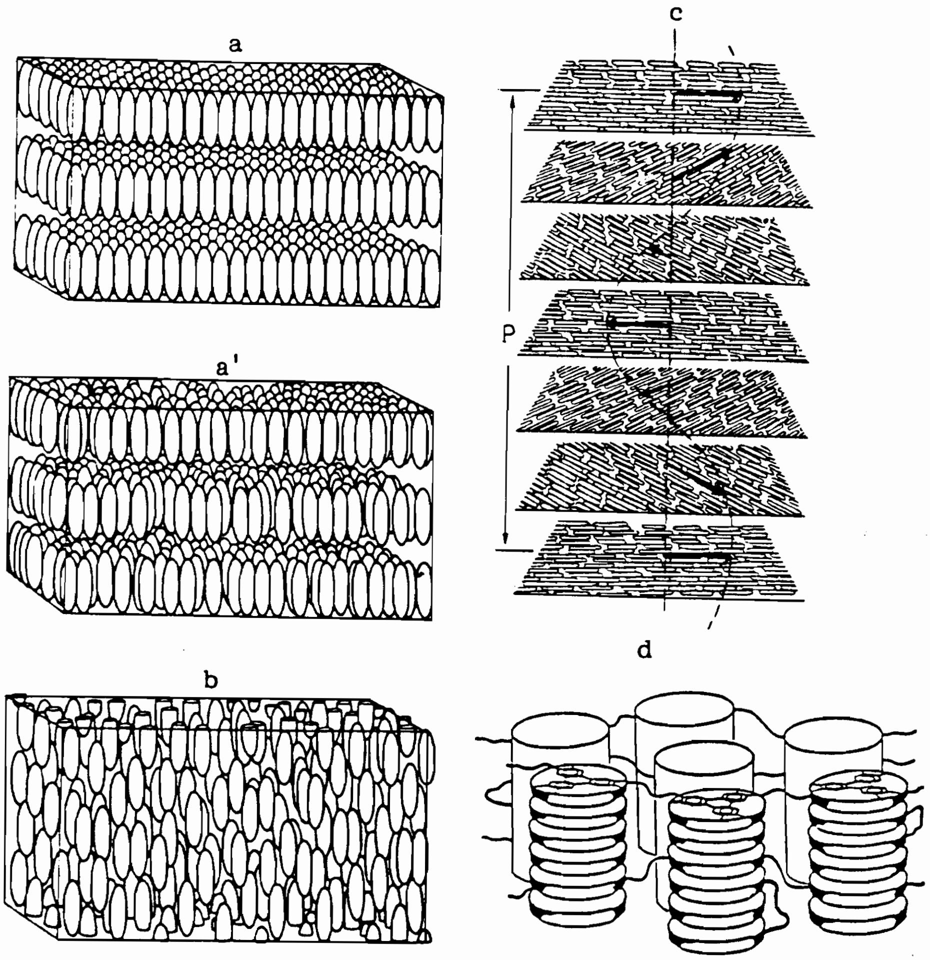


Figure 2.1. Schematic representation of the different types of mesophases:
a). smectic(ordered) b). smectic(unordered) c). cholesteric and
d). discotic[37]

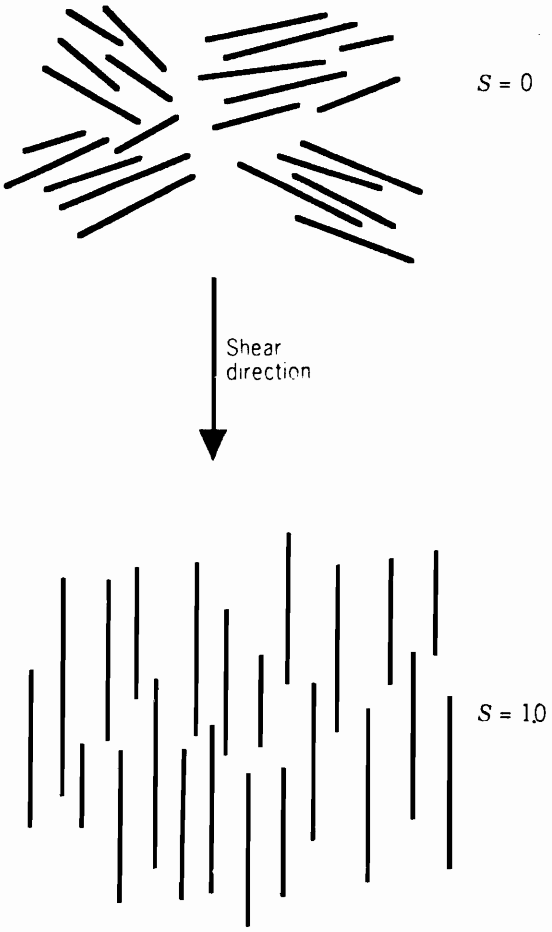


Figure 2.2. Liquid crystalline polymers at rest and in a shear field with perfect alignment[38]

Thermotropic LCPs are characterized by low viscosity, especially under the flow condition. Cogswell [39] visualized the rheological behavior of LCP's in connection with the textures shown in Figure 2.3. Region I is the zone of low shear rates. As the domains rotate, slip past each other and tumble, a small decrease in viscosity is observed, which is characterized by a low order parameter. Region II represent when the shear rate increases and the domains are broken down to smaller sizes. The increasing surface area of the domains may cause an increased resistance to flow. At even higher shear rates (region III) the whole structure is homogenized, the order increases significantly and, most importantly, the viscosity drops by several decades. The low viscosity super domain is stable under shear for thermotropic LCPs, but for a lyotropic solution, the concentration must be above the critical point to maintain mesophases as well as its low viscosity.

2.3.3 Thermotropic liquid crystalline polymers

In 1974, Eastman and Carborundum reported the discovery of the first generation of thermotropic liquid crystalline polymers separately. Eastman's LCPs were poly(ethylene terephthalate) (PET) and p-hydroxybenzoic acid (PHB) based copolymers, whereas, the LCPs of Carborundum were copolyesters based on terephthalic acid/4,4'-biphenol/4-hydroxybenzoic acid. In 1975, various LCPs prepared with substituted hydroquinones and different acid monomers were disclosed by DuPont and in early 1978 the first Celanese LCPs based on 2,6-oriented naphthalene monomers were disclosed. Three most important LCPs are shown in Scheme 2.5[3].

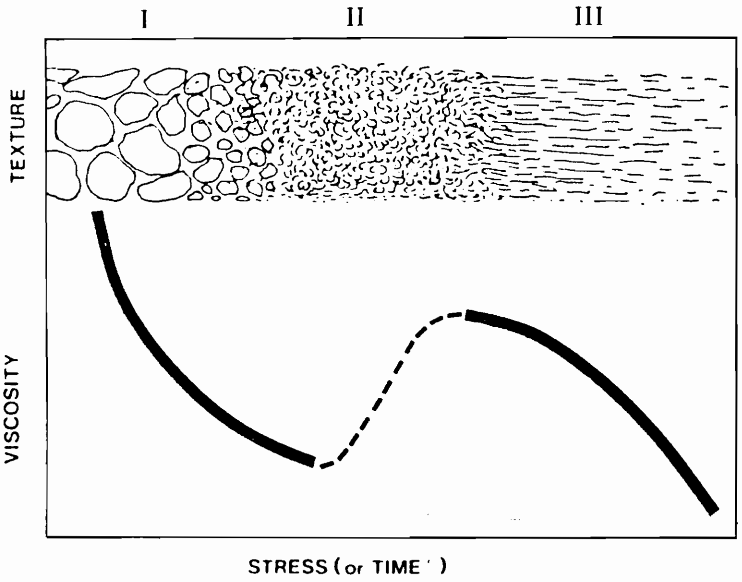
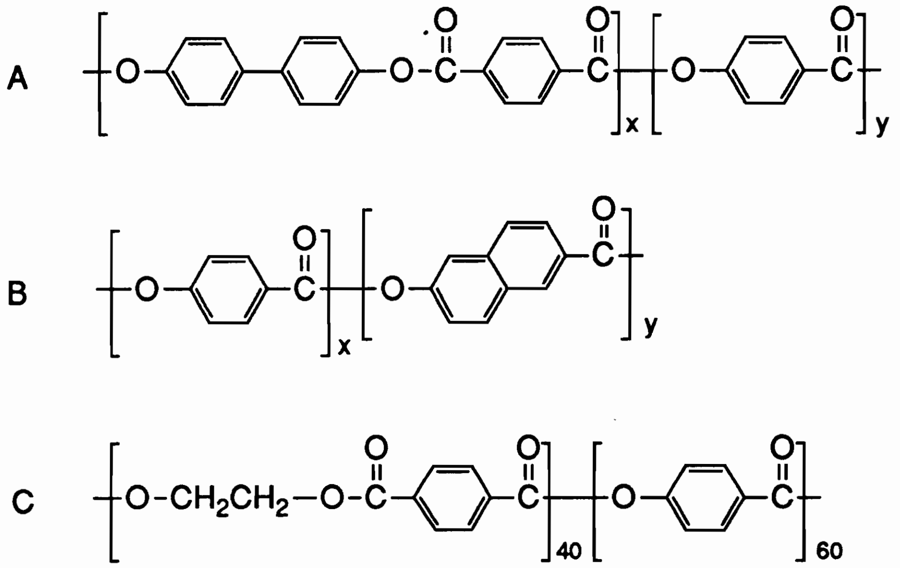


Figure 2.3. Relationship between morphology and rheology[37]



Scheme 2.5. Commercially available (or potentially available) LCPs a). Xydar® (Amoco) b). Vectra®(Celanese) c). POB-PET(Eastman)[3]

Some questions regarding the nature of the micro-structure of the copolyesters being either random or block-like arises from the relative intractability of the copolymers. There are almost an equal number of publications describing the micro-structures of the copolymers either way [3] Economy pointed out that the micro-structures largely depend on the thermal history of the materials [3]. He also stated that, in the nematic melt, mixtures of polyesters can undergo rapid transesterification and lead to a random micro-structure[40]. Recently, some authors have used kinetic analysis to investigate the reactivity of different monomers (e.g. 4-hydroxybenzoic acid vs. 4, 4'-biphenol) [41]. This study also leads to the nature of the micro-structures.

In our laboratory (27, 28) and eleswhere(42-45) new types of polyesters have been synthesized by reacting 4-acetoxybenzoic acid (PABA) with 4(4'-acetoxyphenoxy) benzoic acid (PAPBA) or 3(4'-acetoxyphenoxy)benzoic acid. These two copolyester systems exhibit liquid crystalline properties over a wide range of compositions.[27, 44] It has been shown that PABA / PAPBA at molar ratio 65/35 has the lowest crystal melting transition temperature (280-295°C). In our research, we have incorporated some branching agents into PABA / PAPBA and successfully synthesized randomly star branched LCPs which can be transformed to LC foams by supersaturation of carbon dioxide followed by thermally blowing (46, 47).

From the disclosed LCP syntheses, there are four different approaches to obtain polyesters with the lowest possible melting temperature for better processability in the LC state [9] These approaches include:(Scheme 2.6)

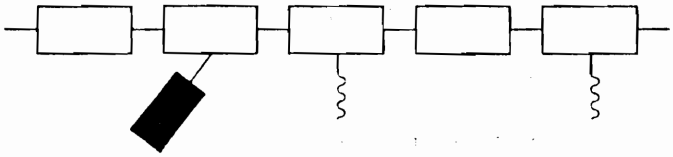
(a) Introduction of lateral substituents on the aromatic rings.
(b) Introduction of flexible spacers of different length and type in a regular or random manner.
(c) Introduction of different size co-monomers to form linear LCPs.
(d) Introduction of a nonlinear (kinked) unit into the linear rigid-rod structure.

During the past few years, our research has involved all approaches except the introduction of flexible spacers to control the melting transitions of new LCPs. [27, 28, 48]. All these approaches are based on the fact that reduced chain packing efficiency results in decreased crystal melting temperature.

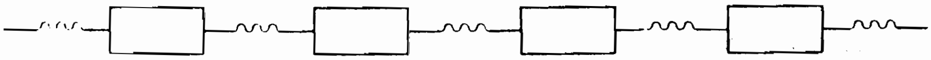
2.4 Poly(ethylene terephthalate) (PET)

Poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are the two most important engineering aromatic polyesters. In contrast to PBT, which has a rapid crystallization rate suitable for injection molding processes, PET has a low crystallization rate, which makes it unsuitable as a molding material unless appropriate chemical modification or nucleating agents provide a commercially acceptable rate of

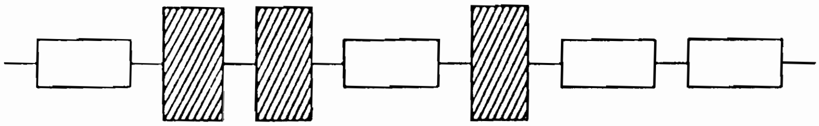
(a) Introduction of lateral substituents in random fashion



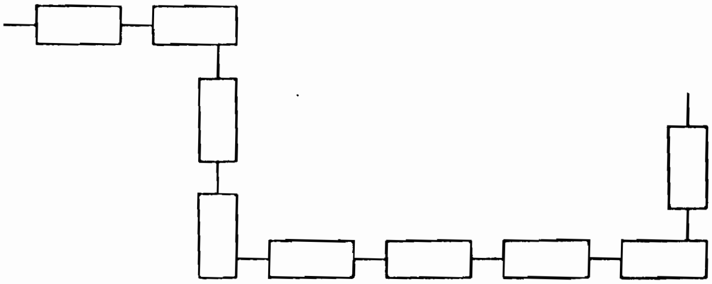
(b) Introduction of flexible spacers within the chain backbone



(c) Introduction of mesogenic counits of different shape and size



(d) Introduction of colinearity kinks



Scheme 2.6. Representation of the structural designs adopted for improving the bulk tractability of LCPs[24]

crystallization [11, 62].

The major applications of PET are fibers, films and beverage bottles. The beverage bottle application results in a dramatic enhancement in the PET production rate. The bottle grade PET usually is produced from dimethyl terephthalate (DMT), or terephthalic acid (TPA) and ethylene glycol (EG) in a continuous melt polymerization process, followed by a solid-state polymerization process at a temperature below the melting point. The last step reduces aldehyde content, which is a by-product of the polymerization process [11-13, 49]. Aldehyde contents have been obtained as low as 2 ppm by solid-state postpolymerization in contrast to about 24 ppm from melt processes[50]. Solid-state polymerization is usually not required for fiber and film production because aldehyde content is not a problem here. In recent years, fire retarding materials have attracted more and more attention. Studies related to the addition of a phosphorus compound to PET to change the flammability of PET have been conducted[13, 49, 51, 61]. Our efforts have focused on the influence of triarylphosphine oxide comonomers on PET copolymers[52].

2.4.1 Synthetic methods for poly(ethylene terephthalate)

PET can be obtained either by direct esterification from TPA and EG or by transesterification from DMT and EG. A typical process diagram for the manufacture of PET is shown in Figure. 2.4 [13]. For many years, PET was prepared exclusively from DMT and EG. This was because TPA was not available with a sufficiently high purity[12, 13, 53, 54]. In addition, poor reaction control due to the heterogeneous reaction condition was another problem(TPA has higher mp and low solubility in EG). The major organic impurities in TPA from p-xylene oxidation are shown in Table 2.3.

