# Synthesis and Characterization of New Phosphine oxide and Ketone Containing Poly(Arylene Sulfide Sulfone)s

Yongning Liu

(ABSTRACT)

High molecular weight poly(phenylene sulfide sulfone) (PPSS) homo- and statistical copolymers have been reproducably synthesized using a known, but complex procedure utilizing 4,4'-dichlorodiphenyl sulfone (DCDPS), sodium hydrosulfide, sodium hydroxide, sodium acetate, and deionized water, in NMP at elevated reaction temperatures and pressure. The effect of these variations, e.g., reaction temperatures and times, molar ratios of $H_2O$-to-NaSH, NMP-to-$H_2O$, etc. were investigated. Optimized conditions were defined, which produced $T_g$ as high as 222°C, very high refractive index (1.70), and tough/solvent resistant films could be prepared by melt fabrication. A two-stage decomposition mechanism in air was demonstrated by dynamic thermal gravimetric analysis.

The melt stability of PPSS was improved by incorporating thermally stable endgroups, such as diphenyl sulfone, 4-chlorophenylphenyl sulfone, and t-butylphenoxide. The chemical structures of the endgroups were confirmed by $^{13}C$ and $^{1}H$ NMR spectra. Compared with mercaptide endcapped PPSS, the new systems showed higher initial degradation temperatures (2% and 5% weight loss), higher char yield at 650°C in air and a more stable melt viscosity at 300°C.

A greatly simplified synthesis of both homo and copolymers has been successfully developed using the new A-A or A-B type thiol-functional monomers, such as bis-(4-mercaptophenyl) sulfone, 4-chloro-4′-mercaptodiphenyl sulfone and 4-chloro-4′-mercapto benzophenone, instead of sodium hydrosulfide. A series of high molecular weight triphenyl phosphine oxide and/or diphenyl ketone containing PPSS copolymers were subsequently synthesized from the bis-(4-mercaptophenyl) sulfone by reaction with 4,4'-

dichlorodiphenyl sulfone, bis-(4-fluorophenyl) phenyl phosphine oxide, and 4,4'-difluorobenzophenone in DMAc in the presence of $K_2CO_3$ at 160$^o$C. The new phosphine oxide containing PPSS copolymers were completely amorphous, showed improved solubility in common organic solvents and exhibited very high char yields in air at 750$^o$C. Surface (XPS) analysis results suggested that the phosphorus moieties in the polymer backbone can form phosphate-like layers on the polymer surface which protects the inner materials from further decomposition in air at high temperatures. The diphenyl ketone containing PPSS copolymers showed very high char yields at 750$^o$C in a nitrogen atmosphere, compared to sulfide sulfone homopolymer and phosphine oxide containing copolymers, possibly because of higher bond energies.

Semi-crystalline poly(phenylene sulfide ketone) homopolymers and sulfone containing copolymers with sulfone/ketone mole ratio (S : K) ≤ 25 : 75 were synthesized by a novel base catalyzed self-polycondensation of 4-chloro-4′-mercaptodiphenyl sulfone and/or 4-chloro-4′-mercapto benzophenone in N-cyclohexyl-2-pyrrolidinone (CHP) at 290$^o$C. Amorphous copolymers with S : K ratios > 25 : 75 were prepared in DMAc at 160$^o$C. These materials exhibited an increase in glass transition temperature with increasing sulfone content. TGA and micro cone calorimetry analyses showed that the semi-crystalline materials with high ketone content had much higher char yields and significantly lower heat release rate and total heat release, compared to the poly(phenylene sulfide sulfone) and poly(pheylene sulfide) controls.

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# Chapter 1.0 INTRODUCTION

Poly(phenylene sulfide) (PPS) is an important engineering polymer which has been the focus of intensive research for the past two decades. PPS, which is a semi-crystalline polymer with $T_g$ around 85$^o$C and a $T_m$ of about 285$^o$C (15, 62), is considered to possess inherent fire resistant and excellent solvent and chemical resistance. Due to its overall combinations of properties, PPS is an important molding resin and has been used as a matrix material for thermoplastic composites. A related sulfide sulfone polymer, has also been investigated, although somewhat briefly, in the patent or commercial trade literature. The poly(phenylene sulfide sulfone) (PPSS) has been described in the literature as an amorphous polymer with a $T_g$ around 217$^o$C (119). Poly(phenylene sulfide sulfone)s are prepared by the nucleophilic polycondensation reaction of sodium sulfide and 4,4′-dichlorodiphenyl sulfone as the activated aromatic halide in N-methyl-2-pyrrolidinone (NMP) at elevated temperature and pressure (120, 123). Although there have been several reports in the patent literature about the effect of polymerization conditions on molecular weights of PPSS (119-120), a detailed study has not been reported. Thus, this thesis will describe new research studies that have been directed towards the effect of reaction temperatures, reaction time, and water as an additive on molecular structure, as well asinvestigate the relationship of molecular weights and thermal and mechanical properties.

One of the problems associated with poly(phenylene sulfide sulfone)s has been its relatively low melt stability and poor processibility, perhaps due to the presence of mercaptans or metal sulfides as end groups on polymer chains (189-191). Some patent literature has disclosed a method to produce PPSS having increased melt stability by treating the polymer with a zinc source, thereby incorporating zinc cations into the polymer (192-193). However, for certain poly(phenylene sulfide sulfone) applications, such as creating injection molded parts and producing composites, it is desirable for the polymer to exhibit a high degree of clarity and purity. Therefore the process whereby melt stability of PPSS is increased could result in introducing impurities into the polymer, which affect the clarity of molded parts and interfere with the resin/fiber interfacial bonding. Therefore it is the objective of this study to develop a method for preparing PPSS with increased melt stability, while not adversely affecting the purity and clarity of the polymer. This thesis will describe the synthesis of poly(phenylene sulfide sulfone)s with three different thermally stable end groups, diphenyl sulfone, t-butylphenoxide, and 4-chlorophenylphenyl sulfone. Their chemical structures and thermal properties are characterized and evaluated in comparison with the normal mercaptide endcapped PPSS.

The second part of this thesis focuses on the synthesis and characterization of novel aryl phosphine oxide and/or ketone containing PPSS derivatives. It is interesting to incorporate the hydrolytically stable aryl phosphine oxide moiety into the PPSS backbone because of its high temperature stability, flame resistance, and improved interactions between the polar phosphine oxide groups of the polymer matrix and functionalized carbon or glass fibers. The presence of ketone units in the polymer structure contributes to the improvement of solvent and chemical resistance, as well as high temperature stability. According to our previous study (194), however, it is difficult to prepare high molecular weight phosphine oxide containing PPSS polymers via the traditional high pressure procedure, possibly due to the different reactivities of the aromatic dihalides and unusual condensation reaction mechanisms. By using the newly prepared A-A or A-B type thiol-functional monomers, bis-(4-mercaptophenyl) sulfone, 4-chloro-4′-mercaptodiphenyl sulfone, and 4-chloro-4′-mercaptobenzophenone, instead of sodium hydrosulfide, a new simplified method was developed, which eliminates the necessity of high pressure and temperature, as well as the use of water and sodium acetate as additives. These new phosphorus and/or ketone containing PPSS related polymers have been synthesized by incorporating bis-(4-fluorophenyl)phenyl phosphine oxide (BFPPO) and/or 4,4′-difluorobenzophenone (DFBP) as a partial or total replacement for the normal 4,4′-dichlorodiphenyl sulfone (DCDPS) component via the new method in DMAc in the presence of potassium carbonate. This research has investigated the synthesis, solubility, thermal behavior, dynamic mechanical properties, fire resistance, and optical characteristics of these new polymers.

This research also focused on the synthesis and characterization of new semi-crystalline poly(phenylene sulfide ketone) homopolymers and sulfone containing copolymers via a novel self-polycondensation of new A-B type thiol-functional monomers. The synthesis and relationship of molecular structure and crystallinity, thermal stability, and flame resistance of the polymers were also investigated in this research.

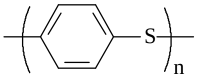
# Chapter 2.0 BACKGROUND

## 2.1 Poly(Phenylene Sulfide) (PPS)

### 2.1.1 Historical Development

Poly(phenylene sulfide), PPS, has a long history in the chemical literature. In fact the synthesis of PPS or PPS-related resins dates back almost 100 years. The structure of poly(phenylene sulfide) was first assigned as a largely insoluble material “melting” at 295°C by Grenveses in 1898 (1). The product was obtained by heating benzene with sulfur in the presence of aluminum chloride. Similar procedures were used by other scientists at the turn of the century. For example, Deuss (2) obtained similar products by reacting thiophenol with aluminum chloride. Glass and Reid (3) also obtained a resinous product by heating benzene with sulfur at 350°C. In all cases, however, ill-defined polymers were obtained, and the presence of many by-products, such as thiophenol, phenyl sulfide, phenyl disulfide, and thianthrene, resulted in very low polymer yields (4).

Interest in the synthesis of PPS was reborn in 1948 when Macallum discovered the first nucleophilic displacement route to poly(phenylene sulfide) resins (5). The Macallum process involves reacting elemental sulfur, sodium carbonate and dichlorobenzene at 275-300°C, in the melt, in a sealed vessel. However, due to the nature of the melt reaction, the polymerization reaction was highly exothermic and difficult to control. Elemental analyses of polymers prepared by this route generally contained more sulfur than was predicted by the structure of the repeat unit.



Although the polymerization reaction was highly exothermic and difficult to control, the Macallum PPS process generated interest within the industrial sector. Eventually, his process patents (6) were licensed in 1954 to Dow Chemical Company. R. W. Lenz and others at Dow laboratories during the late 1950s and early 1960s reported a detailed study of the Macallum polymerization, as well as the structures and characteristics of the polymers (7-9). Despite these efforts, the initial problems associated with the severe reaction conditions, control of the exothermic reaction, and unpredictable polymer yields and properties remained largely unsolved (10).

PPS remained an attractive polymer with an excellent combination of properties, which led Dow researchers to explore alternative synthetic routes. One improved synthetic procedure consisted of the self-condensation reaction of copper(I) *p*-bromobenzene-thiolate (9). This nucleophilic substitution reaction was carried out at 200-250$^{o}$C in the solid state or, alternatively, in the presence of materials such as pyridine as a reaction medium, to produce linear polymer. However, the monomer and process were costly and they experienced considerable difficulty in removing the by-product, copper(I) bromide, from PPS made by this process (11). Thus, Scale-up was not feasible.

By studying model coupling reactions involving nucleophilic displacement of aryl halides by sulfur nucleophiles, researchers at Monsanto found that amide solvents were unexpectedly efficient (12). At the same time, scientists at Phillips Petroleum Company developed a new synthetic route to PPS, which involved the production of PPS from *p*-dichlorobenzene and sodium sulfide in a polar organic solvent at elevated temperature. In 1967, Phillips Petroleum Company was granted a US Patent for this process (13), and in 1973 the world's first PPS plant was commercialized in Borger, Texas. The product is marketed today under the trade name of Ryton® Polyphenylene Sulfide.