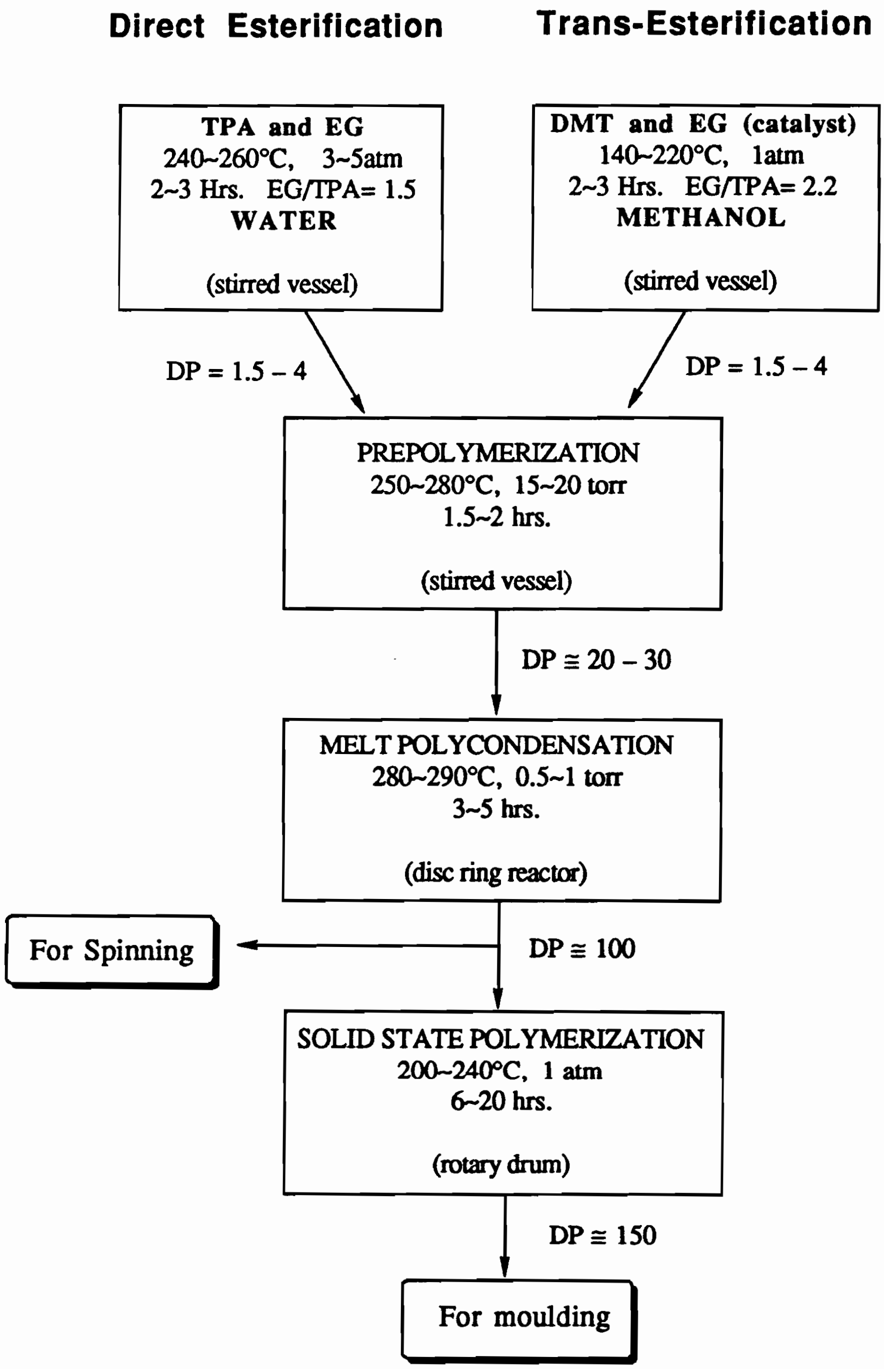
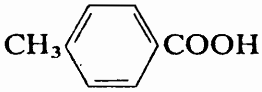
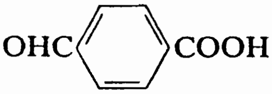
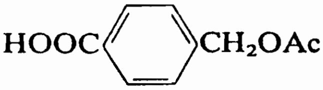
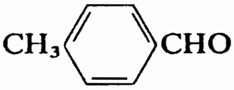
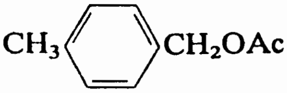
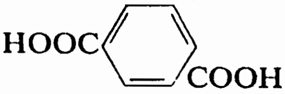
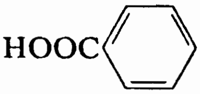
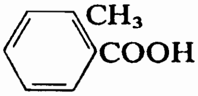
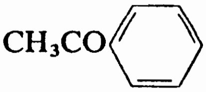
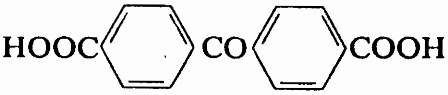
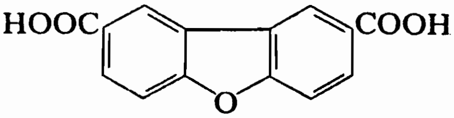
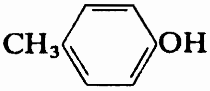


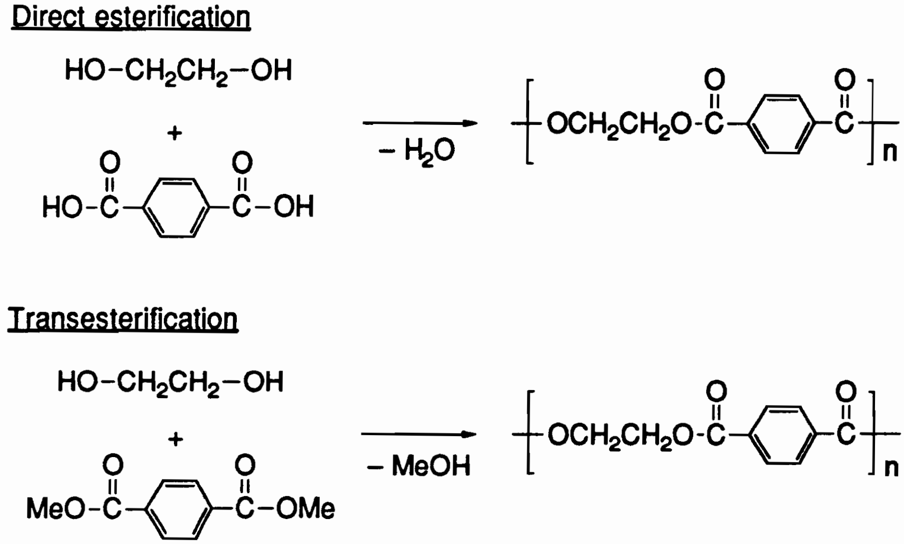
Figure 2.4. Operating conditions of different stages in PET synthesis[13]

Table 2.3. Impurities in terephthalic acid[13]

p-Toluic acid	
p-Carboxybenzaldehyde	
p-Acetoxymethylbenzoic acid	
p-Tolualdehyde	
p-Methylbenzyl acetate	
Isophthalic acid	
Benzoic acid	
o-Toluic acid	
Acetophenone	
p,p'-Dicarboxybenzophenone	
3,6-Dicarboxyfluorenone	
p-Cresol	

Among these impurities, three main impurities, p-toluic acid, p-carboxybenzaldehyde and benzoic acid are monofunctional compounds which limit the polymerization rate and the molecular weight of the polymer. Recently, the availability of high purity TPA and improvements in the reaction technique have made direct esterification the preferred process because of higher reaction rate, reduced catalyst requirements and environmental consideration, wherein water is preferred by-product relative to methanol as the by-product from the transesterification process.

In the direct esterification process, the first stage of reaction is done under pressure (3-5 atm) at high temperature (240-260°C) with elimination of water. At the end of the first stage there is a mixture of oligomers with an average degree of polymerization about equal to three. Since the carboxyl groups of TPA can modestly catalyze the direct esterification, a metal catalyst is not always required for this process at this stage. However, in order to increase the initial reaction rate, an excess of diol(EG) is often employed(molar ratio of EG/TPA = 1.5). The excess diol is subsequently removed in



Scheme 2.7. Synthesis of poly(ethylene terephthalate)s via direct or transesterification

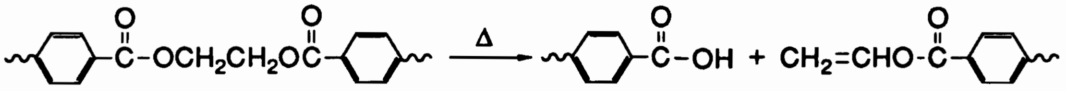
monomeric form via an alcohol-ester exchange reaction in the last period of polymerization, so that the initial imbalance of the functional group does not affect the molecular weight of the final polymer(Scheme 2.7).

In the transesterification process, the first step of transesterification is conducted at atmospheric pressure at 170-210°C using catalysts such as lead, zinc, manganese, calcium, or cadmium acetates[12,13,49]. DMT has a lower melting point, higher solubility in diols and is usually available in a higher purity grade than TPA. Therefore, transesterification processes traditionally have advantages in the production of better quality products and easier process control. However, in contrast to direct esterification, transesterification proceeds very slowly in the absence of catalysts[55, 56]. Large excess of diol(EG/DMT = 2.2) is commonly employed to increase the reaction rate and to obtain complete evolution of methanol at the end of the first stage. If some methyl ester groups are left over to the second stage, both the polymerization rate and the degree of polymerization may be limited [13,49].

At the second stage, a second catalyst, such as Sb_2O_3, GeO_2 or antimony acetate is added and the reaction is carried out at 275-290°C under reduced pressure. Titanium alkoxides are also very good catalysts for both stages, but they may sometimes lead to discoloration of PET. As discussed earlier, a solid-state polymerization process is always an option to produce very high molecular weight.

2.4.2 Degradation reactions during PET synthesis

During PET polymerization processes, chain scission or transformation of reactive end groups into less reactive or non-reactive sites can reverse the chain growth reaction and lead to a decay in the properties of the polymers. Chain-scission of PET can occur randomly by pyrolysis or possibly abstraction of a β-hydrogen from the glycol functionality via a cyclic transition state (equation 2) This produces a carboxyl group and a vinyl ester end-group [49,57,58]. These chain ends can undergo further reactions leading to acetaldehyde, polyene chains or other by-products [13, 49, 59, 60]. The chain scission reaction has been reported to be first order for the ester group. The catalysts used for polymerization usually remain in PET, and it has been found that they may sometimes affect the PET thermal and hydrolytic degradation reaction[49]. PET is somewhat hygroscopic and in its melt state the resin hydrolyzes easily to produce lower molecular weight[11]. Therefore, before processing PET resin, the moisture level should be reduced below 0.02% and maintained at that level.



(2)

2.5 Solid State Polymerization

Solid state polymerization(SSP) is a somewhat vogue term, but usually refers to either two aspects; e.g. the starting materials are either crystalline monomers or the concept of semicrystalline pre-polymers [63, 64a]. In the first case, the monomer is usually transformed into a polymer at a temperature lower than the melting temperature of both monomer and polymer. The interest in this type reaction is limited the polymers which usually cannot be prepared by other polymerization methods. There are a few examples of polymerization reactions, where the SSP is conducted in solutions. For example, poly(arylene ether ketone) reportedly can be synthesized in chlorinated solvent at low temperature by using AlCl3 as catalyst[64b].

In the second case, the prepolymers are synthesized via known techniques followed by SSP at a temperature below the crystal melting transition(Tm), but well above Tg of the polymers. It is generally accepted that the post-polymerization step of the semicrystalline polymer proceeds by step reactions in the amorphous regions. Polymers produced are then treated by SSP often exhibit improved properties becauseof the higher molecular weight and because side reactions (leading to defects in the chemical structure or to undesirable by-products) are limited or avoided.

2.5.1 Solid State Polymerization of Polyamides and Polyesters

Since the capability of polyamides to further increase their molecular weights in the solid state was recognized more than 40 years ago[65], a number of papers and patents have been published for the SSP of prepolymers[66-72]. Major attention has been devoted to polyesters derived from terephthalic acid (PET and PBT in particular) and to aliphatic polyamides (nylon 6 and nylon 6,6) for their commercial interest. Some authors also report that SSP is applicable to thermotropic LCPs (or polyarylates) [27, 73, 74]. In general, molecular weight plays an important role when polyesters and polyamides have to be used as engineering thermoplastics. For certain processing techniques, such as blow-molding and extrusion, a high molecular weight polymer with high viscosity is usually required to prevent collapse in the soft pre-formed state. However, high melt viscosity polymers are very difficult to synthesize by conventional step polymerization processes in bulk. This is because polymer melts with high viscosity are difficult to handle and to remove from the reaction vessel. An increase in temperature to reduce viscosity may result in side reactions. These disadvantages can be limited or avoided by conducting SSP right after the regular polymerization processes.

In general, SSP processes are carried out by heating low or medium molecular weight pre-polymer in the form of chips or powders in a stream of inert gas or under vacuum at a temperature above the glass transition temperature Tg of the polymer but below the melting point Tm. The main factors that can affect SSP include size, initial molecular weight, number and type of the end group, percent crystallinity, temperature, time and the method to remove by-products. Among these factors, the temperature is probably the most important factor [64]. Commonly, the process is carried out at a temperature close to the melting point of the polymer (10-40°C lower).

Usually SSP exerts a skin-core effect[75-77]. This effect caused by the fact that the by-products diffuse out from the surface much more easily than the center. As shown in Figure 2.5, reaction times are also very important. For example, the molecular weight first increases to a maximum then it decreases. This decrease in molecular weight is considerde to be due to scission reactions becoming predominant after long reaction times[75, 78]. In the case of PET, the process is conducted at 200-240°C for 6-20 hours [13, 64].

2.6 Polymeric Foams

Foamed plastics can be considered as the blends of thermoplastics, thermosets or elastomers with gases and are often called cellular plastics. They are classified according to their hardness, cellular structure, or the polymeric materials on which they are based. The walls of the foam cells can be either closed or opened. In the opened cell foams, gases can freely move from one cell to the others, but this movement is confined in the closed cell foams. Perhaps the first commercial cellular polymer was sponge natural rubber, introduced between 1910 and 1920[79].

Rigid foams usually have a high glass transition temperature and both their tensile strength and compressive strength increases with foam density (Figure 2.6). In contrast, flexible foams have low glass transition temperatures, which lie considerable below the application temperatures. Since foams have low densities and elastic behavior, they are

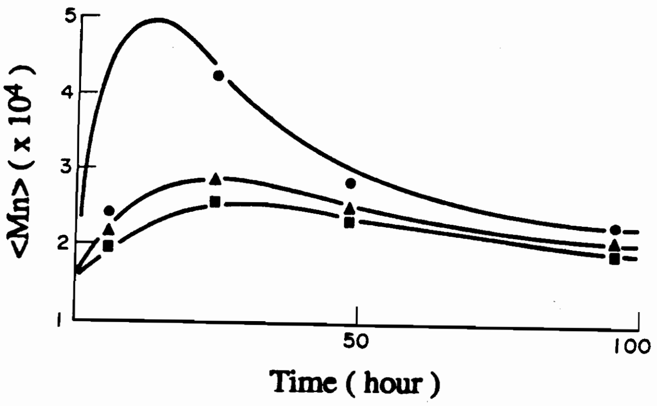


Figure 2.5. Number-average molecular weight vs. SSP reaction time for samples removed from the surface(•), the center(■]) and at intermediate depth[▲] of a planar sheets of 3 mm thick PBT[64, 76]

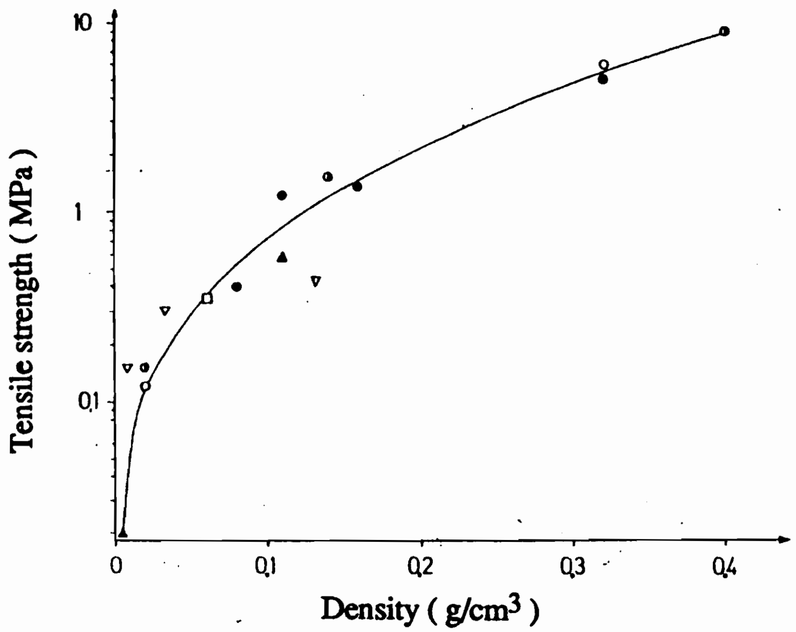


Figure 2.6. Tensile strength of rigid foams as a function of density[82]

used as shock-absorbing packaging materials. For example, structural foams, which are closed cell foams generally not uniform in cell structure with a dense outer skin and a low density in interior, have a favorable ratio of rigidity to mass as well as a high strength. They exhibit very good thermomechanical properties. Generally, foams also exhibit low thermal conductivity, and so are used as insulating materials.

A variety of methods can be used to generate foams. These methods can be classified as chemical, physical and mechanical processes. In the first process, blowing agents such as azo-compounds or ammonium hydrogen carbonate are added into polymers followed by a thermal decomposition reaction. The blowing agents decompose into different gases, which blow the polymers into foams. The foam-producing gases can also be produced in the polymerization reaction or by thermal decomposition of a synthesized co-polymer with a labile composition.

For the physical process, liquid or gas is usually added into polymer matrix under pressure. Upon heating or shock volatilization, the liquid or gas expands and produces foam. The mechanical foam-producing process requires vigorus stirring or whipping of the foam materials. After the foam is formed, a chemical crosslinking reaction is necessary to fix the shape.

In this research, novel liquid crystalline foams were generated. The LCP foams generated were designed to be closed cell foams.

3. EXPERIMENTAL

3.1 Monomer Source and Purification

Bisphenol A : Bis A was obtained as monomer grade material from DOW Chemical. It was used without purification.(Mp 158°C, MW 228.27)

4,4'-Biphenol: Biphenol was purchased from Fisher. It was recrystallized from acetone. (Mp 279°C, MW 186.22)

Hydroquinone: High purity, polymer grade hydroquinone was obtained from Eastman Chemical Co. It was used without purification.(Mp 172°C, MW 110.12)

4-Hydroxybenzoic acid: High purity, polymer grade hydroxybenzoic acid was obtained from Amoco Chemical Co.. It was used without purification.(Mp 217°C, MW 138.12)

Dimethyl terephthalate(DMT): DMT was obtained from Eastman Chemical Co. It was recrystallized from methanol.(Mp 140-142°C, MW 194.19)

Ethylene glycol(EG): EG was also obtained from Eastman Chemical Co. It was distilled over molecular sieves which was dried at 100°C in vacuum.(Bp 196-198°C, MW 62.07).

3.2 Synthesis of Monomers

3.2.1 Diacetoxy Monomers from the Corresponding Bisphenols

In this section, three diacetoxy monomers were generated via a same method by refluxing the corresponding bisphenols with acetic anhydride. These three monomers were used to synthesize amorphous triaryl phosphine oxide containing polyarylates and liquid crystalline polyarylates.

3.2.1.1 2,2'-(4-Acetoxyphenyl) Propane (Bisphenol A Diacetate)

Bisphenol A (40g) was refluxed with 100ml acetic anhydride at ~ 140°C and a catalytic amount of sodium acetate in a 3-neck flask, which was equipped with a condenser and a nitrogen inlet. After 1 hour, the excess of acetic anhydride was distilled off. In the same flask, ethanol and water were then added to recrystallize the product. Yield 92%, mp. 83°C.

3.2.1.2 4,4'-Biphenol Diacetate (BPDA)

4,4'-Biphenol diacetate was prepared by a method similar to the preparation of bisphenol A diacetate. 4,4'-Biphenol (50g) was refluxed with 100ml of acetic anhydride in the presence of sodium acetate for 1 hour. The recovered product was then recrystallized in ethanol/water mixture. Yield 95%, mp. 162°C.

3.2.1.3 Hydroquinone Diacetate

Hydroquinone diacetate was prepared by the same procedure as discribed above for the two diacetate monomers. The product had a yield of ~92%, mp. 121°C.

3.2.2 4-Acetoxybiphenyl

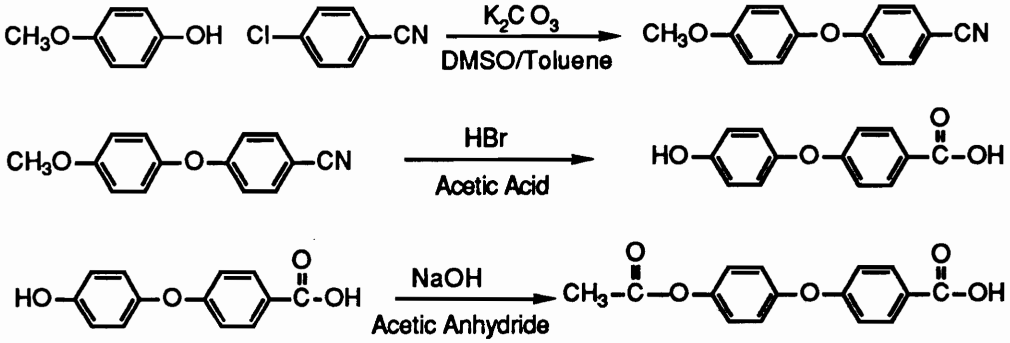
4-Phenylphenol (20g) was dissolved into a stoichiometric amount of aqueous potassium hydroxide solution at 0°C. Then, an excess of acetic anhydride (30ml) was added and the solution was stirred for 1 hour. The collected solid was then recrystallized in ethanol/water mixture mixture. Yield 92%, mp. 76°C.

3.2.3 4-Acetoxybenzoic Acid (PABA)

4-Hydroxybenzoic acid (100g) was dissolved into an aqueous potassium hydroxide (84g) at 0°C. Acetic anhydride (150ml) was then added. After stirring for 1 hour, the solution was acidified with concentrated HCl (60ml). The resulting white product was filtered, washed with water, and recrystallized in ethanol/water mixture mixture. Yield 92%, mp. 189°C.

3.2.4 4(4'-Acetoxyphenoxy)benzoic Acid (PAPBA)

The 4(4'-acetoxyphenoxy)benzoic acid was prepared in a series of 3 reactions[27, 44], begining with the reaction of 4-methoxy phenol with 4-chlorobenzonitrile. (Scheme 3.1)



Scheme 3.1 Synthesis of 4(4'-acetoxyphenoxybenzoic Acid

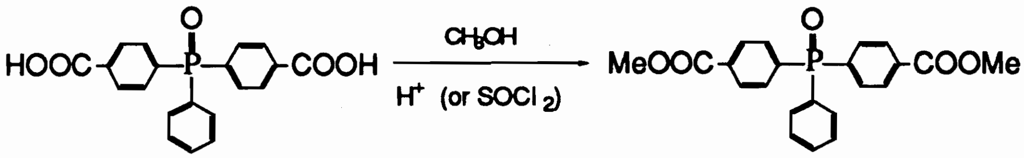
The first reaction was performed as follows: 4-Methoxyphenol (124.14g, 1 mole) and potassium bicarbonate (83g) were added into a 2000 ml 3-neck flask which was equipped with an overhead stirrer, Dean Stark trap and nitrogen inlet. DMSO (1250ml) and toluene (300ml) were then added. The temperature was increased to 140°C for 4 hours under N_2 flow. Then, 4-Chlorobenzonitrile (137.57g, 1 mole) was added into the flask when the temperature reached 100°C. Then, the reaction was performed at 160°C for another 8 hours. After the solution was cooled to 80°C, it was filtered and 1200 ml water was added to precipitate the product out of the solution. The collected product was recrystallized from ethanol/water mixture. Yield ~93%, mp. 110°C.

The second step was to cleave the methoxy group and to hydrolyze the nitrile group by HBr/acetic acid mixture: 4(4'-Methoxyphenoxy)benzoic acid (197g, 0.875 mole) was refluxed in 48% hydrogen bromide (500ml) and acetic acid (1000ml) mixture for 12 hours. A precipitate was formed after water was added. The collected product was then recrystallized from ethanol/water mixture. The yield of the white product was ~95%, mp. 192°C.

The last step is similar to the preparation of 4-acetoxybenzoic acid. 4(4'-Hydroxyphenoxy)benzoic acid (191g, 0.83 mole) was dissolved into aqueous sodium hydroxide solution at O°C. Acetic anhydride (164ml) was then added and the reaction mixture was stirred for 1 hour. The product was recrystallized from ethanol/water mixture. Yield 95%, Mp. 155°C.

3.2.5 Bis(4-methoxycarbophenyl)Phenyl Phosphine Oxide

This dimethyl ester was synthesized from the corresponding dicarboxylic triaryl phosphine oxide which was discussed in Part I (section 4.1.8). Two methods have been used to prepare the dimethyl ester. (Scheme 3.2) The first method is a condensation reaction of the diacid and methanol in the presence of a strong acid such as sulfuric acid. For example, bis(4-carboxy phenyl)phenyl phosphine oxide (30g) was refluxed in 150 ml of anhydrous methanol and 10 ml of concentrated sulfuric acid as a "catalyst" for 20 hours. Then, water (~100 ml) was added to help precipitate the product. This product



Scheme 3.2 Bis(4-methoxycarbo phenyl)phenyl phosphine oxide.

was recrystallized in methanol/water mixture. The yield was about 80%. The second method was to reflux the diacid with thionylchloride (e.g. 5 g/ 15ml) for 5 hours followed by removal of the excess thionyl chloride under reduced pressure. Methanol was then added into the acidchloride, and the product was observed to form immediately. Recrystallization from methanol/water affords a colorless product. Yield ~90%, Mp. 160-161°C.

3.2.6 Branching Agents

In this section, four branching reagents were prepared, which were respectively tri-, tetra- and hexa-functional monomers.

3.2.6.1 1,3,5-Triacetoxybenzene

1,3,5-Triacetoxybenzene was prepared by the method similar to bisphenol A diacetate. 1,3,5-Trihydroxybenzene dihydrate (or phloroglucinol dihydrate) (10g) was refluxed with acetic anhydride (40ml) in the presence of a catalytic amount of sodium acetate for two hours. The excess of acetic anhydride was distilled off and the product was recrystallized in ethanol/water mixture. Yield ~90%, Mp 106°C.

3.2.6.2 Tris(4-acetoxyphenyl)Phosphine Oxide

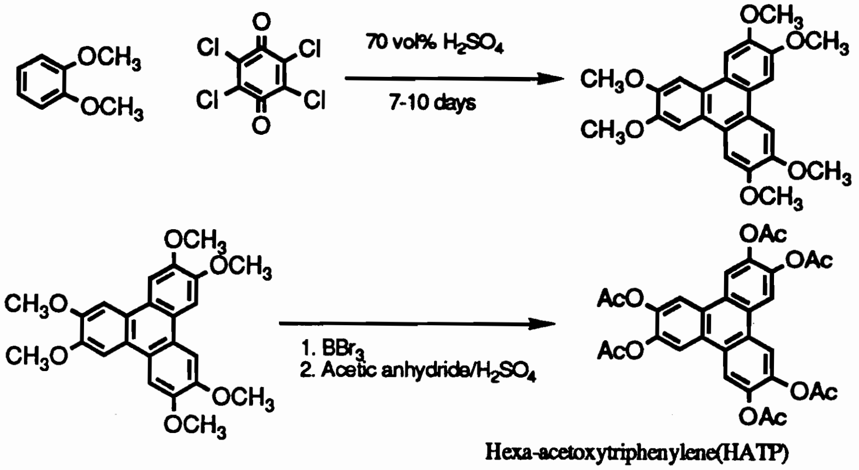
Tris(4-acetoxyphenyl)phosphine oxide was synthesized from tri(4-hydroxyphenyl) phosphine oxide by the same procedure as that described for bisphenol A diacetate. Yield ~92%, Mp 143°C.

3.2.6.3 2,2',4,4'-Tetraacetoxybenzophenone

2,2',4,4'-Tetraacetoxybenzophenone was synthesized from 2,2',4,4'-tetrahydroxybenzophenone by the same procedure as for bisphenol A. The yield was 92%, 141°C.

3.2.6.4 Synthesis of 2,3,6,7,10,11-Hexaacetoxytriphenylene

1,2 Dimethoxybenzene(veratrole) (22g, 159mmole) in 70 vol% aqueous sulfuric acid 300ml was trimerized by reacting with tetrachlorobenzoquinone(78g, 306mmole), which acts as a hydrogen acceptor. After 1 hour of shaking and a reaction period of 8 days, water (800ml) was added and the solid was collected. The product was repeatly washed with water and ethanol. The blue solid was then extracted with chloroform. After the solvent was removed, the solid was treated with ethanol, benzene then chloroform/silica-gel which provide a crude powder. It was recrystallized two or three times in trifluoroacetic acid and a colorless crystal, 2,3,6,7,10,11-hexamethoxytriphenylene, resulted with a 52% yield. Boron tribromide was used to cleave the methoxy group in dry benzene. Subsequent acetylation was conducted in excess acetic anhydride (as



Scheme 3.3 Synthesis of 2,3,6,7,10,11-Hexaacetoxytriphenylene

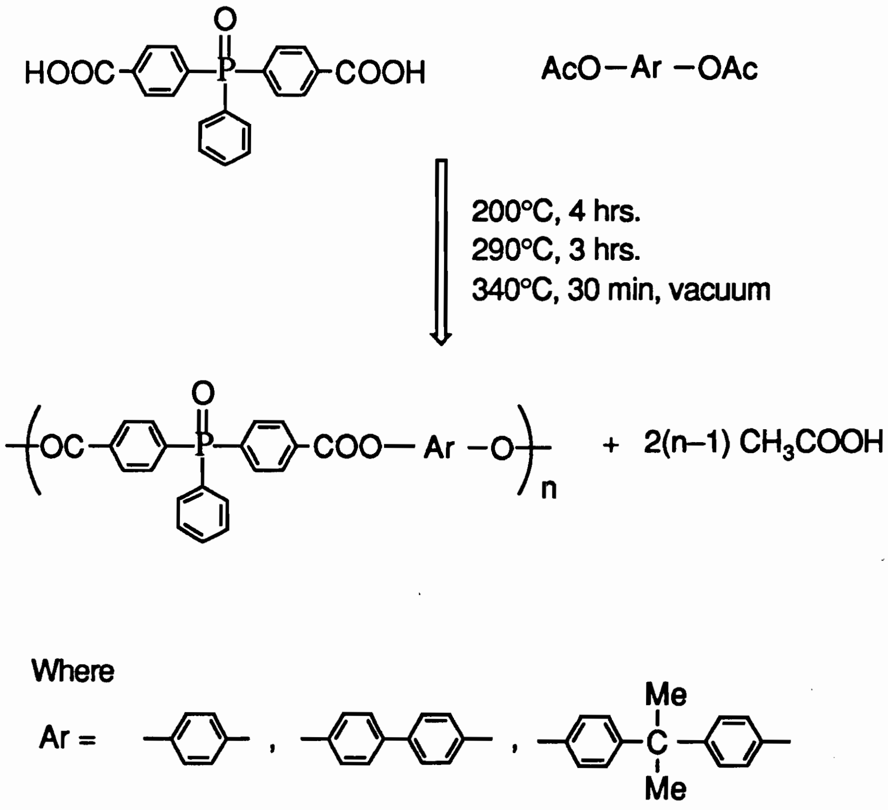
reactant and solvent) in the presence of sulfuric acid. The resulting hexaester was extracted with chloroform and recrystallized in nitromethane. The yield was 55%[83, 84].

3.3 Triaryl Phosphine Oxide Containing Polyarylates via Melt Acidolysis

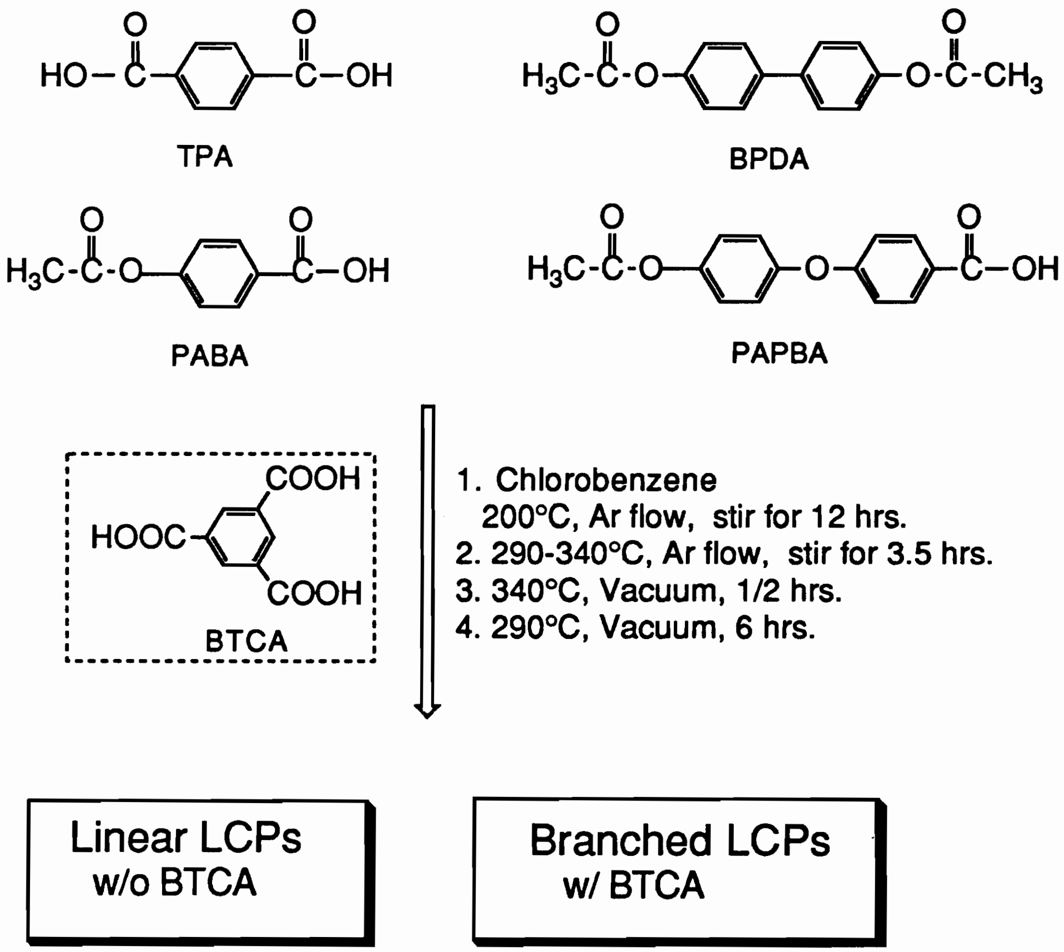
A melt acidolysis technique was used to synthesize the polyarylates containing the triarylphosphine oxide comonomer, as shown in Scheme 3.4. A typical reaction as follows: Bis(4-carboxyphenyl)phenyl phosphine oxide (9g, 24.6 mmole) and bisphenol A diacetate(7.67g, 24.6 mmole) along with chlorobenzene (3ml) were added into a melt reactor which was equipped with a nitrogen inlet and a high torque overhead stirrer and heated in a sand bath. The temperature was initially raised to 200°C for 4 hours. At this point, the reaction mixture became a homogeneous fluid with low viscosity, which was then slowly increased to high viscous state after the temperature was raised to 290°C for 3 hours. The viscosity was reduced when the temperature was increased to 340°C for 30 min. At this stage, the most of chlorobenzene and acetic acid were volatilized and removed by the nitroge stream. Then, a vacuum around 0.5 torr was applied to the reactor. Within 30 minutes, the polymer solidified at this temperature (340°C). The high torque stirrer was not able to stir this reaction mixture any more. After cooling, polymer was brittle and transparent. It was noticed that the solidification behavior was also observed for the hydroquinone or biphenol diacetate reacted with dicarboxylic triarylphosphine oxide monomer.