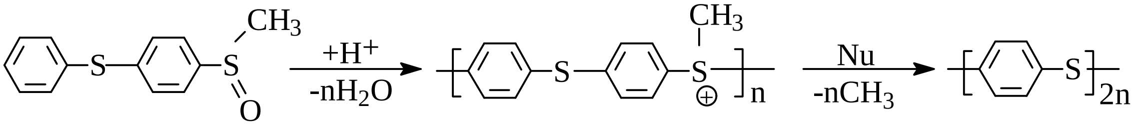
### 2.1.2 Synthetic Methods and Reaction Mechanisms

The outstanding thermal, oxidative, and chemical resistance of PPS has justified the pursuit of many synthetic routes to produce it. In fact, at least four different methods have been reported. The most commenly used industrial process proceeds through a nucleophilic aromatic substitution reaction (14-15). Melt polymerization of 1,4-diiodobenzene and sulfur (16-17), thermolysis of bis(4-halophenyl) disulfide (18), and copolymerization of cyclic (arylene disulfide) oligomers with dihaloaromatic compounds (19-20) have also been described as proceeding by free radical mechanisms. The solution polymerization of salts of 4-bromobenzenethiol is thought to be a single electron transfer process (21-22). Furthermore, the oxidative polymerization of diphenyl disulfides or methyl phenyl sulfide may undergo electrophilic substitution reactions (23-26). Most of these methods and mechanisms are reviewed in this chapter.

#### 2.1.2.1 Electrophilic Substitution

The earliest references to phenylene sulfide structures were described as an electrophilic substitution reaction (1, 27). Genvresse, in 1897, was the first to assign the PPS structure to an amorphous, insoluble resin that was prepared by heating benzene with sulfur in the presence of aluminum chloride (1). However, the resulting products had low molecular weight and contained too much sulfur to be classified as pure PPS. A variety of these reactions have been reported (2, 4, 28-30). Although the electrophilic reactions are straightforward, they display a lack of selectivity and produce only low molecular weight products. In 1984, the electrophilic substitution reactions of benzene and sulfur in the presence of aluminum chloride was reinvestigated (4, 31). Improved analytical methods allowed the detection of structures that contained thianthrylene sulfide linkages, phenylene sulfide linkages and polysulfides, which were unstable under these reaction conditions. It was concluded that the formation of linear high molecular weight poly(arylene sulfide)s in the presence of Lewis acids such as aluminum chloride is, therefore, highly unlikely.

Recently, new electrophilic substitution reactions for the preparation of a high molecular weight linear PPS have been reported (23-26, 33-35). Tsuchida et al. synthesized high molecular weight PPS via the soluble precursor of poly(sulfonium cation) under mild conditions using a sulfoxide-acid system (25, 32). Scheme 2.1.2.1.1 shows that this polymerization proceeds through an electrophilic reaction (32). The protonated sulfoxide, methylhydroxyphenyl sulfonium cation, is an active species that electrophilically attacks the phenyl ring of the monomer to yield a sulfonium cation of the dimer, accompanied by the elimination of water. Therefore, the reaction was influenced by the acidity of the mixture. Trifluoromethanesulfonic acid, a strong protic acid, is highly effective for the formation of the sulfonium cation, unlike weaker acids such as $CH_3COOH$ or $CF_3COOH$, which do not promote the electrophilic reaction. The polycation, poly(methyl[4-(phenylthio)phenyl] sulfonium trifluoromethanesulfonate) (PPST), is soluble in common solvents such as acetonitrile, acetone, dimethyl sulfoxide, and formic acid. In order to convert to PPS from PPST, the demethylation was carried out using pyridine as a nucleophile. PPST was dissolved in refluxing pyridine at 110°C for 20 h. White powder was precipitated during the reaction. The IR spectrum of the resulting polymer agrees with that of the commercially available PPS (Ryton V-1). The molecular weight of the polymer was determined to be 1.2 x $10^5$ by high temperature GPC. However, the $T_m$ (260°C) was lower than that of the Ryton V-1 (285°C), which may be caused by the existence of a small amount of the sulfonium cation units or ortho substitutents of the sulfide bond in the main chain of the PPS. In addition to the lower melting point, another drawback associated with this method is the requirement for a high concentration of strong acids.

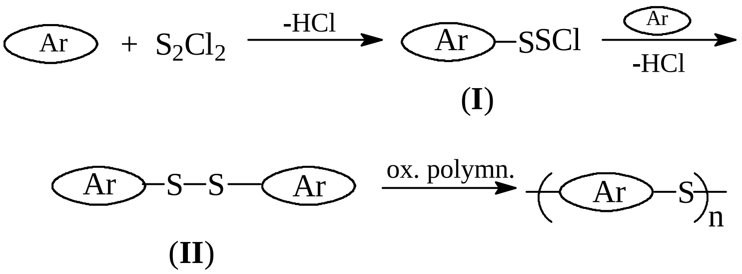


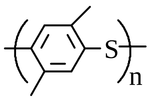
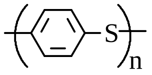
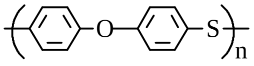
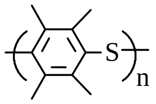
Scheme 2.1.2.1.1 Synthesis of PPS by oxidative polymerization via a soluble poly(sulfonium cation)

Yamamoto et. al. reported that poly(thioarylene)s could be synthesized by reacting aromatics with $S_2Cl_2$ under ambient atmosphere at room temperature, followed by oxidation of the disulfide compound with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (26). This polymerization with $S_2Cl_2$ is applicable to various aromatic compounds, such as *p*-xylene, diphenyl sulfide, diphenyl ether, and 1,2,4,5-tetramethylbenzene (durene). Aromatic compounds having electron-donating substituents are suitable for this polymerization because the reaction is promoted by active electrophilic substitution. Diphenyl ether generates the corresponding polymer in 100% yield. However, benzene and *p*-dichlorobenzene were not sufficiently active due to their low π-electron density.

The polymerization proceeds efficiently in low basicity solvents such as chloroform dichloromethane, and carbon tetrachloride. In particular, dichloromethane is the most suitable solvent for the polymerization (26), while Lewis bases, such as THF, NMP, and DMF, retard the polymerization. These results suggest that the polymerization proceeds via a cationic mechanism, wherein basic solvents deactivate the cationic species and suppress the polymerization (26).

The polymerization mechanism is assumed to be that shown in Scheme 2.1.2.1.2. Here, the $S_2Cl_2$ attacks the aromatic compound electrophilically to form arenethiosulfenyl chloride (**I**). **I** is then coupled with another aromatic to yield the corresponding disulfide compound (**II**). **II** is oxidized with DDQ in the acidic reaction mixture to yield the sulfonium cation. The cation is considered to act as the active species for the polymerization and electrophilically reacts with the benzene ring to yield poly(thioarylene)s (24, 26). The formation of the disulfide compounds is the rate-determining step in this polymerization (26).



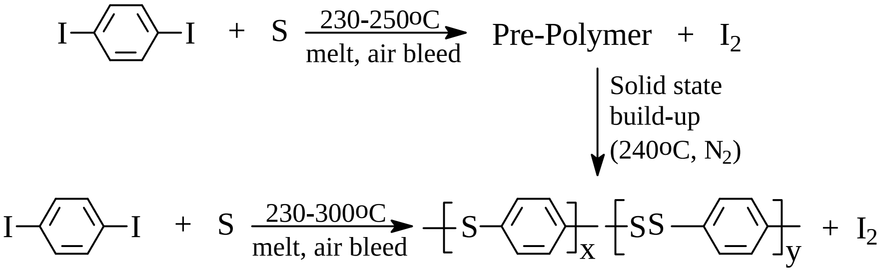
| aromatics | polymer | yield (%) | $T_m$ (°C) |
|---|---|---|---|
| p-xylene |  | 95 | 306 |
| diphenyl sulfide |  | 98 | 183 |
| diphenyl ether |  | 100 | 184 |
| durene |  | 92 | 275 |

Scheme 2.1.2.1.2 Oxidative polymerization of aromatics with $S_2Cl_2$

In the classical Friedel-Crafts reaction of $S_2Cl_2$ with an aromatic catalyzed by a Lewis acid, many side products, such as polysulfides and thianthrene, could be observed. These are formed through the homogeneous exchange and/or electrophilic reactions of disulfide with $S_2Cl_2$. However, the following oxidation suppresses these side reactions and provides a selective formation of poly(thioarylene). The disulfide once formed by the electrophilic reaction of $S_2Cl_2$ is rapidly oxidized without side reactions (26). Unfortunately, the polymers prepared via this method have low molecular weights due to the reduced solubility of the resulting semi-crystalline poly(thioarylene)s in dichloromethane, and also have low melting points (26, 36-37).

### 2.1.2.2 Free Radical Reactions

Recently, a new process, referred to as the "RFWL" process or melt process, for the synthesis of the important semicrystalline engineering thermoplastic poly(phenylene sulfide), PPS, was developed by Fagerburg et al. (16, 38-42). This process, based on the reaction of *p*-diiodobenzene and sulfur at elevated temperatures (230-300°C), generates a polymeric material containing *para*-substituted aromatic groups connected by sulfide or disulfide linkages (Scheme 2.1.2.2.1).

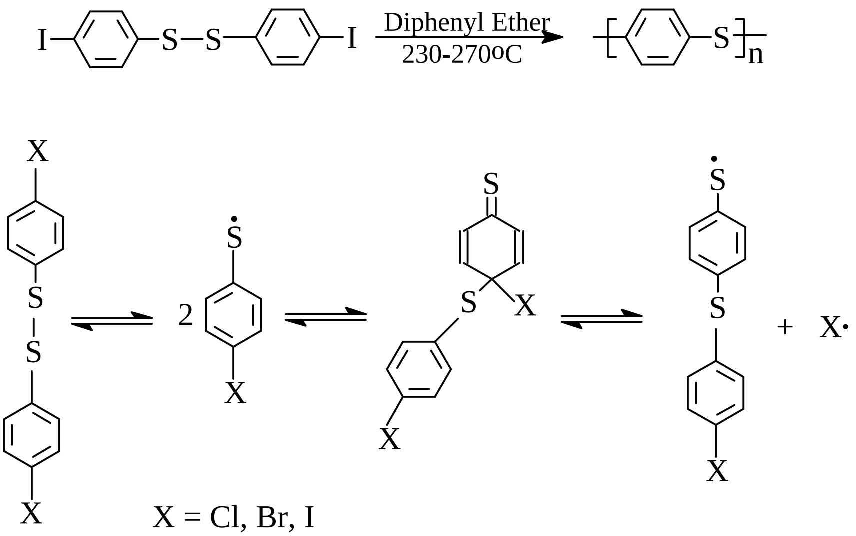


Scheme 2.1.2.2.1 Synthesis of PPS/DS via the RFWL process

The high temperature electron paramagnetic resonance spectroscopy (EPR) provided the first direct observation that free radicals are present during the synthesis of PPS from diiodobenzene and sulfur between 230°C and 300°C, in the presence of air. Radicals observed include a sulfur radical and a carbon radical. The iodine or iodo substitution enhances the stability of these systems to generate free radicals thermally, relative to unsubstituted compounds. EPR experiments indicate the importance of polysulfide linkages, such as disulfide, between phenyl groups with or without iodine for the formation of these radicals. Based on the EPR experiments, Fagerburg et al. proposed a melt reaction mechanism wherein an initial polysulfide radical attacks an iodoaromatic species, followed by subsequent S-S bond cleavage to form a radical for further reaction

(17, 43). PPS of high molecular weight (Mn = 27,500), good yield, and high melting point ($T_m$ = 280°C) was easily obtained via this melt phase reaction (16-17). However, some disulfide linkages were formed in the final product, which is the major drawback of this process.