3.4 Linear and Branched Polyarylates Based on PABA, TPA, BPDA and PAPBA (Xydar® with 28 mole% of POPB)

The 28 mole% of polyoxyphenoxybenzoate(POPB) modified Xydar® polyarylates have a relatively low crystal melting transition temperature (eg. Tm 262°C according to



Scheme 3.4 Triarylphosphine oxide containing polyarylates via melt acidolysis



Scheme 3.5 Linear and star-branched polyarylates based on modified Xydar® system

earlier data [27]). The linear and star branched polyarylates of the modified Xydar® copolymers were synthesized via melt acidolysis at this composition. For the linear polyarylates, 4-acetoxybiphenyl (PABP) was used to control the molecular weight. For the "star-branched" polyarylates, 1,3,5-benzenetricarboxylic acid was the branching reagent utilized. (Scheme 3.5)

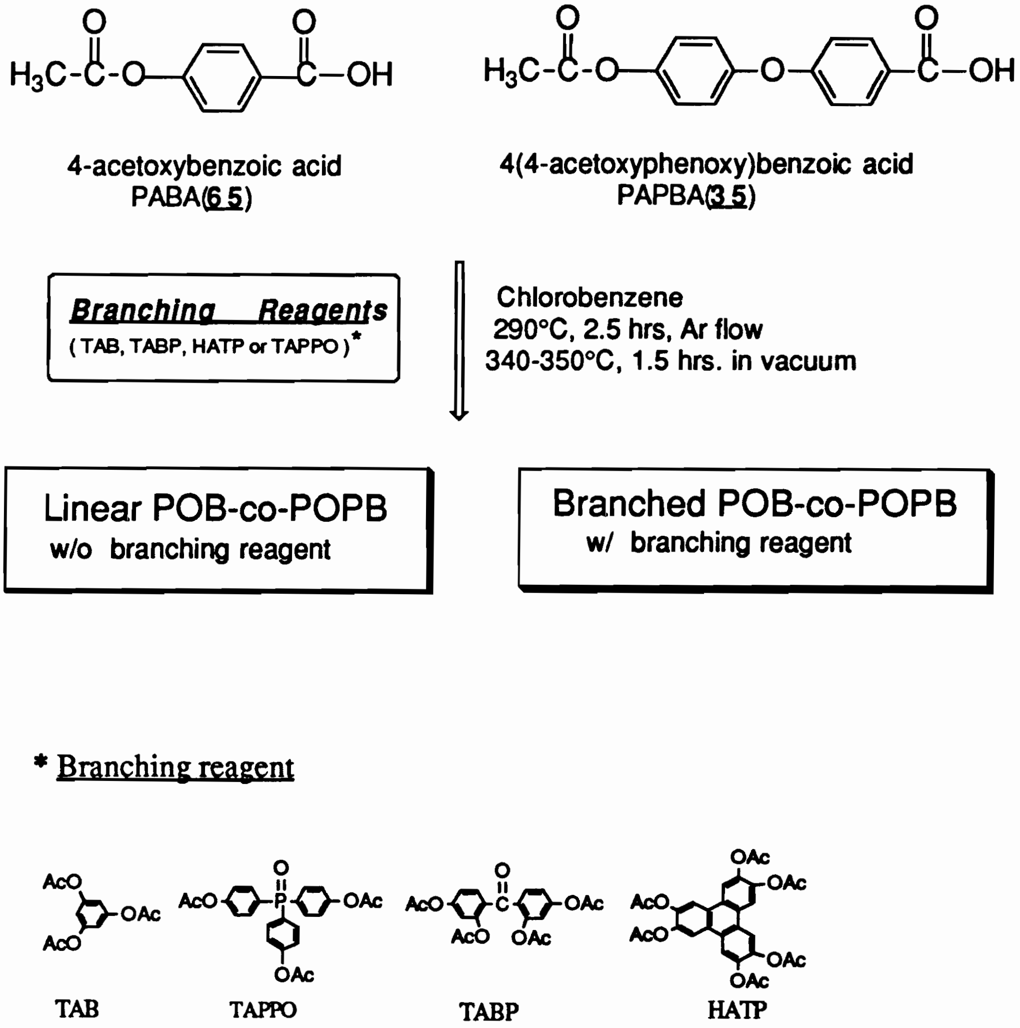
A list of materials used for the synthesis of linear modified Xydar® of non-controlled copolymer in a melt acidolysis is illustrated as follow :

4-Acetoxybenzoic acid	(PABA)	12.00g	66.6 mmole
4,4'-Biphenol diacetate	(BPDA)	9.00g	33.3 mmole
Terephthalic acid	(TPA)	5.53g	33.3 mmole
4(4'-Acetoxyphenoxy)benzoic acid	(PAPBA)	10.57g	38.4 mmole
Chlorobenzene	5 ml		

__Note:__ (TPA + BPDA) : PABA : PAPBA=24 : 48 : 28(in mole%).

The reaction was conducted under argon flow at 200°C for 12 hours. The by-product acetic acid was detected by indicator paper at 200°C after 2~3 hours and the viscosity only increased to medium range at the end of this stage. After the reaction was heated to 290°C for 3 hours, the viscosity was greatly increased and it was reduced at 340°C for 30 minutes. Once the vacuum (0.4 torr) was applied to the system at 340°C (30 minutes), the reaction mixture became a porous material and it was not able to flowunder agitation. Finally, the temperature was reduced to 290°C under vacuum for another 6 hours. At this stage, polymer was not agitated. The polymer was light brown in color.

The monofunctional end-cap monomer, 4-acetoxybiphenyl(PABP), was used at 1, 3 and 5 mole% incorporation by the same procedure as described for uncontrolled linear polyarylate synthesis. For the "star-branched" polyarylates, the trifunctional BTCA was used at 0.1, 0.5 and 1% incorporation. The resulting "branched" polyarylates were impossible to be stirred once the vacuum was applied to the system at 340°C. These properties were not observed for the corresponding linear polyarylates.



Scheme 3.6 Synthesis of Linear and Branched POB-POPB

3.5 Branched Polyarylates Based on POB-POPB System

This polyoxybenzoate-co-polyoxyphenoxybenzoate (POB-POPB) was synthesized via melt acidolysis as mentioned above for the two polyarylate systems. Two AB monomers were used for the reaction and the monofunctional monomer, PABP was used to control the molecular weight of the linear POB-POPB. For the star branched POB-POPB, multi-functional monomers were used to control the molecular weight of the polymers as well as a branching agent(Appendix B). The reactions are shown in Scheme 3.6.

The stoichiometric amounts of monomers for the synthesis of the linear and branched POB-POPB copolymers were calculated as shown in Appendix B. For example, the following materials were used to prepare linear POB-POPB with molecular weight of 20,000 g/mole:

4(4'-Acetoxyphenoxy)benzoic acid	13.00g	47.8 mmole
4-Acetoxybenzoic acid	15.98g	88.7 mmole
4-Acetoxybiphenyl	222.5mg	1.048 mmole
Chlorobenzene	3 ml	

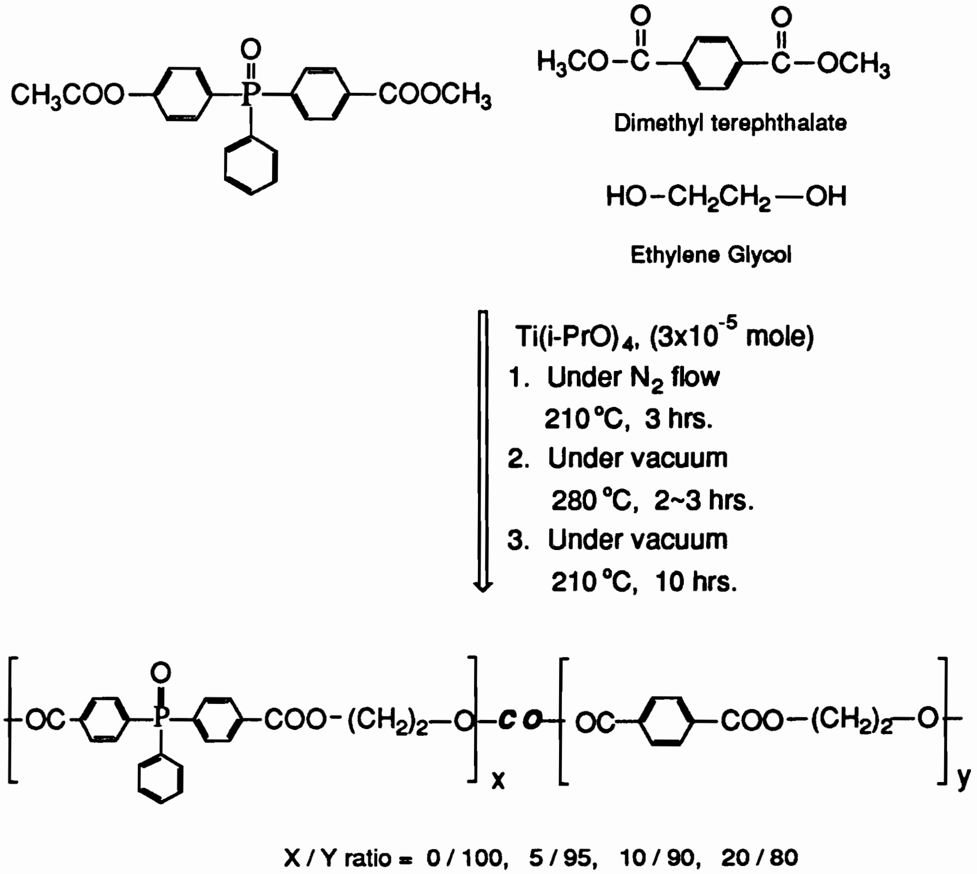
The above materials were charged into a melt reactor equipped with a high torque overhead stirrer, a nitrogen inlet and an outlet adaptor. The temperature was increased to 290°C for 2.5 hours under Ar flow. At this temperature, the acetic acid (detected at 250~260°C by indicator paper) and chlorobenzene were refluxing and the viscosity of the mixture increased from a water like fluid to a very viscous fluid. Then, the temperature was raised up to 340-350°C and a less viscous fluid was observed. Finally, the vacuum (0.5~1 torr) was applied to the system as the temperature reached 340°C(1.5 hours). At this point, the mixture was a fluid with very high viscosity which was able to flow under agitation. The resulting polyarylate was removed from the reactor while still hot.

3.6 Liquid Crystalline Foam Generation

The liquid crystalline foams were generated via a physical process by using carbon dioxide (CO_2) as the blowing gas. The work described in this section was done in collaboration with Wilkes and Risch[46, 47]. This gas supersaturation technique of producing liquid crystalline foams involves three steps. First compression molded plaques of POB-co-POPB copolymers with dimensions of 2.5mm thickness and 25mm diameter were placed in a high pressure cell filled with CO_2 at a pressure of 6500Kpa (950 psi). Samples were periodically removed and weighed to monitor mass uptake of CO_2. After one week, at which point gas saturation was approached in all samples, these samples were removed from their high pressure environment and placed in an oven equilibrated at a foaming temperature above the crystalline melting point of the LCPs. At this point, bubbles nucleated and grew within the LCP melts. After being held at the foaming temperature for 60 seconds, the LCPs were removed from the oven and quickly cooled to room temperature.

3.7 Triaryl Phosphine Oxide Containing Poly(ethylene terephthalate) Copolymer

Poly(ethylene terephthalate) copolymers were synthesized via the transesterification route[52]. (Scheme 3.7). A low concentration of Ti(IV) isopropoxide ($3x10^{-5}$ mole) was used as a catalyst for both stages of the reaction. In a typical PET polymerization, an excess of ethylene glycol (EG) and a stoichiometric amount of dimethyl terephthalate (DMT) and the phosphine oxide dimethylester monomer were charged in a melt reactor at the molar ratio of 2.2 moles EG/1 mole DMT & P(O) monomer. The initial reaction temperature was 210° for three hours. Next, the temperature was raised to 285°C and vacuum (0.4-0.6 torr) was applied to the system for 2-3 hours. At this stage, the viscosity of the mixture increased from non-viscous to very viscous as the excess of ethylene



Scheme 3.7 Synthesis of triaryl phosphine oxide containing PET copolymers

glycol was removed. In a post reaction (solid-state polymerization) step, the product was held at 210°C for 10 hours under vacuum. Finally, in order to remove the copolymer from the reaction vessel, the temperature was increased to 270°C and the copolymer was removed while still hot. The triarylphosphine oxide containing PET copolymer was deep yellow color which was presumably due to the use of the titanate catalyst.

3.8 Characterization

3.8.1 Monomer Analysis (NMR, FTIR, MS, Elemental Analysis)

The instruments and methods used to analyze the monomers were the same as in Part I.

3.8.2 Intrinsic Viscosity Measurement

The IV measurements for phosphine oxide containing PET copolymers were conducted in phenol/tetrachloroethane mixture at the ratio 50/50 by weight (25°C).

3.8.3 Thermal Analysis (TGA & DSC)

Both TGA and DSC thermal analysis were performed with a Perkin-Elmer 7 Series Instrument for the PET copolymers. The TGA tests were conducted in air, at a heating rate of 10°C/minutes. DSC measurements utilized two heating cycles from 30–280°C at a heating rate 10°C/mininutes.

For the LCPs and polyarylates, the DSC was performed on a Du Pont DSC-912 instrument and the TGA was performed on a Du Pont TGA-951.

3.8.4 Dynamic Mechanical Analysis (DMA)

DMA measurements were by using a Perkin-Elmer 7 Series instrument in the extension mode at a heating rate 10°C/min and 1 Hz

4 RESULTS AND DISCUSSION

4.1 Synthesis and Characterization of Monomers

4(4'-Acetoxyphenoxy)benzoic acid (PAPBA) was synthesized similar to earlier reported procedures [27, 44]. Alternate methods to prepare the PAPBA or its precursor, include Ullmann condensation [42,85] and halogenation of diphenyl ether followed by a series of additional reaction steps [86]. Fig 4.1 shown the ^{1}H-NMR spectra of the PAPBA monomer.

4.2 Synthesis and Characterization of Triarylphosphine Oxide Containing Polyarylates

The synthetic reaction employed for the synthesis of the triarylphosphine oxide containing polyarylates are illustrated in Scheme 3.4. The reactions temperatures were initially raised to 200°C to minimize the possibility of sublimation of the diacetate monomers. The small quantity of chlorobenzene used for the reaction plays an important role in returning the sublimed diacetate monomer back into the reaction mixture. The sublimation problem was reduced as the viscosity becomes higher. The temperature was stepwise increased to 290°C and 340°C. At 290°C, the viscosity of the reaction mixture was very high and it was reduced at 340°C. However, this fluid solidified rapidly once the pressure was reduced. The solidified material was transparent and the high torque stirrer was not able to stir the reaction mixture at 340°C. The materials were basically brittle, very possibly because of unknown degradation reactions under these conditions. The analysis results on the materials are summarized in the Table 4.1.

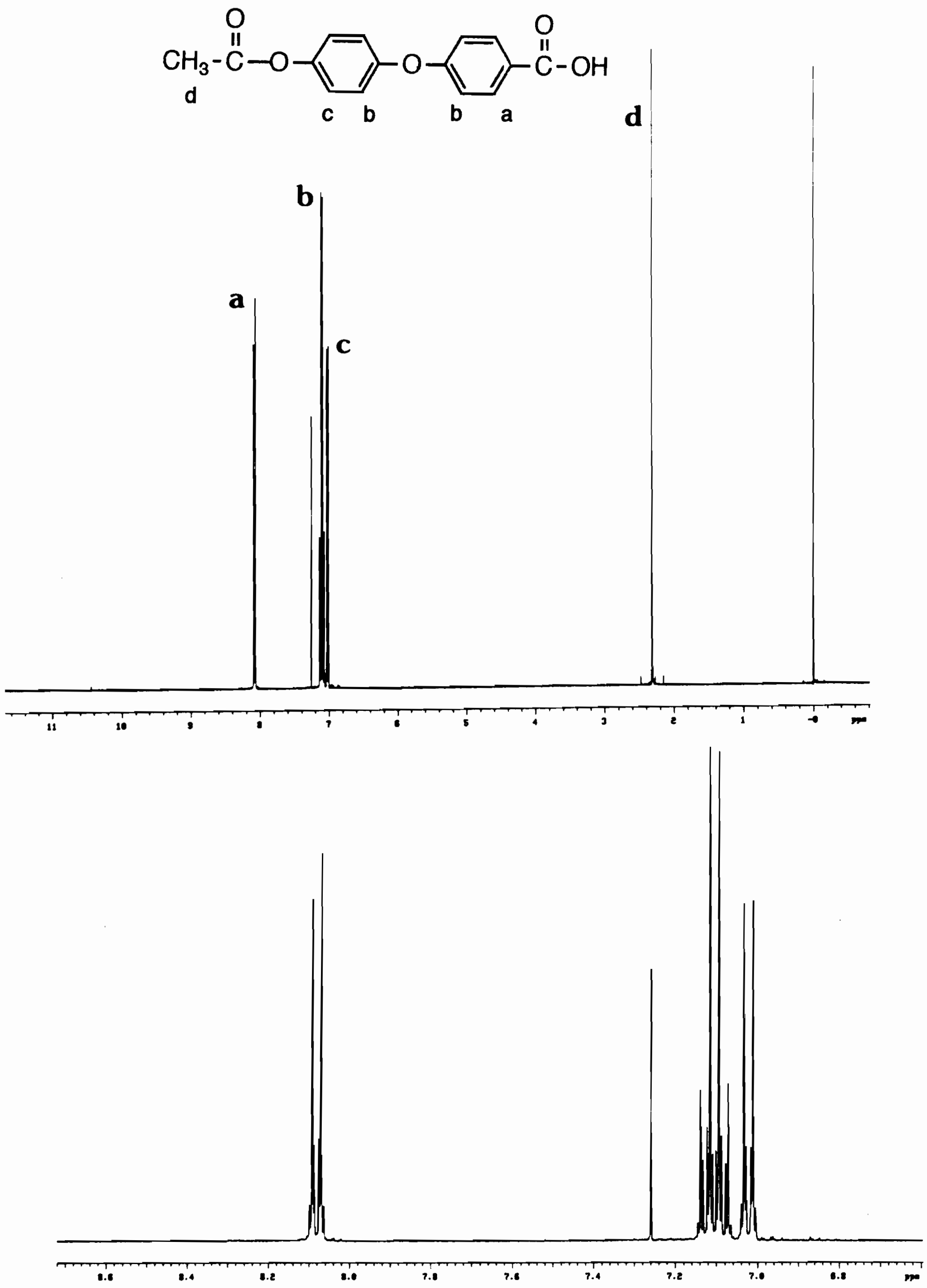


Figure 4.1 1H-NMR of 4,4'-acetoxyphenoxybenzoic acid

Table 4.1 Triarylphosphine oxide containing polyarylates

Bisphenol component	η^1 (dl/gm)	Tg^2 (°C)	TGA^3 (°C)	Char% in N_2(Air)
Bisphenol-A	0.24	207	448	33 (30)
Hydroquinone	0.20	202	433	32 (27)
Biphenol	0.27	227	455	37 (34)

* Polyarylates : $—(OCC_6H_4–P(O)(Ph)–C_6H_4COO–Ar–O)_n—$
1. In methylene chloride at 25°C
2. Second heat of DSC at 10°C/min
3. In air; 5% weight loss

The triaryl phosphine oxide containing polyarylates were soluble in methylene chloride. The intrinsic viscosities of the polymers were not high and their solution cast films did not exhibit good toughness. DSC measurements showed that the Tg of these materials were in the range 200°C to 230°C(Figure 4.2). The char yields of these materials in nitrogen or oxygen at 800°C are about the same, and very high compare to typical organic materials.

There are questions related to the factor that causes the solidification of the phosphine oxide containing polyarylates at high temperatures (340°C). From the table, these materials have Tg just above 200°C. Since they are transparent, soluble in methylene chloride and show no diffraction peaks in the WAXS patterns(i.e., only amorphous halos), these materials can not be semicrystalline polymers. However, the solidification phenomenon was observed and the hardness of the materials at 340°C was enough to ruin the high torque overhead stirrer. No good explanation can be found in the literature for the solidification of the phosphine oxide containing polyarylates. Several authors suggested that the solidification properties were associated with the crystallization of the

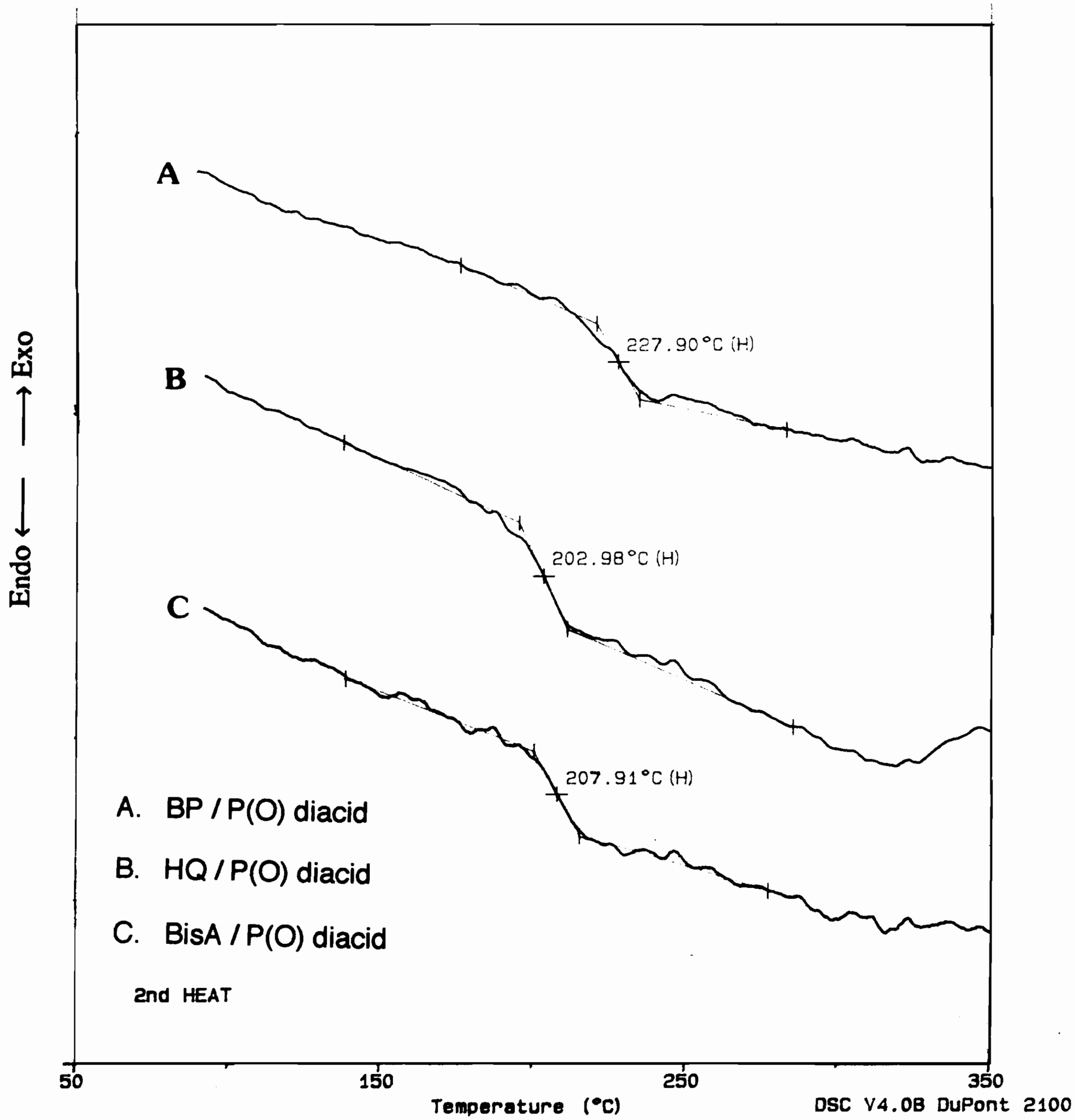


Figure 4.2 DSC traces of triaryl phosphine oxide containing polyarylates

triarylphosphine oxide containing polyarylates[88]. However, from our observation, these polymers were not semi-crystalline polymers. In general, the corresponding P(O) containing polyarylates that have been reported were synthesized via the solution acid chloride route have been very low molecular weight products. The solidification behavior was not observed for the synthesis of phosphine oxide containing poly(arylene ether)s (Part I) via high temperature melt processes. It is suggested that this solidification behavior is a manifestation of an unknown degradation process and that this is a main reason limiting the molecular weight by the melt acidolysis reaction. Elimination of by-product acetic acid at 340°C, may be part of the problem, particularly.

4.3 Synthesis and Characterization of Linear and Randomly Star-Branched Polyarylates Based on Xydar® and 28 mole% of POPB

Xydar® is a commercial LCP marketed by the Amoco Chemical. It was synthesized from 67mole% of PABA and 33mole% of TPA/4,4'-BPDA and has a Tm or possibly liquid crystalline transition of 388°C. In this thesis, Xydar® was modified with 28 mole% of PAPBA and had a Tm of 262°C (after annealing at 240°C for 50 min)[27]. This lowered Tm of the modified Xydar® allows processing at a relatively low temperature before degradation takes place. The polyarylate of this described composition was the first chosen material to be studied for the generation of a liquid crystalline foam. As illustrated in Section 3.4, a series of linear and "star-branched" polyarylates were prepared via melt acidolysis. Data of these polyarylates are shown in Table 4.2.

The molecular weight of linear modified Xydar® was controlled by the addition of 4-acetoxybiphenyl and the "star-branched" polyarylates were made by the addition of 1,3,5-benzenetricarboxylic acid. For the synthesis of linear polyarylates, the polymers at

Table 4.2 Thermal behavior of linear and branched polyarylate based on modified Xydar and POPB

Bran. Mono. mole%*	End-cap mole%	Tg(°C)	Tm(°C)	TGA**(°C)	Remark
0	0	111	274	503	linear
0	1	113	276	496	linear
0	3	107	273	482	linear
0	5	108	275	488	linear
0.1	0	112	274	499	crosslinked
0.5	0	113	278	501	crosslinked
1	0	129	no	512	crosslinked

* 1,3,5-benzenetricarboxylic acid

** In air, 5% weight loss at 10°C/min

340°C and under vacuum have exhibited very high viscosity under low agitation rates; however, the polymers could still be stirred. In other words, the polymer flows under agitation. For the synthesis of "Star-branched" polyarylates, a different observation was obtained. The shape of the polymer was basically unchanged once the vacuum was applied to the system. Although the polymers were soft at high temperatures (340°C), they did not flow under agitation. This phenomenon may be caused by the crosslinking of the "branched" polyarylates. The modified Xydar® consists of four main monomers. Among them the TPA and 4,4'-BPDA were AA, BB type monomers. These AA, BB monomers will result in crosslinked structures if a multi-functional monomer is present. Therefore, even for the polymers with very low mole% of BTCA incorporation (eg. 0.1mole%), the polymer did not flow under agitation. The next approach was to use only AB monomers plus multi-functional monomers to generate the star-branched liquid crystalline polymers to avoid the crosslinking.

4.4 Synthesis and Characterization of Linear and Randomly Star-Branched LCPs Based on POB/POPB System

The homopolymers of poly(oxybenzoate)(POB)[87] and poly(oxyphenoxybenzoate) (POPB)[27,42,44] both have very high melting transitions (above 400°C). The high Tm of the homopolymers limits their use as melt-processable materials. However, the copolymers of POB-POPB may have relatively low Tm, depending on their composition. It was reported that the copolymers at 65/35 molar ratio exhibited a Tm lower than 300°C [27,44].

POB-POPB was synthesized from two AB type monomers as shown in Scheme 3.6. The molecular weights of the linear and branched polymers can be easily calculated by the method described in Appendix B. The resulting polymers basically have the expected topology (i.e., no crosslinked structures). This property (combined with their low Tm) suggests that the POB-POPB system should be good materials for generating liquid crystalline foams.

The analyses of the linear and the star-branched POB-POPB copolymers are summarized in Table 4.3. All the copolymers have the same ratio of POB/POPB (i.e. 65/35 in molar ratio). At this ratio, the copolymer exhibited liquid crystalline properties [27, 44]. The 3-arm POB-POPB copolymers described in the table 4.3 used 1,3,5-triacetoxybenzene, not tri(4-acetoxyphenyl)phosphine oxide, as the branching agent because of the previously described "solidification" problem. It was observed that if the branching agent was the tri(4-acetoxyphenyl)phosphine oxide, the reaction mixture slowly solidified to a white opaque solid at the end of the first stage. This solid did not form a homogeneous melt even when the temperature was raised to 350°C. In contrast to the polyarylates with 50 mole% of the triarylphosphine oxide comonomer (Section 4.2), this reaction only had 0.77 mole% of the trifunctional phosphine oxide monomer. The unusual solidification phenomenon appears to be directly related to the triarylphosphine oxide compound and high temperatures, since this problem was not observed for the other POB-POPB reactions.

Dynamic TGA behavior of the POB-POPB liquid crystalline branched copolymer showed good thermal stabilility, with 5 % weight loss being observed around 480-490°C in nitrogen. A typical dynamic TGA experiment is shown in Figure 4.3. DSC experiment were conducted by a DuPont DSC-912 instrument, which showed that the copolymers have a Tg of about 126°C and a "Tm" around 283°C for samples annealed at 240°C for 50 min. The Tm of the linear and the star-branched POB-POPB were very similar. This indicated that for the polymers containing long chain branches, such as the star-branched polymer, the high temperature transition did not change significantly with the incorporation of branching agent. However, the crystallinity was affected by branching. In general, the higher branching density translated into a less ordered

Table 4.3 Thermal behavior of linear and star-branched liquid crystalline POB-POPB copolymers

Architecture calculated Mn	Tg	Tm[a]	TGA[b]	ΔH(J/g)	% Branching[c]
linear-control	125	283	482	1.94	no
linear-10K	123	283	482	2.06	no
linear-20K	124	282	482	1.59	no
linear-30K	125	283	483	2.70	no
3 arm-10K	128	----*	487	—*	1.54
3 arm-15K	126	287	482	0.40	1.03
3 arm-20K	126	289	492	0.95	0.77
3 arm-30K	129	283	494	1.16	0.51
3 arm-45K	126	285	489	1.26	0.40
4 arm-10K	126	—*	490	—*	1.54
4 arm-20K	126	284	488		0.77
6 arm-30K	128	—*	475	—*	0.51
6 arm-90K	126	290	475	0.39	0.17

a. DSC, 2nd heat of annealed samples(240°C, 50 minutes)