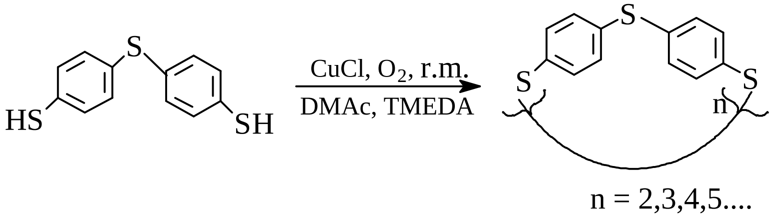
High molecular weight PPS has also been synthesized by the thermolysis of bis(4-halophenyl) disulfides (Scheme 2.1.2.2.2) (18, 44). Polymerizations were carried out in diphenyl ether at temperatures of 230-270°C, and polymers were obtained in high yields as off-white or pale yellow solids with melting points ranging from 270 to 282°C. The polymerization takes place readily at about 230°C, as evidenced by the formation of iodine. The completion of the polymerization was indicated by the cessation of iodine evolution. It should be noted that the degree of polymerization was very temperature dependent. For example, at 220-230°C it took nearly 2 days to complete the polymerization, which resulted in a low molecular weight PPS (DP ~ 50) that still contained a high percentage of iodine. As the reaction temperature was increased, however, the required reaction time shortened dramatically and the degree of polymerization increased significantly. Polymerization at 260-270°C took place in 8 h to yield polymer that had a number-average molecular weight of approximately 20,000 (DP ~ 180).



Scheme 2.1.2.2.2 Thermolysis of bis-(4-halophenyl)disulfide and a reaction mechanism

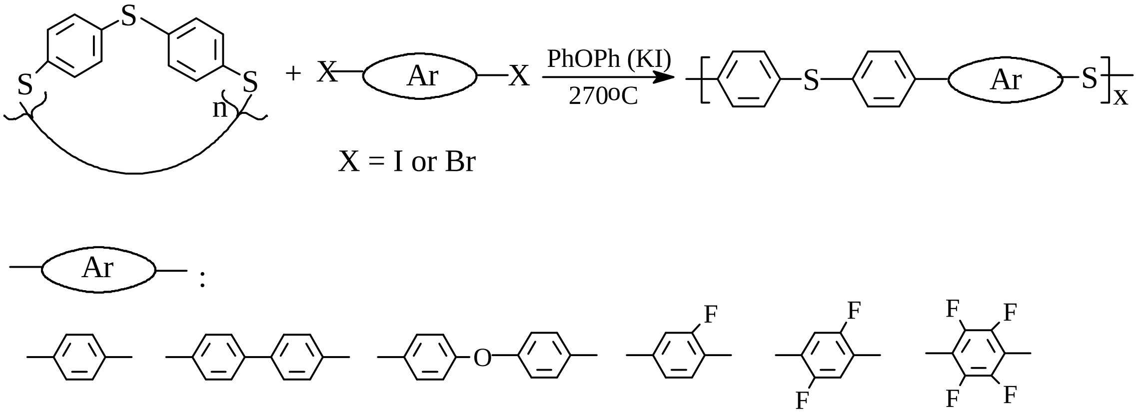
The polymerization of bis-(4-iodophenyl) disulfide would be expected to proceed initially by thermal homolysis of the disulfide bond to the corresponding thiophenoxy radical. Analogous to the quinone-ketal mechanisms, the thiophenoxy radical could then dimerize to give a dithioquinone ketal, which could subsequently rearrange to dimeric thiophenoxy radical, with the release of iodine radical affording iodine (Scheme 2.1.2.2.2). The removal of the by-product iodine is the driving force for the polymerization, as was the case for the melt reaction of sulfur with iodobenzene (RFWL process).

Since the PPS can be prepared by heating bis-(4-iodophenyl) disulfide, as discussed earlier (18, 44), cyclic aromatic disulfide oligomers are also potentially very useful intermediates for the synthesis of aromatic polysulfides by reacting with diiodo or dibromo compounds (20, 45). Recently, Hay et al. synthesized a series of cyclic arylene disulfide oligomers by oxidative coupling of dithiols with oxygen using a copper-amine catalyst under high dilute conditions (Scheme 2.1.2.2.3) (19, 45). DMAc was found to be the most effective solvent for synthesizing cyclic oligomers, due to the fact that both the reactants and resulting products remain soluble. Cuprous chloride and N,N,N′,N′-tetramethylethylenediamine (TMEDA) were used as the copper salt and amine ligand, respectively. The cyclic disulfide oligomer prepared from the Scheme 2.1.2.2.3 had a number average molecular weight ($M_n$) of 380 and a weight average molecular weight ($M_w$) of 570, as determined by GPC.



Scheme 2.1.2.2.3 Synthesis of cyclic aromatic disulfide oligomer

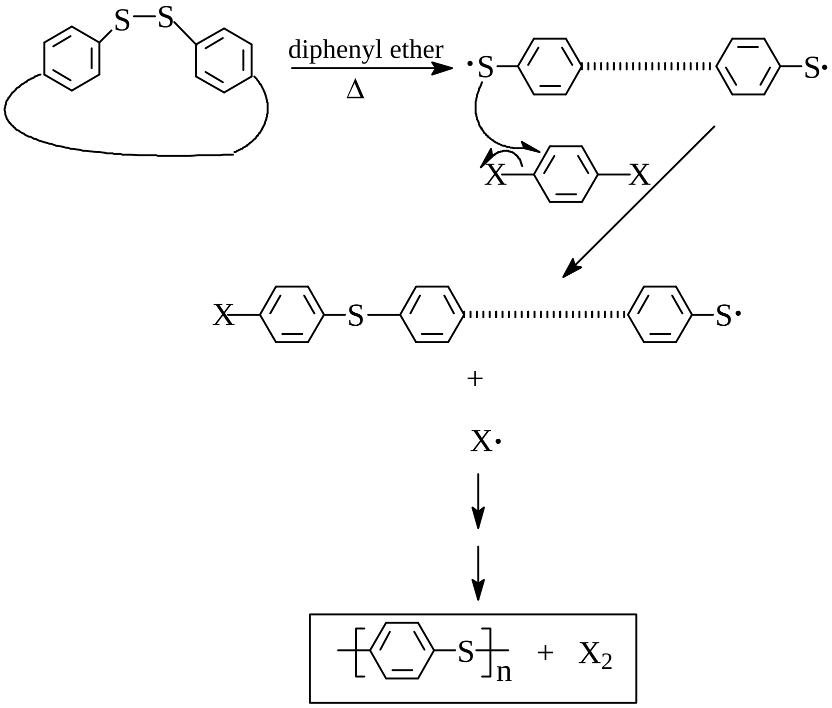
The cyclic arylene disulfide oligomers underwent melt ring-opening polymerization to yield high molecular weight poly(arylene sulfide)s by a free radical mechanism (18, 20). PPS was synthesized by the thermal polymerization reaction of the cyclic disulfide oligomer with the *p*-diiodobenzene in diphenyl ether at 270°C (Scheme 2.1.2.2.4) (20, 45). PPS was also prepared by reacting the cyclic disulfide oligomer with *p*-dibromobenzene in the presence of potassium iodide (45). The molar ratio of the cyclic disulfide oligomer to *p*-diiodobenzene has a significant influence on the crystallization temperature ($T_c$) of the product (45). The 1,4-diiodobenzene has to be used in ~4% excess to obtain PPS with the highest $T_c$, which is assumed to represent the highest molecular weight, since $T_c$ is a monotonic function of molecular weight (18). Presumably, this is due to the decomposition of the iodo compound at high temperatures (46). However, when *p*-dibromobenzene was used, the molar ratio of 1:1 of the reactants was found to be optimum (45). By reacting with the cyclic disulfide oligomer, *p*-diiodobenzene resulted in PPS with a $T_g$ of 88°C and a $T_m$ of 286°C, while *p*-dibromobenzene produced PPS with a $T_g$ of 92°C and a $T_m$ of 275°C (45).



Scheme 2.1.2.2.4 Thermal polymerization reactions between cyclic disulfide oligomer and dihalo aromatic compounds

The polymerization mechanism illustrated in Scheme 2.1.2.2.5 is a typical free-radical *ipso*-substitution reaction (45). At high temperatures, disulfide linkages in cyclic disulfide oligomers are ruptured to generate thiyl radicals, which then ipso-substitute the halogen atom to form biphenyl sulfide linkages and halogen radicals. The iodine radicals afford iodine, which distills from the reaction mixture. However, the bromine radicals are very reactive and brominate the solvent diphenyl ether, thus destroying the stoichiometric balance of reactants necessary to produce a high molecular weight polymer. Potassium iodide serves as a reductant for the bromine atoms that suppress the side reactions caused by the reactive bromine radical.

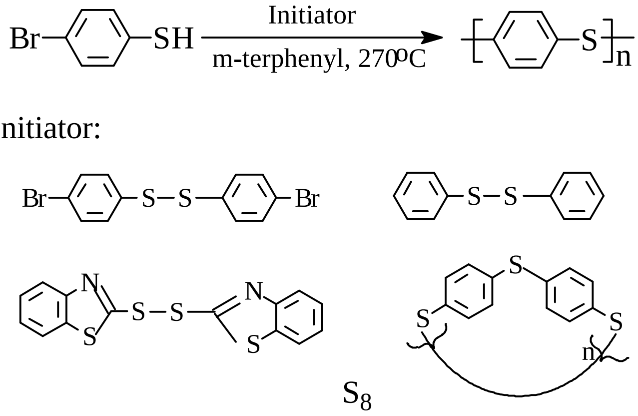
Although a more feasible and economical method of preparing cyclic disulfide oligomers is required, this thermal ring opening polymerization for PPS is interesting and provides the possibility of easy material processing, since the cyclic oligomers have much lower viscosities compared to the linear high molecular weight polymers. In addition, this method can be easily extended to prepare other poly(thioarylene)s by using different dihaloaromatic compounds (Scheme 2.1.2.2.4) (45).



Scheme 2.1.2.2.5 Mechanism of thermal polymerization reactions between cyclic disulfide oligomer and dihalo aromatic compounds.

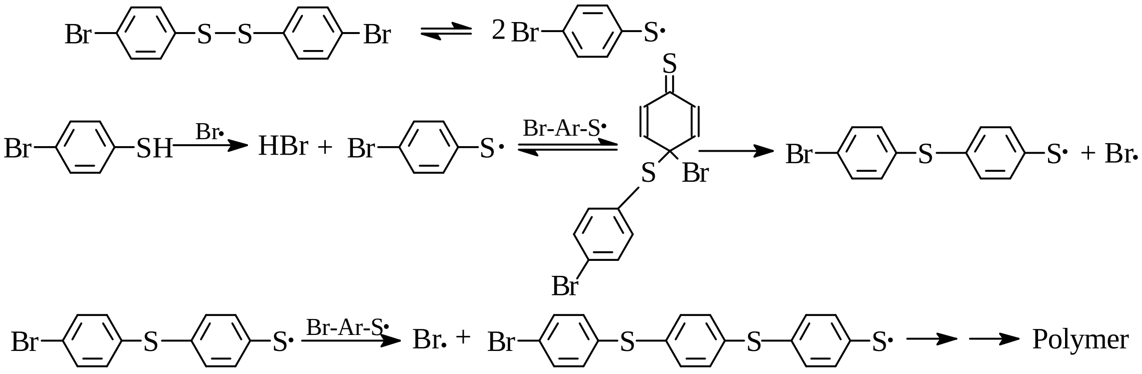
In 1997, Hay et al. also reported the synthesis of PPS via a self-polymerization of 4-bromobenzenethiol in the presence of a free radical initiator (47-48), which was carried out in *m*-terphenyl solution at 270°C (Scheme 2.1.2.2.6). *M*-terphenyl is a high-boiling point solvent (bp 365°C) that is unreactive to the thiyl radical. The purpose of using a high-boiling point solvent is to maintain the growing polymer chains in solution, since the boiling point of 4-bromobenzenethiol is only 230°C. Different initiators were used to influence the polymerization reaction, such as bis-(4-bromophenyl) disulfide, cyclic disulfide oligomer, diphenyl disulfide, 2,2′-dithiolbis(benzothiazole), and elemental sulfur

(47-48). Based on the $T_g$ and $T_c$ of the products, using bis-(4-bromophenyl) disulfide as an initiator gave the best results. Elemental analysis indicated that PPS obtained from the polymerization of 4-bromobenzenethiol initiated by bis-(4-bromophenyl) disulfide did not contain any significant amount of disulfide linkages. However, PPS initiated by cyclic aryl disulfide oligomers may contain small amounts of disulfide linkages (50). Therefore, bis-(4-bromophenyl) disulfide is strongly recommended as the initiator of choice for the polymerization of 4-bromobenzenethiol. The best results were achieved when 1 mol % of the bis-(4-bromophenyl) disulfide was used as the initiator, which produced a polymer of good molecular weight ($M_n$ = 6,900 and $M_w$ = 19,600) and excellent yield (95%) (48). On the other hand, using 0.5 mol % of the initiator resulted in a PPS of relatively high molecular weight, but a yield of only 61%. This phenomenon later became known as "preferential polymer formation" (9, 49). As the amount of the initiator was increased, the molecular weights of the resulting polymers were lower (48).



Scheme 2.1.2.2.6 Polymerization of 4-bromobenzenethiol with different initiators

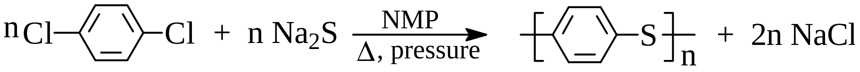
The proposed mechanism for the polymerization using bis-(4-bromophenyl) disulfide as initiator is shown in Scheme 2.1.2.2.7 (47). The bromine radicals here play a key role in propagating the chain reaction by reacting with the thiol group to generate HBr and the thiophenoxy radical. The oligomeric radicals formed can then react further to yield PPS. If a different disulfide was used as initiator, the organic moiety would then be expected to be present as a chain end. This novel process produces PPS without the formation of any salt. Instead, HBr is formed as the sole side product. However, this process has the drawback of producing relatively low molecular weight polymers.



Scheme 2.1.2.2.7 Proposed mechanism for the polymerization of 4-bromobenzenethiol

### 2.1.2.3 Nucleophilic Substitution ($S_NAR$)

Edmonds and Hill (13) first developed a commercially feasible synthetic route for PPS. The process involved the polycondensation of *p*-dichlorobenzene with sodium sulfide or sodium hydrosulfide/sodium hydroxide in N-methyl-2- pyrrolidinone (NMP) at 260$^o$C and elevated pressure (Scheme 2.1.2.3.1). This reaction produced PPS with a molecular weight in the range of 15,000-20,000. Recently, a similar reaction scheme has been investigated by Rajan, Ponratham, and Nadkarni (51), who studied the kinetics of the polycondensation reaction of *p*-dichlorobenzene with $Na_2S$ in NMP at 195$^o$C and 2 atm. The reaction followed second-order kinetics, but followed a two step process. There was a slow initial rate up to 50% conversion, followed by a faster rate at higher conversion (≈ 2.5 times faster). The slow initial rate was partially attributed to the limited solubility of sodium sulfide in NMP. They also analyzed the degree of polymerization with reaction time by intrinsic viscosity measurements and observed that intrinsic viscosity reached a plateau after 6 hours. Furthermore, Radhakrishnan et al. (52) studied the effect of reaction time and stirring speed on the crystallinity, particle size, and morphology of PPS synthesized by the same method. The crystallinity determined by X-ray diffraction techniques modestly decreased from 74 to 68% after 6 hours, which was attributed to the presence of low molecular weight species at the beginning of the reaction that can easily crystallize at higher rates. The particle size and polymer yield increased with reaction time in a very similar way. The particles seemed to be porous in nature, with a general spherical shape containing a “sheaflike” structure or “lettuce-like” structure, as these authors described it. The stirring speed affected the morphology by producing larger and more compact particles as the speed was increased. Moreover, the particle size distribution was sharp.

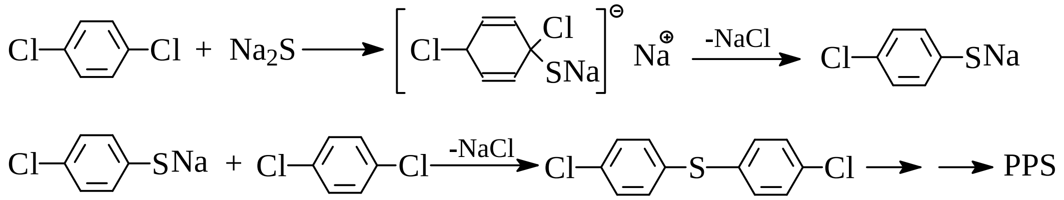


Scheme 2.1.2.3.1 Synthesis of PPS by nucleophilic substitution reaction

The structure of the species present in PPS synthesized by the Edmonds and Hill process (13) has been extensively studied (53-54). Reents and Kaplan (53) used methylene chloride extraction, high performance liquid chromatography, and solid probe mass spectroscopy (MS) to analyze the oligomers presented after synthesis. These authors found the presence of cyclic as well as linear *p*-phenylene sulfide oligomers. The linear species were either dichloro terminated, single chlorine terminated, or had no chlorine end groups. They also noticed the presence of dibenzothiophene. A comparative study of the oligomers presented in the synthesis of poly(*o*-phenylene sulfide) (*o*-PPS), poly(*m*-phenylene sulfide) (*m*-PPS), and poly(*p*-phenylene sulfide) (*p*-PPS) was performed by Montaudo et al. (54). The *o*-PPS isomer produced mostly thianthrene species. In contrast, the *m*-PPS isomer showed cyclic oligomers from trimers to heptamers, with the cyclic trimers as the most abundant. These authors, however, reported that only traces of cyclic oligomers were observed in *p*-PPS.

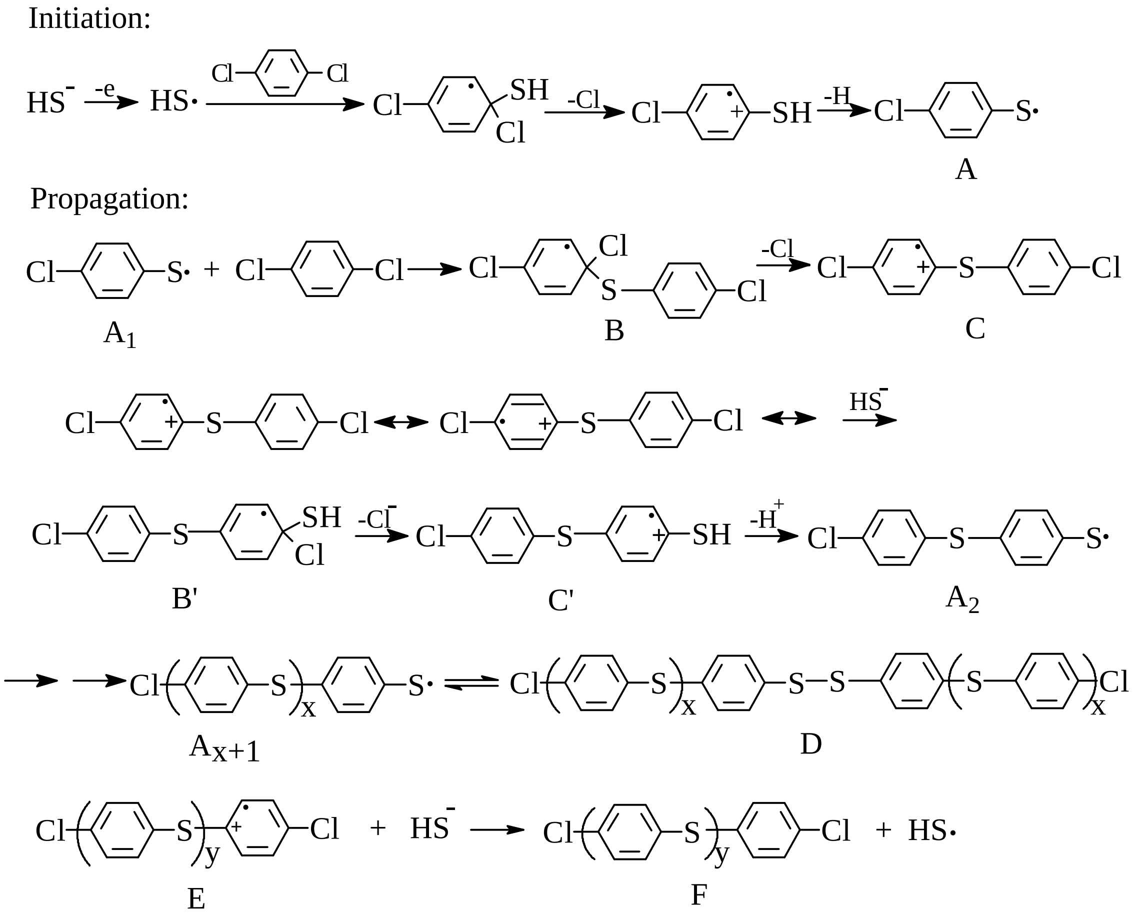
The reaction mechanism is believed to be essentially a nucleophilic displacement reaction that leads to the formation of PPS and sodium chloride as a by-product (14, 55). Scheme 2.1.2.3.2 depicts the initiation reaction of an inorganic sulfide with the monomer, *p*-dichlorobenzene, followed by the beginning of polymer chain growth as the product of initiation reacts with additional *p*-dichlorobenzene. These reactions may be extended to include the reaction of sodium sulfide and sodium *p*-chlorobenzenethiolate with chlorophenyl end groups on polymeric species. Analogously, thiolate nucleophile end groups on polymer molecules can react with any other aryl chloride. However, this polymerization does not seem to exhibit classic condensation polymerization behavior (14-15, 56). That is, polymers of higher molecular weight than predicted by the Carother's equation are produced at low conversions (15) and even at unequal *p*-dichlorobenzene to $Na_2S$ ratios (56). This behavior was rationalized by Fahey and Ash (14) as a natural consequence of the sensitivity of the $S_NAr$ mechanism to the substituents on the aryl chloride, and to the nucleophilicity of the sulfur anion for each individual growth step. Most of the growth steps have rate constants higher than that for the initial condensation of the two monomers. More specifically, the enhanced activating ability of a para sulfur substituent, relative to chlorine, provides the driving force for developing a high molecular weight polymer at low initial monomer conversions.