b. In air, 5% weight loss at 10°C/min

c. Mole % of branching monomer

* Tm peak found on 1st heat

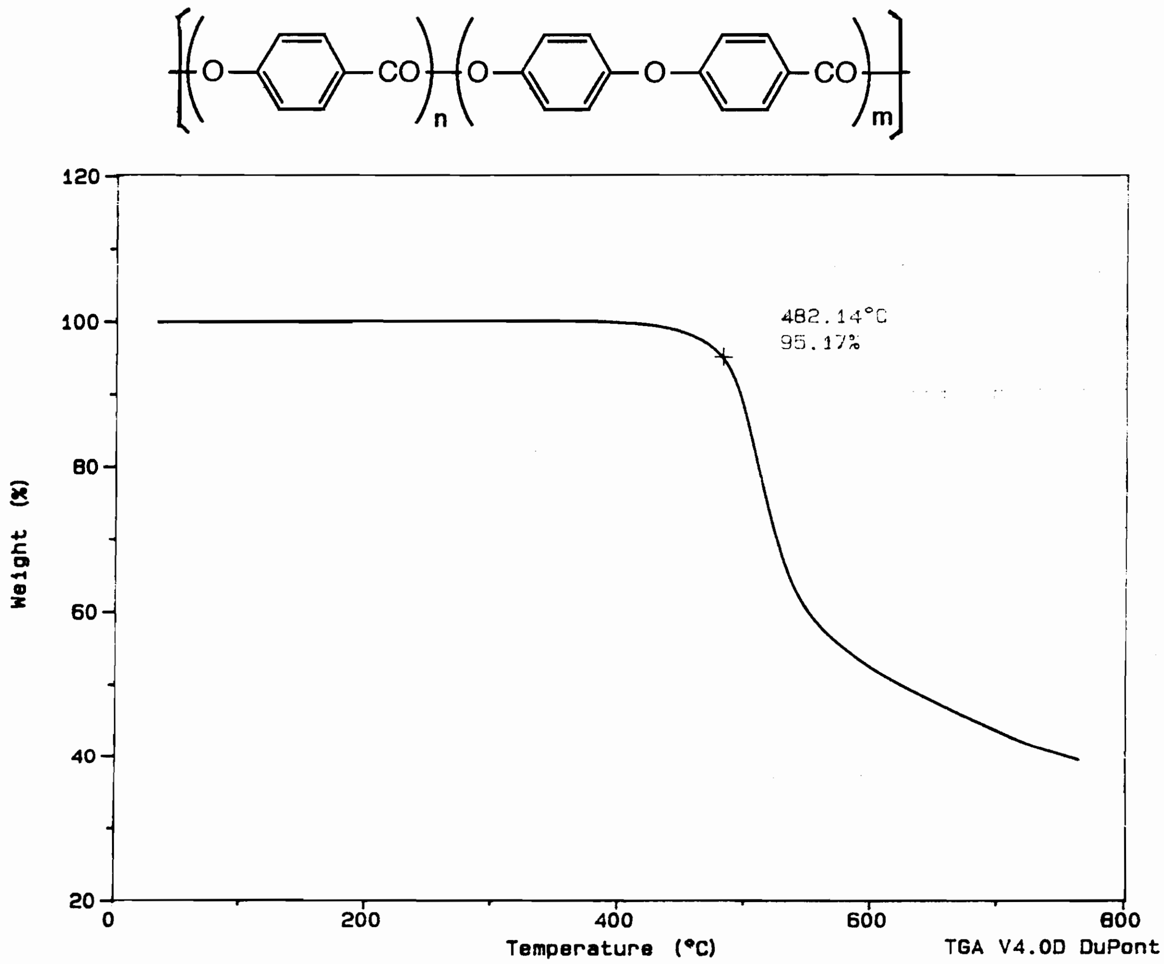


Figure 4.3 TGA thermogram of the POB-POPB copolymer

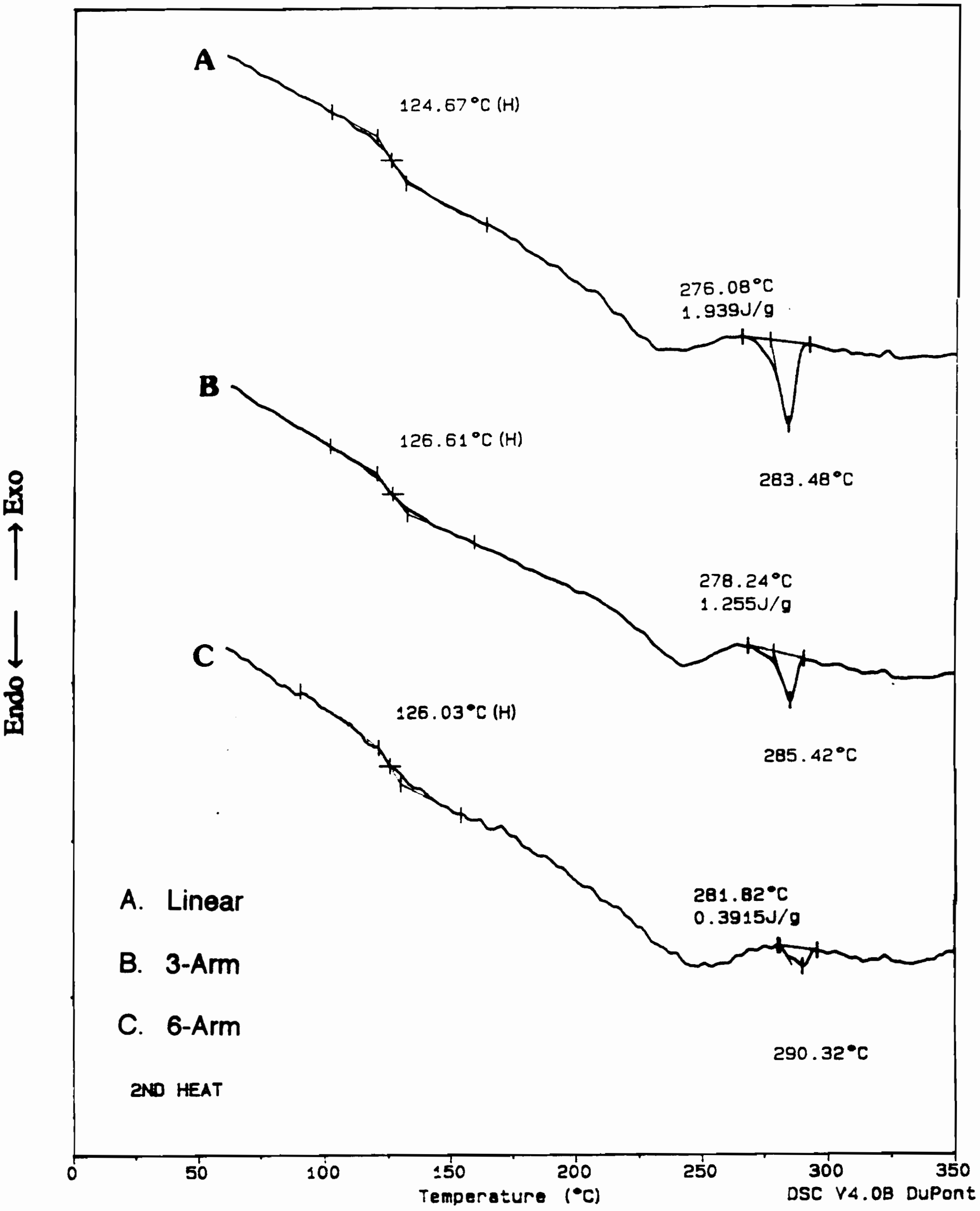


Figure 4.4 DSC traces of the linear and branched POB-POPB copolymers

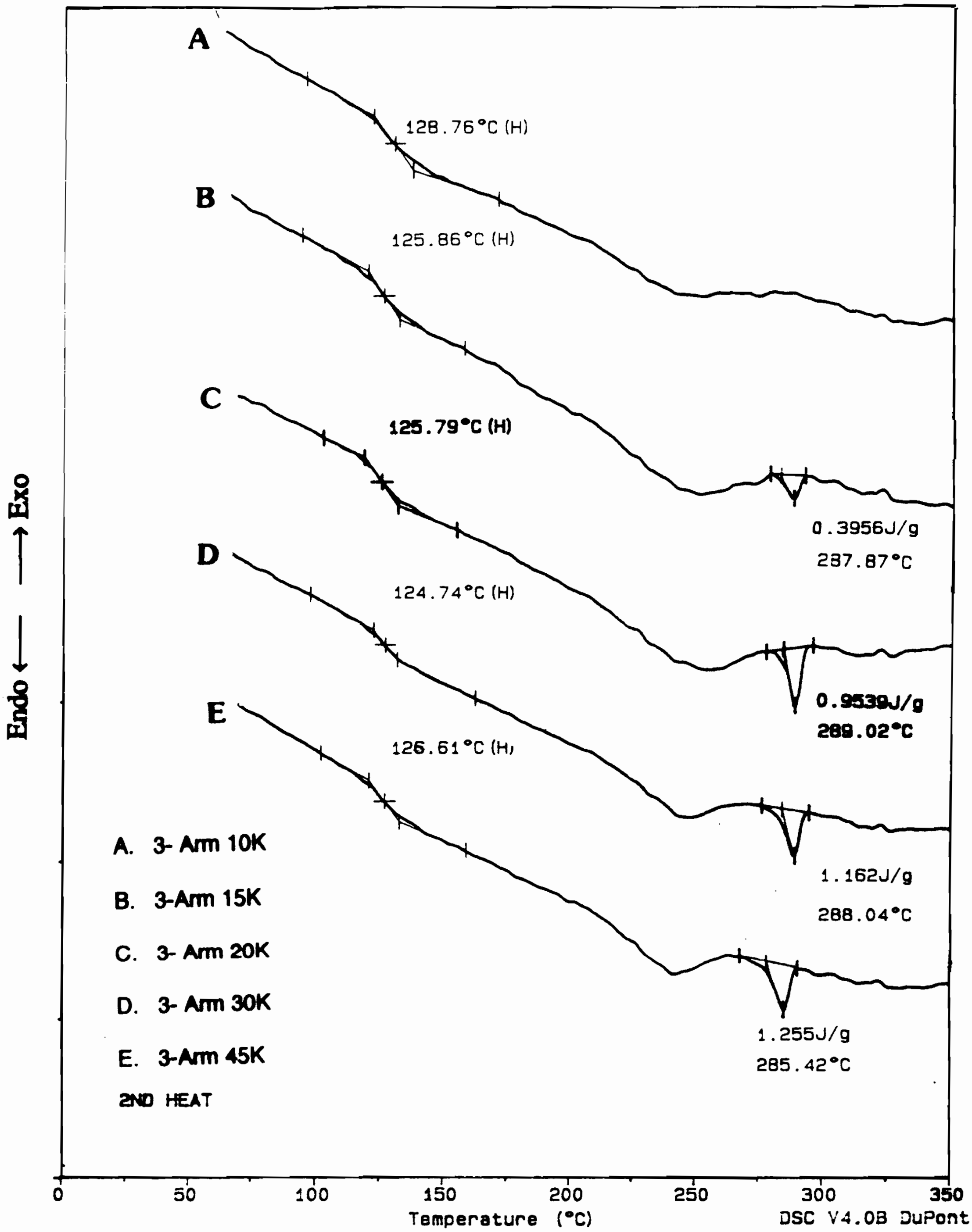


Figure 4.5 DSC traces of the 3-arm POB-POPB copolymers with variation in branching density

morphology. Table 4.3 clearly shows this trend for heat of fusion (ΔH). Figures 4.4 and 4.5 are representative DSC curves by DuPont instrument for the linear and star-branched POB-POPB copolymers. As shown in Table 4.3, the Tm did not change but ΔH decreased with an increase in the branching density.

The arm size may, of cause also have some influence on the crystallinity or morphological order of the copolymers. Fore example, longer arms provide higher crystallinity. The trend is very clear from Figure 4.5 of the DSC traces of the 3-arm POB-POPB copolymers with different arm sizes. If the arm size of the star branched copolymer is too small, e.g. each arm being less than 5K, the copolymers usually do not show an endothermic peak. However, a crystalline melting transition endotherm was observed for the first DSC heat. This can also be seen from Table 4.3. One possibility is that the crystallinity of the short arm LCPs was generated during the stirring process(i.e., under shear).

4.5 Generation of Liquid Crystalline Foams and Their Characteristics

Although a series of branched POB-POPB were successfully prepared via a melt acidolysis, attempts to generate liquid crystalline foams were only focusd on the 4-arm LCP, which had calculated controlled molecular weights of 10,000 and 20,000 g/mole. The 4-arm POB-POPB(10K) and the 4-arm POB-POPB(20K) had mole fractions of 1.56 and 0.77% of the four functionality branching agent, respectively.

The extent to which the liquid crystalline order was disrupted within 4-arm POB-POPB copolymer is evident through the DSC scans and the wide angle X-ray diffraction (WAXS) measurements. The DSC scans in this case were performed at 10°C/minute on a SEIKO™ thermal analysis instrument. A decrease in the magnitude of the melting

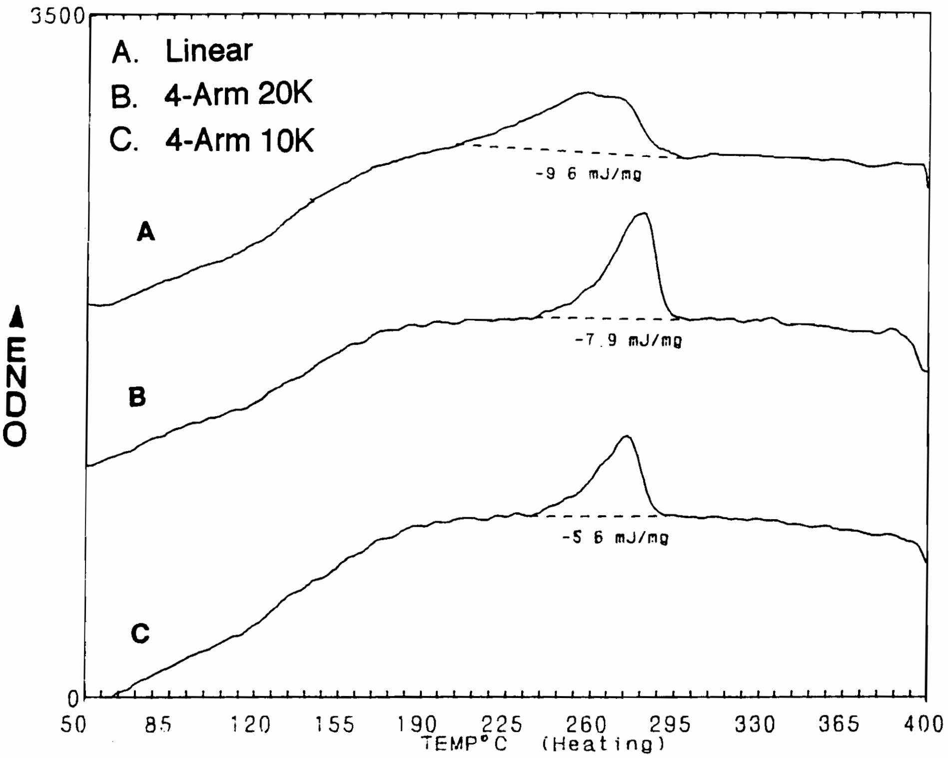


Figure 4.6 DSC traces of linear and 4-arm branched POB-POPB (65/35) copolymers

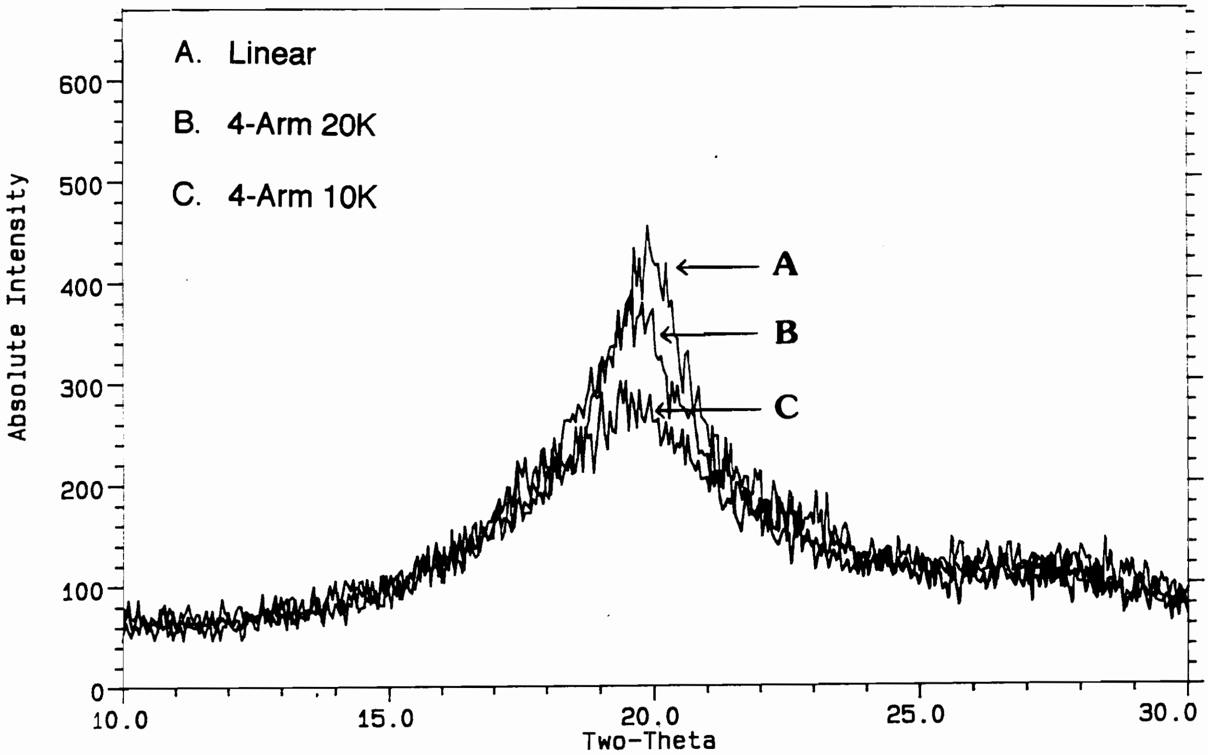


Figure 4.7 WAXS of linear and 4-arm branched POB-POPB(65/35) copolymers

transition between 280°C and 300°C was observed with increasing branching-point concentration, as discussed earlier(Figure 4.6). The decrease in the melting endotherm suggested that some disruption of the order within the LCPs occurred for those systems containing the branching-point.

The WAXS patterns of the POB-POPB copolymers are shown in Figure 4.7. The intensity of the diffraction peaks at $2\theta \sim 20^\circ$ systematically decreased with increasing branch-point concentration, also indicating that the branch-points cause a disruption of the liquid crystalline order. Although the order is disrupted, however, the WAXS patterns indicate that the ordered phase is still present, even in the sample with 1.56% branch-point content(e.g., 4-arm 10K POB-POPB).