Achieving a high molecular weight polymer depends on the use of NMP as the reaction medium (13). The ability of the NMP solvent to facilitate $S_NAr$ processes by dissociating ion pairs is well documented (12, 57-58). However, the special qualities that NMP brings to this process go well beyond that of a conventional solvent. Fahey and Ash reported that when hydrated $Na_2S$ dissolves in NMP at elevated temperatures, a chemical reaction occurs, yielding an isolable product with the empirical formula $Na_2S \cdot NMP \cdot H_2O$ (14). The $^1H$ and $^{13}C$ NMR spectra of this product clearly reveal that the NMP ring has been hydrolytically opened to yield an equailmolar mixture of sodium 4-(N-methylamino)-butanoate (SMAB) with sodium hydrosulfide. The SMAB is considered to both solubilize NaSH and act as a proton acceptor (14).

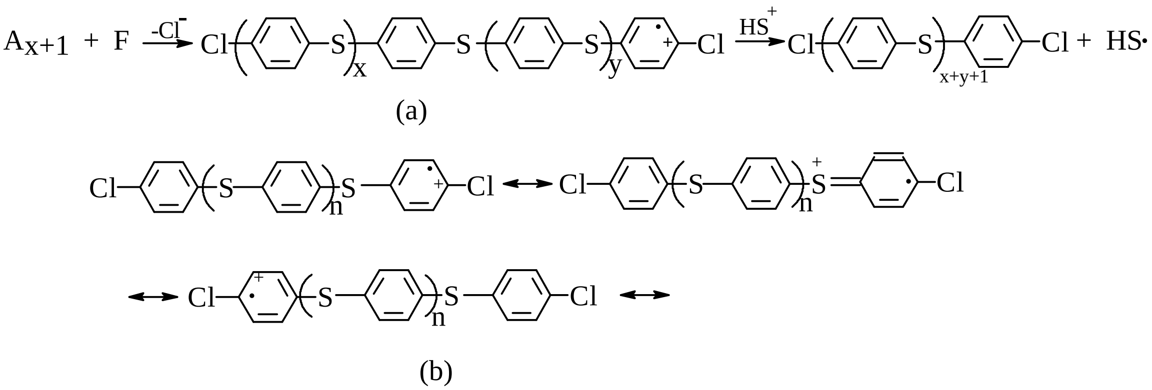


Scheme 2.1.2.3.2 $S_NAr$ mechanism for PPS step growth

Campbell (56) developed an improved process for synthesizing PPS with a higher molecular weight (35,000-65,000). The scheme involves the reaction of *p*-dichlorobenzene with $Na_2S$ in NMP in the presence of an alkaline metal salt of acetic acid, propanoic acid, benzoic acid, or phenol at 245$^{o}$C and 5.4-9.5 atm. It has been claimed that by using 1,2,4-trichlorobenzene as a comonomer in this reaction scheme, the molecular weight of PPS can be increased to 200,000 (29). The mechanism of the Campbell reaction was traditionally considered to be a nucleophilic substitution. However, Koch and Heitz (60-61) have proposed an one-electron-transfer process, with radical cations as reactive intermediates as shown in Scheme 2.1.2.3.3 (reactive intermediate polycondensation). This mechanism was proposed in an attempt to rationalize (a) the formation of polymers of higher molecular weight than predicted at low conversions, (b) the formation of disulfides in model compound studies, and (C) the high stability of the radical cations of PPS oligomers in mass spectral analyses (14, 60). This mechanism involves five types of reactive intermediates: sulfenyl radicals (A), aromatic radicals (B and B′), and radical cations (C and C′). Generation of any of these would provide entry into the propagation cycle. The chain is initiated by an one-electron-transfer process to form HS•. Formation of disulfide D is inherent to the mechanism, and explains its presence as a by-product. Furthermore, it indicates the need for high temperature to cleave the disulfide linkage homolytically, without which the chain propagators would be destroyed. The chain propagation occurs by the reaction of sulfenyl radicals (A) with *p*-dichlorobenzene, and with oligomers (F) formed by electron transfer of $HS^{-}$ to the radical cation (Scheme 2.1.2.3.4 a) (61). Unlike “conventional” step or polycondensation, the formation of PPS does not require equal reactivity of the end groups irrespective of chain length, due to the formation of reactive intermediates C and C′, which are of higher reactivity than the monomer. This reactivity decreases with increasing chain length due to increasing conjugation (Scheme 2.1.2.3.4 b) (61), and leads to products with intermediate molecular weight at the beginning of the reaction, even if the reactants are not added in stoichiometric amounts. For example, Figure 2.1.2.3. schematically presents the dependence of molecular weight on the conversion for four types of polymerizations. In the “reactive intermediate polycondensation” proposed by Koch and Heitz (60-61), high molecular weight products are obtained near the end of the reaction, similar to condensation polymerizations. Presumably, radical coupling and hydrogen abstraction process would account for chain termination reactions (62). Because this mechanism is a new mechanistic concept for “nucleophilic” aromatic substitution, its general characteristics and responses to reaction variables have not yet been firmly established.



Scheme 2.1.2.3.3 Radical-cation mechanism for PPS growth proposed by Koch and Heitz (61)



Scheme 2.1.2.3.4 Reaction mechanism proposed by Koch and Heitz (61) for the synthesis of PPS (a) Electron transfer from HS- to radical cation. (b) Stabilization of the reactive intermediate C by conjugation.

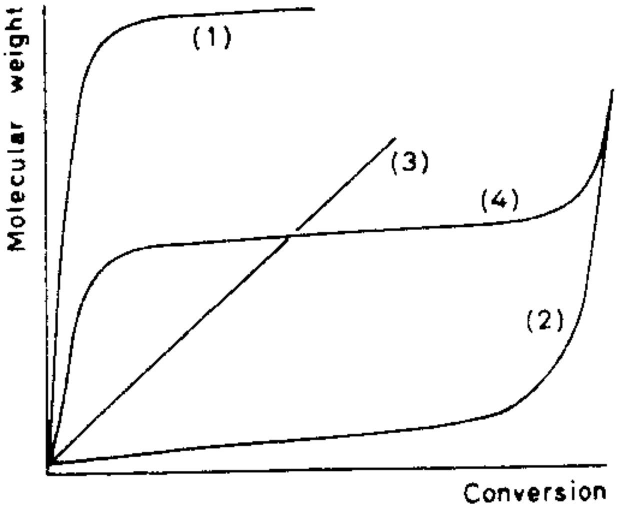
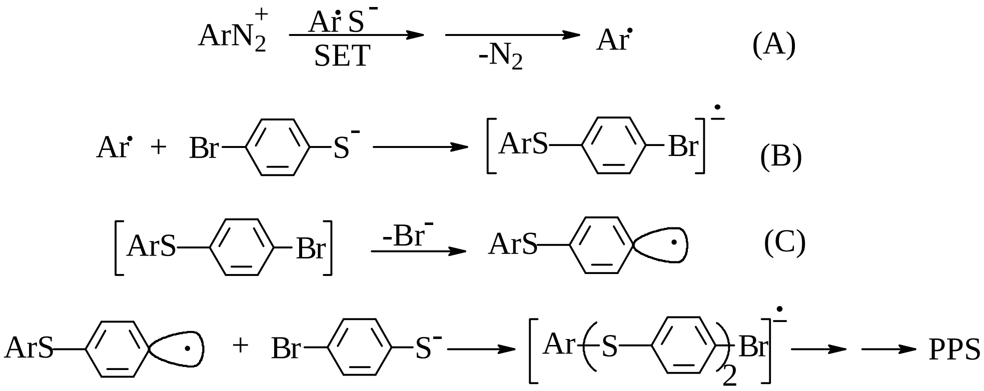


Figure 2.1.2.3 Schematic representation of the dependence of molecular weight on conversion for four types of polymerizations. (1) Radical polymerization, (2) Conventional polycondensation, (3) Living polymerization, (4) Reactive intermediate polycondensation.

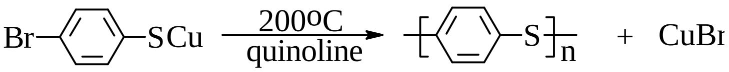
### 2.1.2.4 Single-Electron Transfer ($S_{RN}1$)

Recently, a very different approach for synthesizing PPS has been developed by Novi et al. (63), who used sodium *p*-bromobenzene-thiolate in DMSO at room temperature utilizing catalytic amounts of a diazonium salt (sodium arenediazonium tetrafluoroborate) via a radical, radical-anion chain pathway, conducted in argon. The step sequence of the reaction proposed by Novi et al. is shown in Scheme 2.1.2.4.1 (63). It consists of a single-electron transfer from the thiolate to the initiator to form an aryl radical (A); growth of the chain by radical/anion coupling (B); and expulsion of bromide with formation of a new radical (C). Chain growth may be terminated by the oxidation of a radical anion by residual initiator, or radical/radical coupling, or H-atom transfer to a radical from the medium. Because the polymerizations were carried out at room temperature and semi-crystalline PPS is highly insoluble, it is not surprising that only oligomeric PPS was obtained with repeating units around 9 based on the elemental analysis (48, 63).



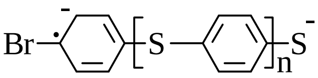
Scheme 2.1.2.4.1 $S_{NR}1$ mechanism for synthesis of PPS proposed by Novi et al.

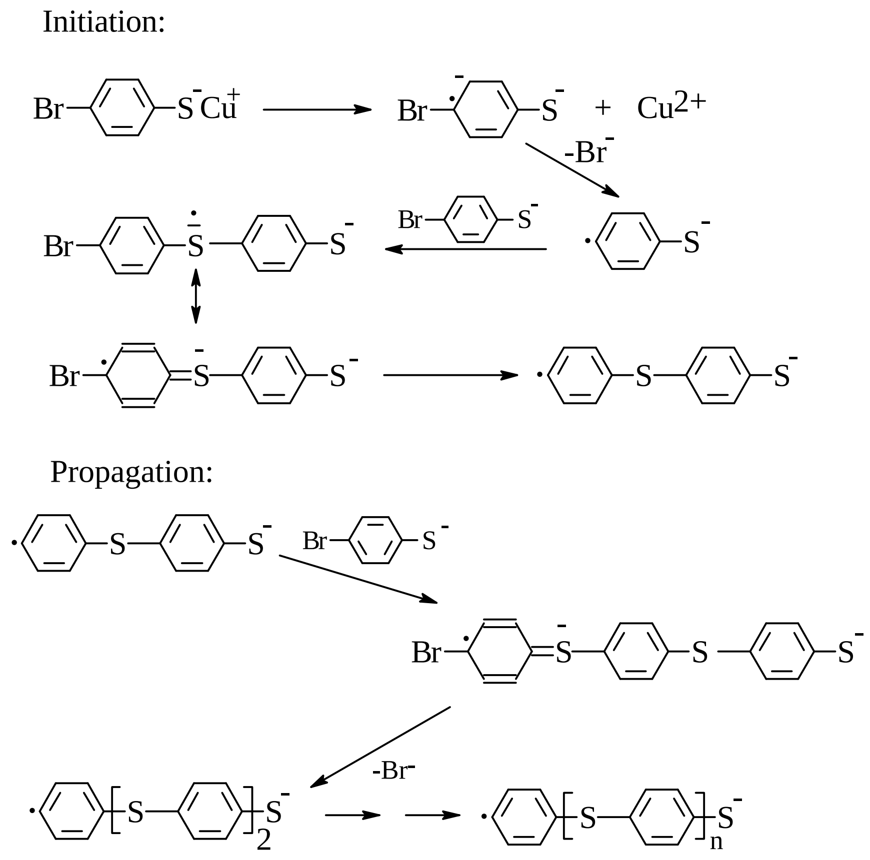
Archer and Lovell reported in 1995 that PPS can be synthesized by a solution polymerization of copper (I) 4-bromobenzenethiolate at 200°C in quinoline under atmospheric pressure (Scheme 2.1.2.4.2) (64-65).



Scheme 2.1.2.4.2 Synthesis of PPS by solution polymerization of copper(I) 4-bromobenzenethiolate

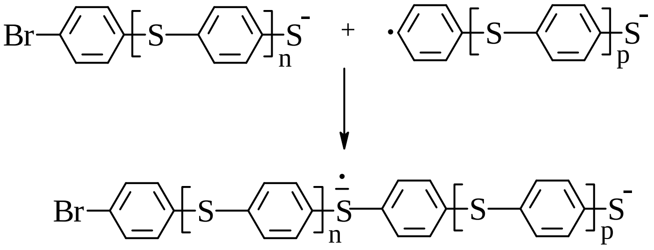
This polymerization method has been monitored as a function of reaction time by electron spin resonance (ESR) spectroscopy and by evaluating the yield and molecular weight of the PPS formed. ESR showed the existence of organic free radicals throughout the polymerization and also revealed the presence of $Cu^{2+}$ ions during the period, up to about 2h reaction time, when PPS yield and molecular weight increased rapidly. An $S_{NR}1$ type mechanism that is consistent with the experimental observations on solution polymerization of copper (I) 4-bromobenzenethiolate is proposed in Scheme 2.1.2.4.3 (65). The initiation step is taken to involve formation of a $Cu^{2+}$ ion by single electron transfer (SET) from a $Cu^{+}$ ion; the specific reaction proposed is SET from a $Cu^{+}$ ion to the aromatic ring of a 4-bromobenzenethiolate ion, leading to the formation of an aryl radical-anion and a $Cu^{2+}$ ion. In keeping with the standard $S_{NR}1$ mechanism, the aryl radical-anion then loses a bromide ion to yield an aryl radical, which rapidly couples to the sulfur atom in another 4-bromobenzenethiolate ion. The latter step leads to the formation of a dimeric radical-anion, which also loses a bromide ion to create a terminal aryl radical. Propagation proceeds by sequential coupling of the monomeric thiolate sulfur atoms to the terminal aryl radicals of growing chains, each coupling step being followed by the loss of a bromide ion in order to regenerate the chain carrier. In each of these reactions, the polymer chain can grow only by formation of 1,4-phenylene sulfide repeat units because of the requirement for the loss of a bromide ion from the site of substitution. In accordance with $S_{NR}1$ reactions, the loss of a bromide ion can be expected to be the rate-determining step, leading to the inference that the organic radical species detected by ESR are the aryl radical-anions of general structure shown below.



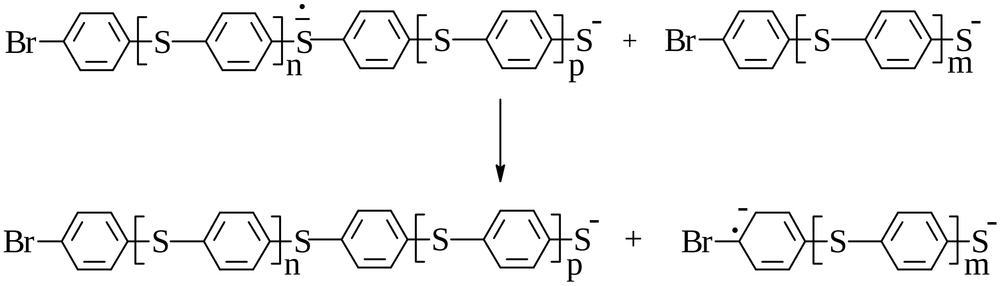


Scheme 2.1.2.4.3 Proposed $S_{NR}1$ mechanism for solution polymerization of Cu(I) 4-bromobenzenthiolate

Since the mechanism proposed in Scheme 2.1.2.4.3 is a chain reaction, it satisfies the general observation that relatively high molecular weight PPS (Mn = 1000 g/mol) is formed at low monomer conversion (64-65). However, as the monomer concentration is reduced, the same chemistry leads to a change in the nature of the polymerization to step-wise growth. This is consistent with the observed two-stage variation of molecular weight with reaction time and results from the fact that all species present (i.e. molecules of monomer, oligomer and polymer) are capable of growth by reaction at both chain ends. Reactions of a monomer with another monomer, an oligomer, or a polymer proceed via a chain reaction mechanism in which the newly added monomer end units automatically become active propagation sites, thus giving rise to the characteristics of chain polymerization. In comparison, the reactions between molecules of oligomer/polymer (which proceed by identical coupling processes to those for reaction of monomer with monomer) leave the active site at the point of coupling (Scheme 2.1.2.4.4) (65), i.e. remote from the chain end, thereby preventing immediate continuation of growth of the chain. These coupled oligomer/polymer molecules can transfer their activity to the end unit of another oligomer/polymer molecule (Scheme 2.1.2.4.5) (65), activating it towards further growth, and thus continuing the kinetic chain of events, resulting in growth of the chains in a step-wise manner.



Scheme 2.1.2.4.4 Coupling of chain species involved in the $S_{NR}1$ mechanism



Scheme 2.1.2.4.5 Chain transfer between chain species involved in the $S_{NR}1$ mechanism

### 2.1.2.5 Other Methods

The patent literature describes several other methods for synthesizing PPS. For example, Sinclair et al. (66) utilized the reaction of alkali metal sulfide with a dihaloaromatic compound in a two-phase solvent, e.g., high molecular weight polyethylene glycol and water. Idel et al. (67-69) reported the reaction of alkali metal sulfide with di- and trihaloaromatic compounds in N-methylcaprolactam utilizing carboxylic amides, anhydrides, esters, and amino acids as cosolvents.

Other synthesis methods for the preparation of PPS have been investigated. For example, Wejchan-Judek and Rogal (70) studied the preparation of PPS by oxidizing thiophenol with thionyl chloride in the presence of $FeCl_3$, $BF_3$, $ZnCl_2$, $TiCl_4$, and $SnCl_4$, while Wejchan-Judek (71) used $WCl_6$, $SbCl_5$, and $H_2SO_4$ as catalysts. The synthesis with $SbCl_5$ was not successful; since no polymer was obtained. The rest of the catalysts produced polymers that contained partly cyclic structures. Polymers synthesized in the presence of $FeCl_3$, $ZnCl_2$, $SnCl_4$, and $TiCl_4$ were amorphous. Polymer synthesized with a $BF_3$ catalyst had crystallinity of the order of 68% (by x-ray diffraction) and showed sequences of a unit cell similar to that of Ryton PPS. Elemental analysis showed that significant amounts of oxygen were present in all polymers, with the exception of those synthesized in the presence of $BF_3$, where it appears that oxygen was present in the form of sulfoxide groups. Kreja et al. (72) synthesized PPS utilizing a modified version of the Grenvesse reaction. They utilized the reaction of benzene, elemental sulfur, and aluminum chloride at $80^{o}C$ under an inert atmosphere. However, they obtained polysubstituted poly(phenylene sulfide)s containing linear, cyclic, and crosslinked species. Nevertheless, none of these approaches is as commercially feasible as the methods of Edmonds and Hill (13), and Campbell (56), mentioned earlier.

### 2.1.3 Physical Properties

PPS is recognized among thermoplastic resins for its remarkable combination of inherently attractive properties and physical characteristics. These include: unusual thermal stability, excellent chemical resistance, inherent flame resistance, high electrical insulation properties and good mechanical properties of molded parts.

#### 2.1.3.1 Thermal Properties

The thermal stability of PPS results from the structure of the polymer, involving only carbon-carbon, carbon-hydrogen and carbon-sulfur bonds, all of which are quite thermodynamically stable. The implication of the thermodynamic stability of the bonds in PPS is that it will take a large input of energy (high temperature) to dissociate any of the bonds (induce thermal degradation). PPS is well suited for use at high temperatures for extended periods of time.

A standard test for assessing weight loss, and thus the thermal stability of a material, is dynamic or isothermal thermogravimetric analysis (TGA). In this test, the percent weight loss is recorded as a function of the temperature of the material. Hill and Edmonds (73) utilized this method to obtain comparative data for PPS and other thermoplastics in a nitrogen atmosphere, as shown in Figure 2.1.3.1.1. Figure 2.1.3.1 shows that no appreciable weight loss was observed in PPS up to about 500°C. In air, degradation of PPS was complete at 700°C (73). On the other hand, in nitrogen there was a 40% weight retention at 1000°C (73). Comparison of PPS with “vinyl” polymers such as polyvinyl chloride, poly(methyl methacrylate), polystyrene, poly(ethylene), and poly(tetrafluoroethylene) indicated a higher thermal resistance for PPS (73).