The disrupted order of the branched 4-arm LCPs suggested that the gas permeability and solubility might be expected to be enhanced. Figure 4.8 shows the gas absorption behavior as a function of molecular weight and topology. The linear LCPs showed poor gas absorption behavior. After one week, the mass fractions of the CO_2 absorbed by the linear LCP of 20K and 10K molecular weight were 1.4% and 1.6% respectively. In the same time period, the 20K molecular weight LCP (with 0.77% branch-point content) absorbed a mass fraction of 3.5% CO_2 and the 10K molecular weight LCP (with 1.56% branch-point content) absorbed a mass fraction of 7.5% CO_2. Thus, the inclusion of branch-points and the resulting disruption of liquid crystalline order dramatically increases the absorption of CO_2 in POB-POPB copolymer.

Although foam structures were generated from the linear POB-POPB copolymers, the produced foams had relatively high densities with highly anisotropic bubbles. On the other hand, both the 10K and 20K 4-arm star-branched POB-POPB copolymers produced well defined foams with densities from 0.3 to 0.4 g/cc, which is about 30% of the initial density of the compression molded plaques (i.e., 1.24 g/cc) (Figures 4.9). These foams contained both open and closed cells, although the cells were predominately

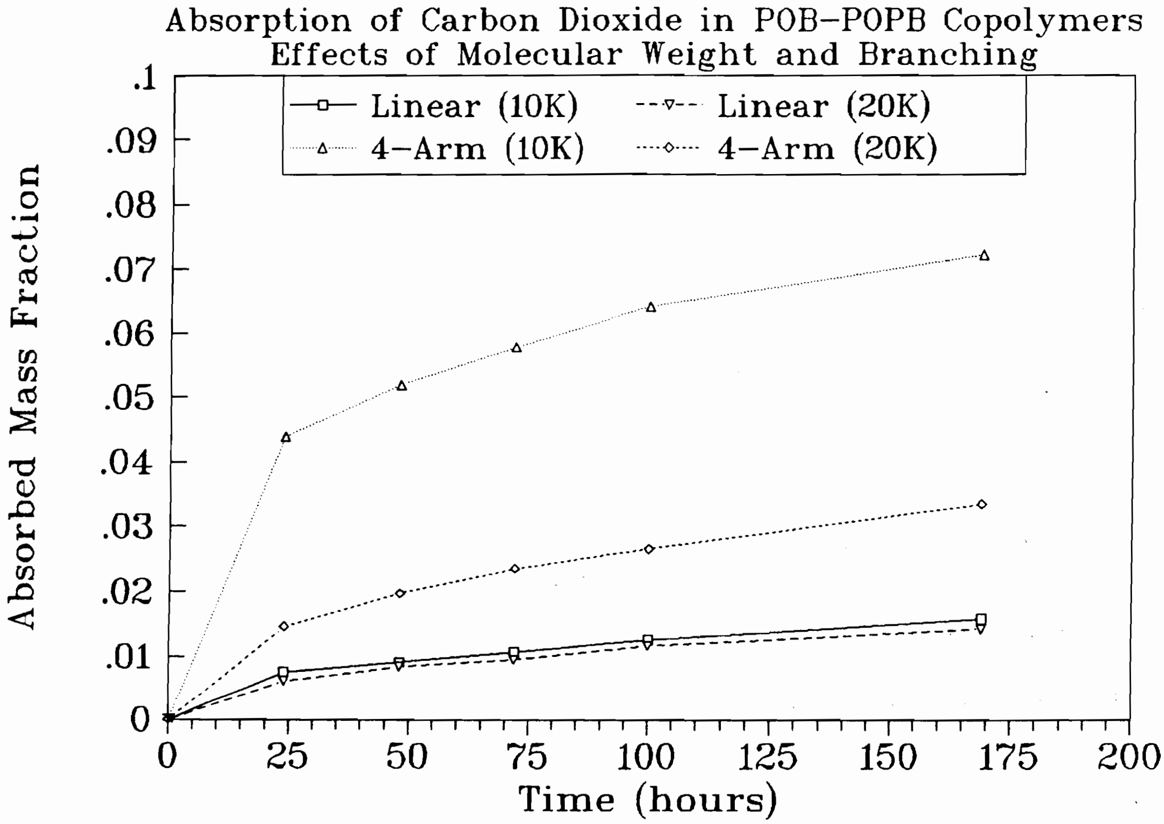


Figure 4.8 Gas absorption in POB-POPB copolymers

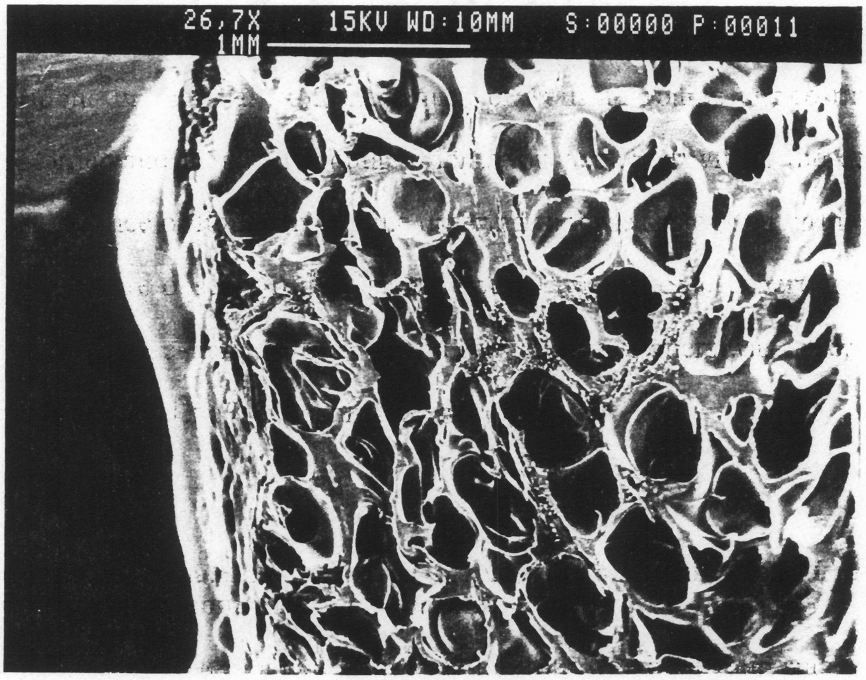


Figure 4.9 SEM cross section of liquid crystalline foams based on 4-arm POB-POPB (65/35) copolyarylates (Mn = 10,000g/mole)

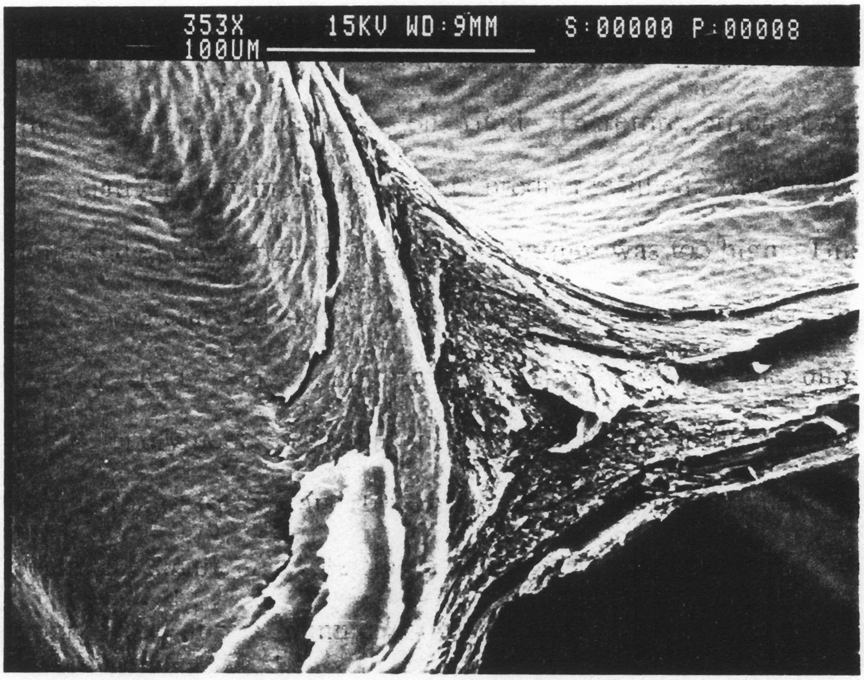


Figure 4.10 Enlargement of a cell edge showing the sheet like structure characteristic a liquid crystalline polymers

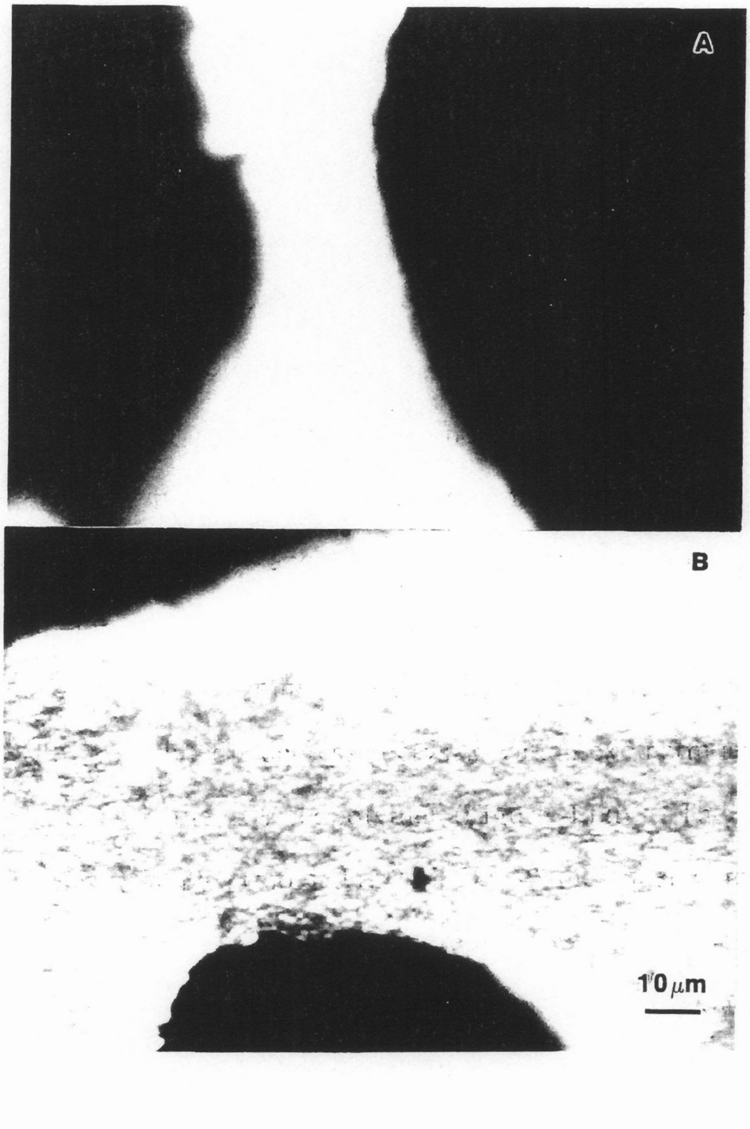


Figure 4.11 Polarized optical micrographs of 4-arm POB-POPB (65/35) copolyarylates; A. 20K, B. 10K

closed. The nucleation density of the bubbles in the 4-arm (10K) foam was greater than in the 4-arm (20K) foam, and the mean cell size in the 4-arm (10K) foam was less than half that of the 4-arm (20K) foam. The nucleation density also appeared to increase with increasing temperature in both systems. Highly anisotropic cell shapes near the outer skins of these foams suggests that molecular orientation which occured during compression molding may have persisted through the subsequent processing of these materials. The characteristic sheet-like structure of liquid crystalline polymers was clearly evident in the walls of the liquid crystalline foams suggesting that liquid crystalline order and high molecular orientation occurred within the cell walls (Fig. 4.10). The presence of liquid crystalline ordering in these systems is further supported by the granular texture observed in polarized optical microscopic experiments (Fig. 4.11). The granular texture characteristic of liquid crystalline polymers was observed in samples with both 0.77% and 1.56% branching agent content.

4.6 Synthesis and Characterization of Triphenyl Phosphine Oxide Containing Poly(ethylene terephthalate) Copolymer

PET was synthesized in a two stage reaction followed by a solid state polymerization process as shown in Scheme 3.7. The first step is the so called transesterification process which generally requires excess ethylene glycol(EG) to increase the desired forward reaction rate and to complete the evolution of methanol at the end of first stage. A low level of catalyst, titanium(IV) isopropoxide ($3x10^{-5}$ mole) was used for the reaction. At the second stage, the temperature was raised to 285°C and vaccum at 0.4 torr was applied to the reaction vessel. By the end of this stage, after three hours the reaction mixture were viscous fluids. Finally, a solid state polymerization step was performed to further increase molecular weight. The results are shown in Table 4.4.

Table 4.4 Characterization of triarylphosphine oxide containing PET copolymers

P(O)% in PET	[η][1] (dl/gm)	Tg[2] (°C)	Tm [2] (°C)	TGA[3] (°C)	Char % (750°C)	Tg[4] (°C)
0	1.04	76	236	401	~0	82
5	1.08	72	209	390	1	83
10	0.61	83	211	401	3.5	91
20	0.40	87	no	394	7.5	95

Note:
1. In 50/50 by weight of phenol and tetrachloroethane at 25 °C
2. Second heat of quench cooled samples (10 °C/min)
3. 5 wt% loss in air
4. By DMA at a heating rate 10°C/min and 1 Hz

The intrinsic viscosities of the copolymers showed that 10% and 20% of the triarylphosphine oxide containing PET copolymers have relatively low values. The main reason for the low IV of the 20% P(O) containing PET probably is due to the unusual solidification problem as mentioned earlier for the synthesis of P(O) containing polyarylates at 340°C under vacuum(Part II, Section 4.2) and POB-POPB at 290°C under inert nitrogen flow(Section 4.4). At the second stage of the copolymerization, it was found that the reaction mixture was not a homogenous melt. Instead, it was a mixture of a soft gel (major component) and a viscous fluid. Therefore, efficient stirring was not possible and a relatively low molecular weight product resulted. Another possible reason is that the solid state polymerization (SSP) temperature was too high. This step usually performed at a temperature 20~40°C lower than the Tm of the polymer. In this case, the temperature was 210°C, which may have been too high for the phosphine oxide containing PET copolymers. A crystal melting endotherm on the second heat of DSC experiments was found for 5% and 10% of comonomer systems, although the melting transition peaks are small. At 20%, the copolymer only had a Tg (Figure 4.12a) The cooling thermalgrams(at 5 °C/minute) of the copolymers showed that the 5% and 10% copolymer systems exhibited a depressed crystallization exotherm and no crystallization peak was observed for the 20% copolymer (Figure 4.12b). The DMA traces of the compression molded samples (molded at 275~280°C, then quench to room temperature) are shown in Figure 4.13 and 4.14. From these two figures, it is clearly seen that the Tg was increased with the phosphine oxide content. Figure 4.15 shows the TGA traces of the copolymers which indicated that the char yields also increased with increasing phosphine oxide content.