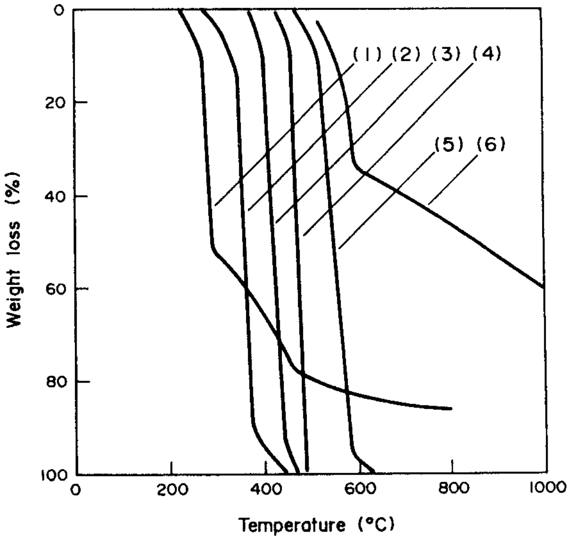
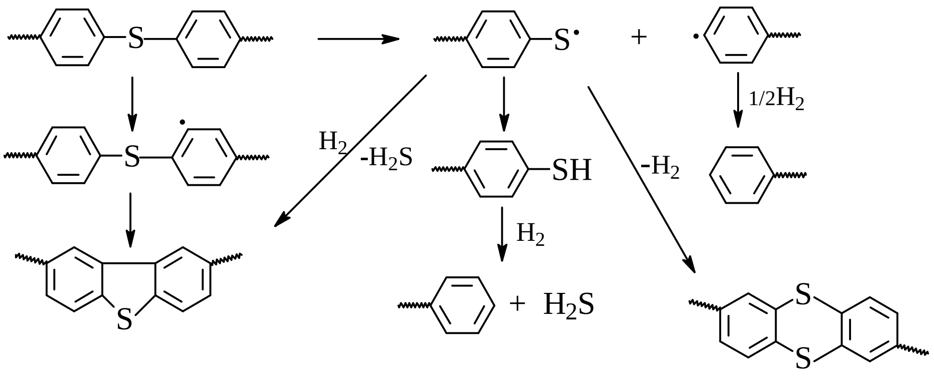


Figure 2.1.3.1 Comparative thermogravimetric analysis of polymers in nitrogen: (1) poly(vinyl chloride); (2) poly(methyl methacrylate); (3) polystyrene; (4) polyethylene; (5) poly(tetrafluoroethylene); (6) PPS

The effect of structural variables on the thermal stability of PPS has been reported. Black et al. (74) reported that branched polymers seem to be more stable than the linear polymers. In addition, molecular weight did not have any obvious effect on the thermal stability of the *p*-phenylene sulfide polymers. Ehlers et al. (75) analyzed the products of pyrolysis of PPS in vacuum at 450°C by mass spectroscopy. They reported that the major decomposition product was a condensate composed of dimeric and trimeric chain fragments, dibenzothiophene, and thianthrene. Other products consisted of $H_2S$, $H_2$, and a residue that suggested a crosslinked species. Moreover, Scheme 2.1.3.1.1 represents a simplified version of the reaction mechanism of the thermal degradation of PPS, proposed by Ehlers et al. (75). The breakdown mechanism could start by cleavage of carbon-sulfur bonds and abstraction of hydrogen to form chain fragments with phenyl and phenylmercapto end groups. Further cleavage of the C-SH bonds and the abstraction of H would lead to the elimination of $H_2S$. The radicals formed by the abstraction of H would cause recombination and crosslinking, and low molecular weight dimers and trimers would be removed at these high temperatures to form a condensate. The dibenzothiophene structure would form from free diphenylsulfide or within the polymer chain, whereas thianthrene would originate from phenylmercaptan or phenylmercapto end groups.



Scheme 2.1.3.1.1 Reaction mechanism for thermal degradation of PPS proposed by Ehlers (75)

PPS is a semi-crystalline polymer and its thermal transitions are appropriate for the melt processing of materials into finished parts. Using differential scanning calorimetry (DSC), PPS shows a high crystalline melting point ($T_m$ = 285°C) and a modest glass transition temperature ($T_g$ = 85°C). Moreover, the polymer crystallizes rapidly above $T_g$ as indicated by an exothermic crystallization peak located at 120-130°C ($T_{cc}$, heating rate of 10°C/min) (76). The polymer also crystallizes rapidly when cooled from the melt. PPS also displays a melt crystallization exotherm at approximately 220°C ($T_{mc}$, cooling rate of 10°C/min) (77). Using the appropriate molding and annealing conditions, a crystalline part can be obtained that is dimensionally stable and possesses good mechanical properties.

Typical heats of fusion for crystalline samples of PPS are in the range of 10-12 cal/g (77). The ability to mold PPS in a crystalline form is critical in achieving solvent resistant and dimensionally stable parts, and to allow those parts to be used at elevated temperatures. According to an X-ray diffraction method described by Brady, fully crystallized PPS has a crystallinity index of about 65% (78).

### 2.1.3.2 Chemical Resistance

PPS also has excellent chemical resistance and there are no known solvents for the polymer below 200$^o$C. Parts molded from PPS can be utilized in a variety of hostile chemical environments where inertness is required. A chemically resistant polymer will maintain its dimensional stability, physical properties, weight and appearance when exposed to hostile environments (79). PPS is affected by high temperature exposure to only a few organic solvents, strong mineral acids, and strong oxidizing reagents (80). The reaction of these reagents is due to the expected chemistry for the structure of PPS. Oxidizing reagents can convert sulfides present in PPS to sulfoxides or sulfones. The aromatic ring can be halogenated, nitrated or sulfonated under appropriate conditions to yield derivatized polymers. Table 2.1.3.2 documents a comparison of PPS with selected engineering polymers when exposed to a variety of reagents (80).

Table 2.1.3.2 Comparative Chemical Resistance of Various Polymers at 93$^o$C/24h (percent tensile strength retained)

| Chemical | Nylon 6,6 | Polycarbonate | Polysulfone | Modified PPO | PPS |
|---|---|---|---|---|---|
| 37% HCl | 0 | 0 | 100 | 100 | 100 |
| 10% $HNO_3$ | 0 | 100 | 100 | 100 | 96 |
| 30% $H_2SO_4$ | 0 | 100 | 100 | 100 | 100 |
| 30% NaOH | 89 | 7 | 100 | 100 | 100 |
| 28% $NH_4OH$ | 85 | 0 | 100 | 100 | 100 |
| $H_2O$ | 66 | 100 | 100 | 100 | 100 |
| NaOCl | 44 | 100 | 100 | 100 | 84 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| Bromine | 8 | 48 | 92 | 87 | 64 |
| Butyl alcohol | 87 | 94 | 100 | 84 | 100 |
| Phenol | 0 | 0 | 0 | 0 | 100 |
| Butylamine | 90 | 0 | 0 | 0 | 50 |
| Aniline | 85 | 0 | 0 | 0 | 96 |
| 2-Butanone | 87 | 0 | 0 | 0 | 100 |
| Benzaldehyde | 98 | 0 | 0 | 0 | 84 |
| Chlorobenzene | 73 | 0 | 0 | 0 | 100 |
| Chloroform | 57 | 0 | 0 | 0 | 87 |
| Ethyl acetate | 89 | 0 | 0 | 0 | 100 |
| Butyl phthalate | 90 | 46 | 63 | 19 | 100 |
| *p*-Dioxane | 96 | 0 | 0 | 0 | 88 |
| Butyl ether | 100 | 61 | 100 | 0 | 100 |
| Gasoline | 80 | 99 | 100 | 0 | 100 |
| Diesel fuel | 87 | 100 | 100 | 36 | 100 |
| Toluene | 76 | 0 | 0 | 0 | 98 |
| Benzonitrile | 88 | 0 | 0 | 0 | 100 |
| Nitrobenzene | 100 | 0 | 0 | 0 | 100 |

### 2.1.3.3 Flame Resistance

PPS possesses outstanding fire retardancy, which can be attributed to its aromatic structure and to its tendency to char. When exposed to flame, PPS will burn with a yellow-orange flame until the flame source is removed. It has a high oxygen index of 44 (77), a low heat release rate (140), a low radiant panel flame spread index (ASTM E 162) and, according to the standard UL 94 laboratory flammability test results, it is classified as V-0/5V (62), i.e., self-extinguishing and non-dripping. The autoignition temperature is 540$^{o}$C. Smoke-density measurements indicate that PPS does not produce copious amounts of smoke in either the smoldering or the flaming stage as do some other aromatic polymers, such as polystyrene, and halogenated polymers, e.g., poly(vinyl chloride) (PVC) (81). Table 2.1.3.3 summarizes the flammability characteristics of PPS (62).

Table 2.1.3.3 Flammability Characteristics of PPS

| Test | Test method | Value |
|---|---|---|
| Oxygen index | ASTM D 2863 | 44-62[a] |
| Flammability | UL 94 | V-0/5V |
| Flame spread index | ASTM E 162 | 50.8 mm |
| Autoignition temperature[b] | — | 540°C |
| Smoke density[c] | NBS test chamber | |
| obscuration time, smoldering | — | 15.5 min |
| obscuration time, flaming | — | 3.2 min |

[a] Unfilled PPS has oxygen index = 44. Filled composites vary with filler and composition.
[b] Ref. 77.
[C] Time required to reach specific optical density of 16. Results from ref.81.

### 2.1.3.4 Electrical Properties

PPS resins and compounds display properties characteristic of good insulators, including high dielectric strength, low dielectric constant, low dissipation factor and high volume resistivity. Table 2.1.3.4 summarizes the electrical properties of two major types of PPS molding compounds used for electronic and electrical applications (62).

Table 2.1.3.4 Electrical Properties of PPS Compounds

| Property | 40% glass filled | Glass and mineral filled | test method |
|---|---|---|---|
| Dielectric strength (1 kHz, V/mil)[c] | 450 | 340-400 | D149[a] |
| Dielectric constant (1 MHz) | 3.8 | 4.6 | D150[a] |
| Dissipation factor (1 MHz) | 0.0013 | 0.016 | D150[a] |
| Volume resistivity (2 min, Ω cm) | $4.5 \times 10^{16}$ | $2.0 \times 10^{15}$ | D257[a] |
| Arc resistance (s) | 35 | 200 | D495[a] |
| Comparative tracking index (v) | 180 | 235 | UL 746A[b] |
| Insulation resistance (Ω) | $10^{11}$ | $10^{9}$ | — |

[a] ASTM.
[b] Underwriters Laboratory.
[C] 1 mil = $10^{-3}$ in.