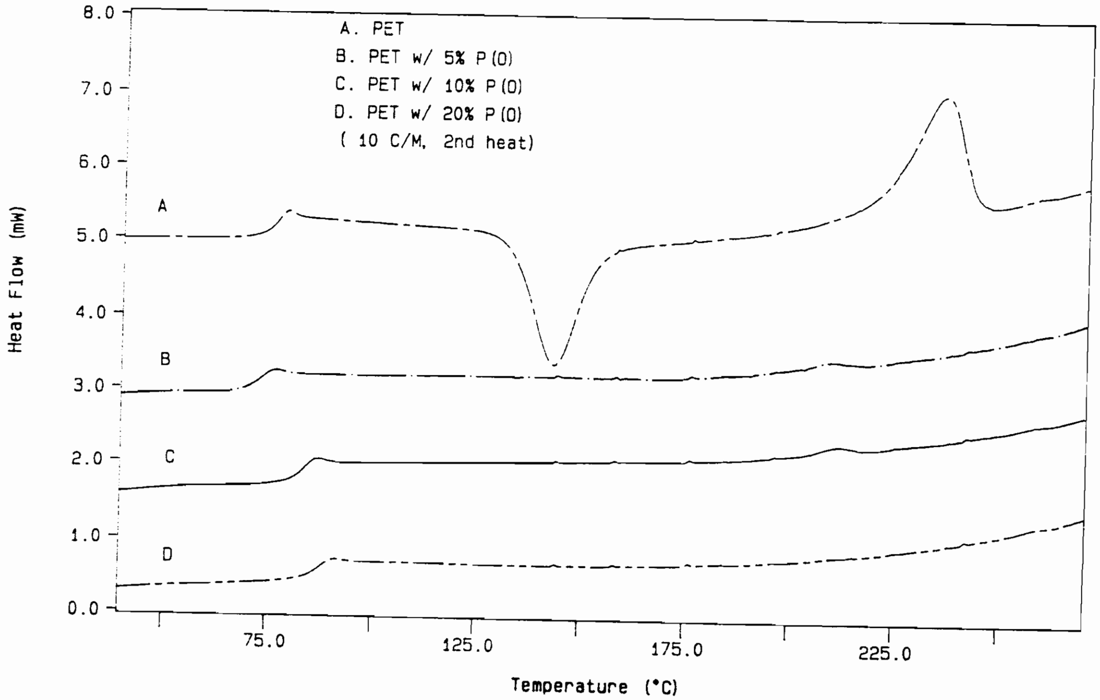


Figure 4.12 DSC traces of triaryl phosphine oxide containing PET copolymers (second heat at 10°C/minutes)

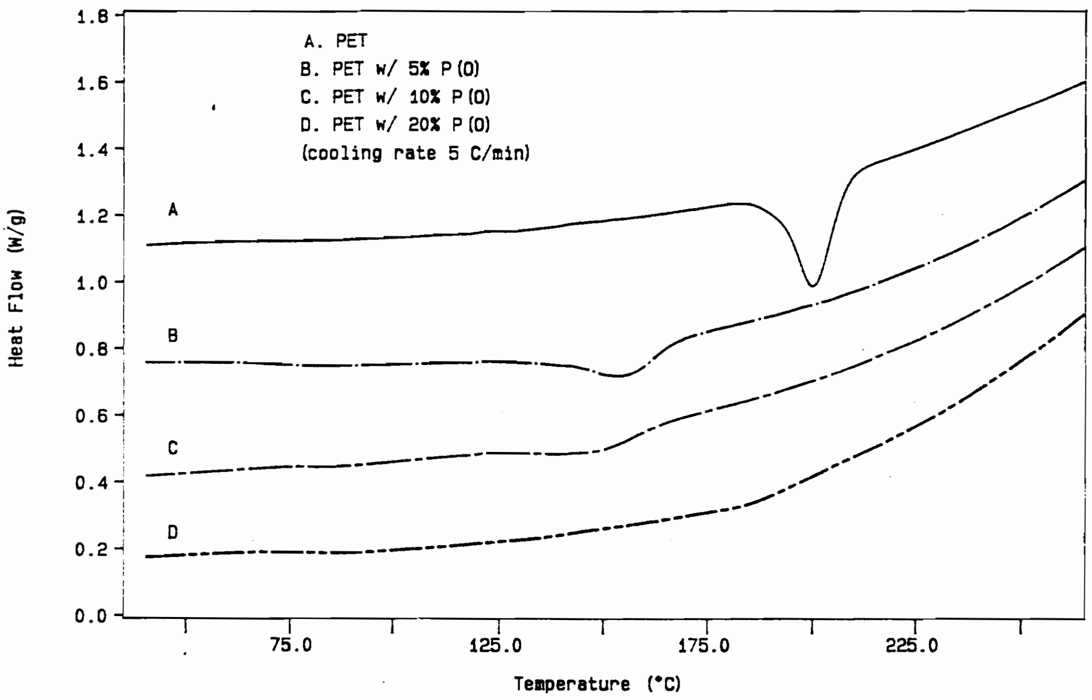


Figure 4.12 b) DSC traces of triaryl phosphine oxide containing PET copolymers (cooling from melt at 5 °C/minute)

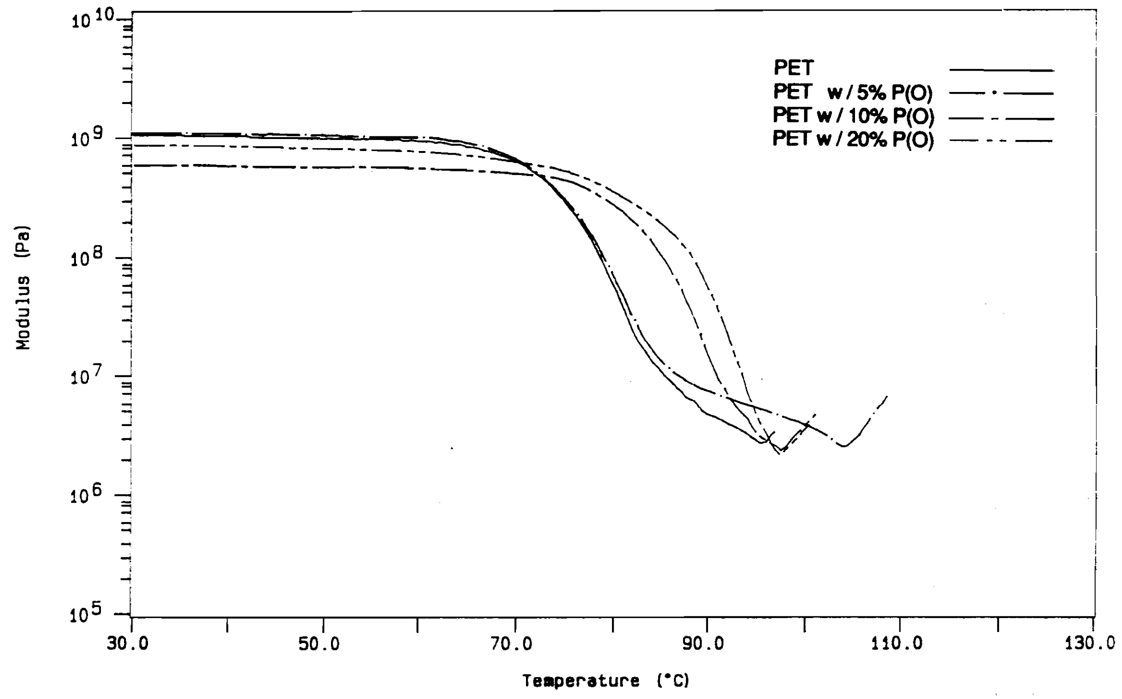


Figure 4.13 DMA traces of triaryl phosphine oxide containing PET copolymers (storage modulus)

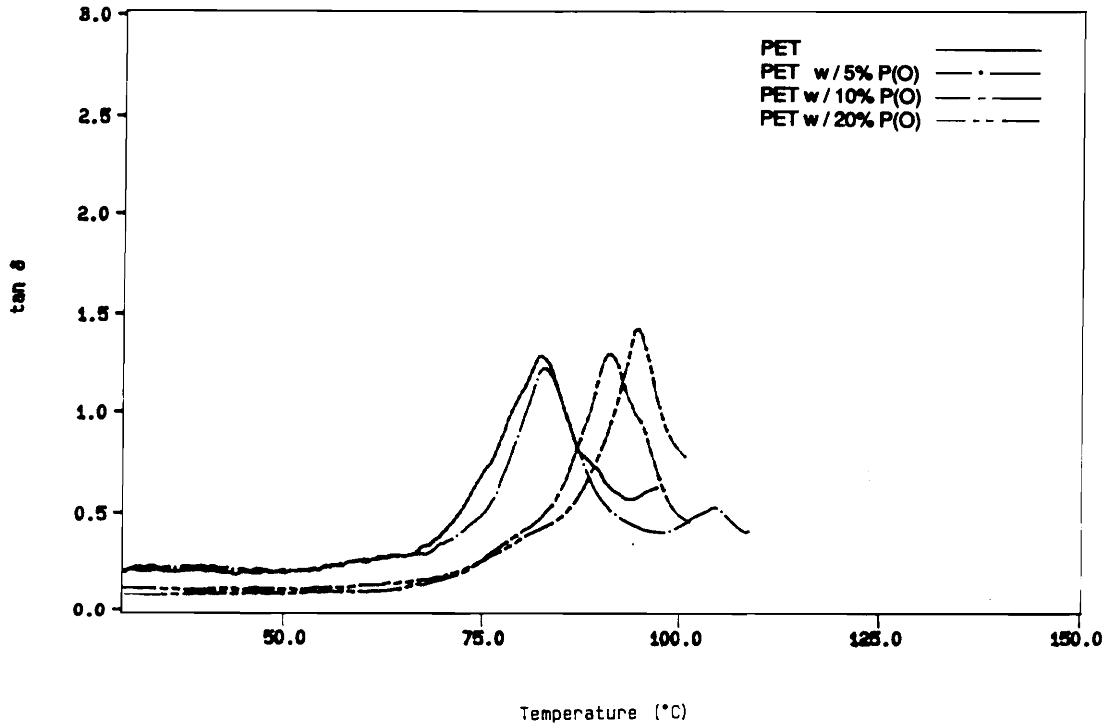


Figure 4.14 DMA traces of triaryl phosphine oxide containing PET copolymers(Tan δ)

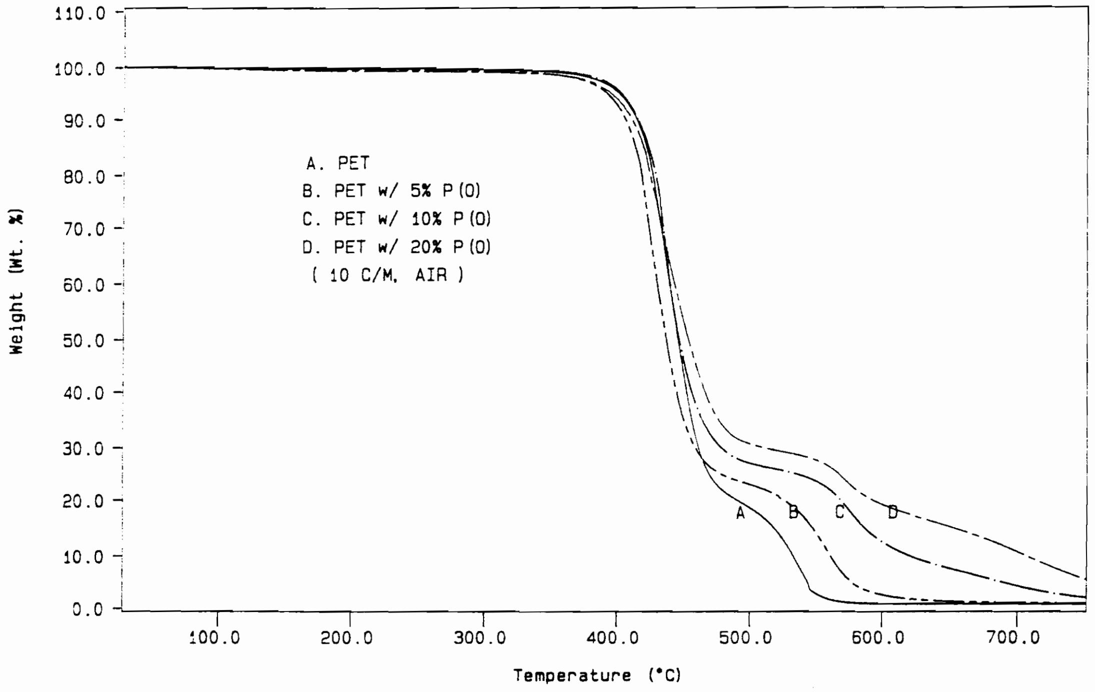


Figure 4.15 TGA traces of triaryl phosphine oxide containing PET copolymers

5. CONCLUSIONS

Several multi-functional branching reagents including three, four and six functionality monomers were prepared. These reagents have been copolymerized with two AB type monomers, 4-acetoxybenzoic acid and 4(4'-acetoxyphenoxy)benzoic acid, to generate randomly star-branched POB-POPB copolymers. Both the linear and branched POB-POPB copolymers exhibited a Tm (or LCP transition) lower than 300°C at the composition investigated(i.e., POB/POPB ~ 65/35 in molar ratio). At this composition, the copolymers are liquid crystalline materials as judged by polarized optical microscopy[27, 44, 47] and scanning electron microscopy[47].

Unlike modified Xydar® which contains 28% of POPB, to control the molecular weight of POB-POPB copolymer systems was relatively straight forward by the addition of monofunctional or multi-functional reagents. The resulting copolymers flow under agitation at a temperature above the Tm. It was shown that the crystalline or liquid crystalline transition were not depressed by the branching, but the order was reduced as the branching density or the number of arms increased. It was found that the AB type monomers are essential to generate processable star shaped LCPs, with no crosslinking. The branching agents were used to control the molecular weight of LCPs, to disrupt the order to some extent and to allow more CO_2 to be absorbed by the polymer matrix.

The 4-arm POB-POPB copolymers were successfully converted to novel LC foams by the gas supersaturation technique. The foams produced had densities ranging from 0.3 to 0.4 g/cc, which is 30% of the initial density(1.24 g/cc). The cells of the foams were predominately closed. Higher blowing temperatures or lower molecular weight of the copolymers could generate foams with larger cells. The new LC foams are stiff structural foams.

Triarylphosphine oxide containing polyarylates were prepared via the melt acidolysis route. This melt acidolysis reaction has been successfully employed to synthesize high molecular weight polyarylates and LCPs. Therefore, it seems that this polymerization technique is also possible in the synthesis of high molecular weight P(O) containing polyarylates. However, the results of the reactions were unusual and inexplicable at this stage because the polymers solidified at high temperatures (340°C). The polymers were amorphous materials as shown by their solubility, their transparent nature, WAXS scans and DSC measurements. The Tg of the P(O) containing polyarylates was around 210 ~ 220°C. These polymers have high char yields of about 30~35 wt% in air.

Triarylphosphine oxide containing PET copolymers were synthesized via the titanium isopropoxide catalyzed transesterification reaction route. The copolymers have very low crystallinity comparing to the nylon 6,6 copolymers. At 20 mole% P(O) incorporation the copolymer was amorphous, but the char yields increased with increasing P(O) content. The PET copolymers became gel-like materials in the melt state with high content of P(O) incorporation(e.g., 20 mole%), which may indicate that it would be difficult to draw fibers from these copolymers. Much more research is required to more properly refine the synthesis process.

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Appendix A : Molecular Weight Control(for AA and BB monomers)

For example : Calculation of the carboxyl terminated poly(arylene ether sulfone) oligomer (PES-COOH) of <Mn> 10,000 gm/mole

Define :

DP = Degree of polymerization(or number of repeat units)
Xn = Number average degree of polymerization
r = Stoichiometric imbalance of functional group

Xn = 2 x DP for AA + BB systems

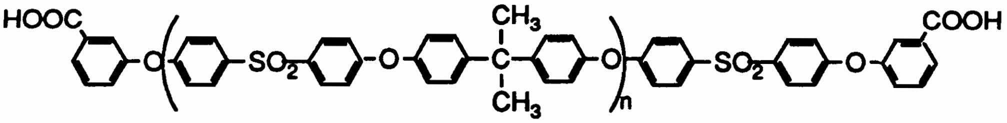
Carothers equation : $Xn = \frac{1+r}{1-r}$ (when P = 1)

(P is the fractional extent of reaction $0 \leq P \leq 1$)

when the amount of 4,4'-dichlorodiphenyl sulfone(DCDPS) is in excess relative to bisphenol A, $r = N_A / N_B$

where N_A and N_B are the number of moles of bisphenol-A and DCDPS respectively. ($2N_A'$ is the number of moles of end capper which is 3-hydroxybenzoic acid)

For PES-COOH of <Mn> 10,000 gm/mole having the formula weight of the repeat unit of 442.5 gm/mole



$$Dp = \frac{10{,}000}{442.5} \qquad \text{Thus, } Xn = 2 \times DP = 45.1977$$

From $Xn = \frac{1+r}{1-r}$ when Xn = 45.1977, then r = 0.9567

and $NA = rN_B$

if N_B (DCDPS) and if one choose to use 20 gm (69.645 mmole)

then, $N_A = N_B \times r = 0.9657 \times 0.069645 = 0.06663$

When the oligomer of PESCOOH is endcapped by 3-hydroxybenzoic acid, the equation becomes :

$$r = \frac{N_B}{N_A + 2\,N_A'} \qquad \text{so,} \quad 2N_A' = \frac{N_B - rN_A}{r} = 0.0061674$$

Therefore, the amount of reagents used are :

N_A : Bisphenol A	15.211 g (66.63 mmole)
N_B : DCDPS	20 g (69.65 mmole)
$2N_A'$: 3-Hydroxybenzoic acid	0.851 g (6.17 mmole)
Potassium bicarbonate	12.1 g (87.5 mmole, 20% ex.)

Appendix B : Molecular Weight Control(for AB monomers)

Define :

<Mn> : Theoretical number average molecular weight

n : Number of repeat unit

Mo : Formula weight of repeat unit

Thus,

$$\frac{< Mn >}{Mo} = n$$

For every "n" repeat units need one end group to cap the linear polymer; therefore, the molar ratio of the end cap to AB monomers is equal to "1/n".

This equation is also suitable for star-branched polymers. For example, the star-branched polymers with the molar ratio of "1/n" (branching agent/AB monomers) are the polymers with equal number average molecular weight (< Mn >) as the corresponding linear polymers. In this case, the molecular weight is controlled by branching reagent and the number of repeat unit of each arm equal to n/# of arms

Vita

I-Yuan Wan was born in Taichung, Taiwan, Republic of China and received his BS. in Chemistry from Tamkang University, Taiwan in 1980. He was then drafted into the army for two years. In 1984, he obtained a MS. degree in inorganic chemistry from National Tsing-Hwa University, Taiwan and then worked in Industrial Technology Research Institute, Taiwan as associate researcher for 4 years. He entered the Ph.D. program at VPI & SU, Virginia, U.S.A. in 1988 under the supervision of Prof. James E. McGrath. He received his Ph.D. degree in chemistry 1994