PPS compounds that contain only glass fillers are better insulators than those containing glass and mineral fillers. Alternatively, compounds containing both glass and mineral fillers provide better arc resistance and tracking index. Both types of compounds, however, provide an excellent balance of electrical properties. The dissipation factor and dielectric constant for a 40% glass-filled PPS compound display excellent stability over a wide frequency range and at elevated temperatures.

PPS (40% glass-filled) compounds also retain their excellent electrical properties, even after exposure to humid environments. For example, the volume resistivity decreases by only one decade ($10^{16}$ ohm cm to $10^{15}$ ohm cm) after immersion in 60°C water for 12 days (62). The unusual combination of good electrical properties and high temperature resistance accounts for the Underwriters Laboratories approval of the use of PPS compounds at high temperatures (200-240°C) (77). These properties make PPS compounds well suited for electronic and electrical applications.

Despite the fact that PPS is an excellent insulator, it can be rendered modestly electrically conducting by the addition of dopants such as arsenic pentafluoride (82-83), antimony pentafluoride (84), sulfur trioxide (84-85) and nitroxy hexafluorophosphate (86). Doped PPS is not unique as a conducting polymer. Many other polymers with πconjugated structures in the backbone of the polymer have been doped with strong electron acceptors to yield conducting polymers. Polyacetylene (87), poly(*p*-phenylene) (88), and polypyrrole (89) are examples of such polymers. These polymers all suffer, however, from processing shortcomings in that they are intractable. Since PPS is easy to process in its predoped state, it has been the object of significant interest as conductive polymers. The reaction of arsenic pentafluoride with PPS appears to result in structural modification of the polymer (90). Dibenzothiophene moieties are produced by the coupling of adjacent phenyl rings in the PPS backbone. These aromatic rings are forced into a coplanar conformation not found in PPS crystal structures (91) or amorphous state studies (92), presumably facilitating π-electron overlap between the aromatic rings. A further consequence of doping PPS with arsenic pentafluoride is the loss of crystallinity (93), due to the above-mentioned dopant-induced disorders. The solvent resistance of PPS is due in part to its crystallinity. Thus, doping PPS with arsenic pentafluoride in the presence of arsenic trifluoride (the solvent for this process) resulted in rapid dissolution of the polymer (94). The resulting solution was intensely blue, conductive and indefinitely stable in dry air. Evaporation of the solvent produced film that had conductivities ranging from $5 \times 10^{-3}$ to 200 S/cm and that possessed good strength and flexibility (94). Extending these technologies to practical electronic and electrical applications is attractive and awaits further development.

### 2.1.3.5 Mechanical Properties

PPS is generally characterized by high strength and stiffness and moderate impact resistance. An unusual property of PPS moldings is its ‘metallic ring’ when given a sharp tap, which is associated with a high modulus (62). Fillers and reinforcing fibers can be easily added to PPS, yielding reinforced compounds with enhanced properties. These compounds are useful for compression and injection moldings, displaying high tensile strength, high flexural modulus, good flexural strength, high heat deflection temperature, low elongation and moderate impact strength. Compounds can be custom-tailored by including other mineral fillers, pigments or fiber reinforcements to suit specific applications. Table 2.1.3.5 summarizes the properties of neat PPS and a variety of filled compounds (62).

Table 2.1.3.5 Properties of PPS Resin and Compounds[a]

| Property | Neat[b] | 40% glass reinforced | Glass and mineral filled | Test method[c] |
|---|---|---|---|---|
| Density (g/cm$^3$) | 1.35 | 1.6 | 1.8-2.0 | D1505 |
| Tensile strength (p.s.i. x $10^{-3}$)[e] | 9.5 | 17.5 | 10.8 | D638 |
| Elongation (%) | 1.6 | 1.2 | 0.54 | D368 |
| Flexural modulus (p.s.i. x $10^{-6}$)[e] | 0.56 | 1.7 | 2.2 | D790 |
| Flexural strength (p.s.i x $10^{-3}$)[e] | 14.0 | 26.0 | 14.5 | D790 |
| Izod impact (lb ft in$^{-1}$)[e] (unnotched) | 1.9 | 4.5 | 1.9 | D256 |
| Compressive strength (p.s.i x $10^{-3}$)[e] | 16.0 | 21.0 | 16.0 | D695 |
| Heat deflection temperature (°C)[d] | 135 | >260 | >260 | D648 |
| Rockwell hardness | R-120 | R-123 | R-121 | D785 |
| Expansion coefficient ($10^{-5}$/°C) | 4.9 | 4.0 | 2.8 | — |

[a] Injection molded into a 135°C mold, samples unannealed unless specified.
[b] Cured feedstock.
[c] ASTM test methods.
[d] Samples annealed at 260°C for four hours.
[e] 1 p.s.i. = 0.00689 MPa; 1 Ib ft in$^{-1}$ = 53.38 J m$^{-1}$.

## 2.2 Poly(Arylene Sulfide) Related Systems

### 2.2.1 Other Poly(Arylene Sulfide)s

Although PPS is the poly(arylene sulfide) that has received the most attention, a variety of other structures have also been synthesized. Copolymers have been prepared (95-96) from mixtures of *p*- and *m*-dichlorobenzene and sodium sulfide (Table 2.2.1.1). Incorporation of *meta* units results in disruption of crystallinity. Copolymers containing

50-100 mol% *meta* structure are amorphous. The 50 and 70 mol% copolymers are quite soluble in tetrahydrofuran (THF).

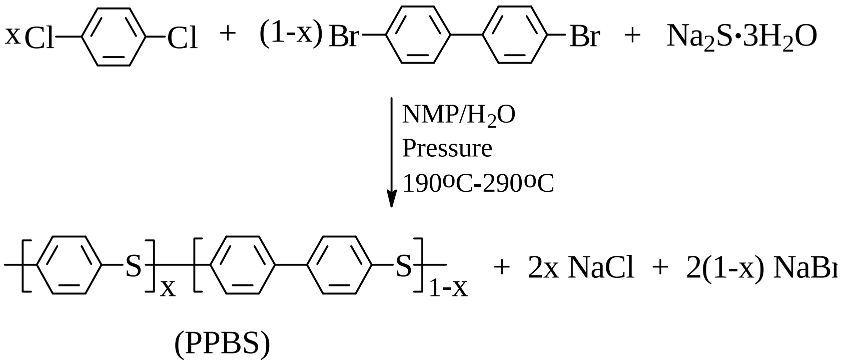
Table 2.2.1.1 Poly(*p*-phenylene sulfide/*m*-phenylene sulfide) Copolymers (95-96)

| *Para*/*meta* ratio | $T_g$ (°C) | $T_m$ (°C) | Solubility[a] |
|---|---|---|---|
| 1/0 | 83 | 283 | insoluble |
| 3/1 | 68 | 205 | insoluble |
| 1/1 | 49 | --[b] | soluble |
| 1/3 | 27 | --[b] | soluble |
| 0/1 | 15 | --[b] | nearly insoluble |
| 1/1[c] | 39 | 271 | soluble fraction |

[a] In refluxing tetrahydrofuran.
[b] Amorphous polymers softening at 90-100°C.
[c] Block copolymer.

The *meta* homopolymer is nearly insoluble in refluxing THF, but is soluble in NMP at 100°C. The molecular weight in this series decreases as *meta* content increases, contributing to a lower $T_g$. The last entry in Table 2.2.1.1 is a block copolymer prepared from a mixture of *meta* and *para* homopolymers (96). It consisted of soluble and insoluble fractions (NMP at 100°C), containing 75 and 25 mol% *meta* units, respectively.

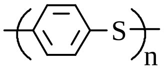
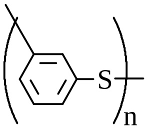
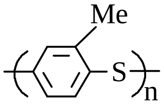
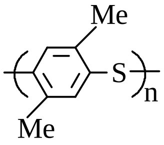
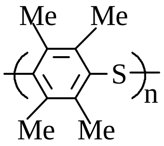
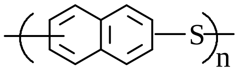
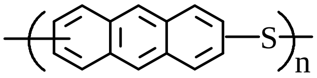
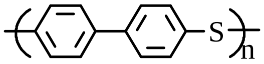
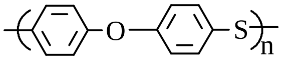
Lee Soon Park et al. recently reported the synthesis of copoly(*p*-phenylene/ biphenylene sulfide)s (PPBS) from sodium sulfide trihydrade ($Na_2S \bullet 3H_2O$), *p*-dichlorobenzene (DCB), and 4,4′-dibromobiphenyl (DBB) comonomers in NMP solvent using an autoclave (Scheme 2.2.1.1) (97). The molecular weights of PPBS copolymers were determined by high temperature (210°C) GPC in 1-chloronaphthalene solvent. The reaction temperature had little effect on the molecular weights of PPBS copolymers with water as additive at the level of 3 mol $H_2O$ per 1 mol $Na_2S$. PPBS copolymer, however, showed maximum molecular weight of $M_w = 24.1 \times 10^3$, with the total water content of 9 mol $H_2O$ per 1 mol $Na_2S$ at an optimum polymerization temperature of 270°C. As more rigid biphenylene repeat units were incorporated in the chain, the PPBS copolymers exhibited increasing $T_g$s and decreasing $T_m$s. The reactivity of 4,4′-dibromobiphenyl (DBB) was higher than that of 4,4′-dichlorobenzene (DCB) toward thiolate anion, resulting in DBB rich copolymer at lower reaction temperatures (97).



Scheme 2.2.1.1 Synthesis of copoly(*p*-phenylene/biphenylene sulfide) (PPBS)

The physical properties of other poly(arylene sulfide)s are summarized in Table 2.2.1.2. The variation in diad structure (head-to-head and head-to-tail) for the 2-methyl derivative accounts for its lack of crystallinity. The addition of symmetrically placed substituents in the 2,6-dimethyl and 2,3,5,6- tetramethyl derivatives does not significantly reduce crystallinity. Structural irregularities in the polynuclear derivatives disrupt crystallinity. Replacement of sulfide groups with ether groups lowers crystallinity. Both nucleophilic and electrophilic synthetic procedures were used in producing these polymers.

Table 2.2.1.2  Other Poly(arylene sulfide)s

| Structure | Softening temperature ($^oC$) | Crystallinity | Solubility | Ref. |
|---|---|---|---|---|
|  | 280 | some | $ClC_{10}H_7$ | 13 |
|  | 100 | none | NMP | 95 |
|  | 100 (1400 | none | $C_6H_6$ | 98-99 |
|  | 170 (220) | slight | $C_6H_6$ | 98-99 |
|  | 290 | some | $0\text{-}C_{l2}C_6H_4$ | 100 |
|  | 130 | none | $CHCl_3$ | 101 |
|  | 105 | none | $CHCl_3$ | 101 |
|  | 430 | high | none | 102 |
|  | 160 | some | DMSO | 103 |

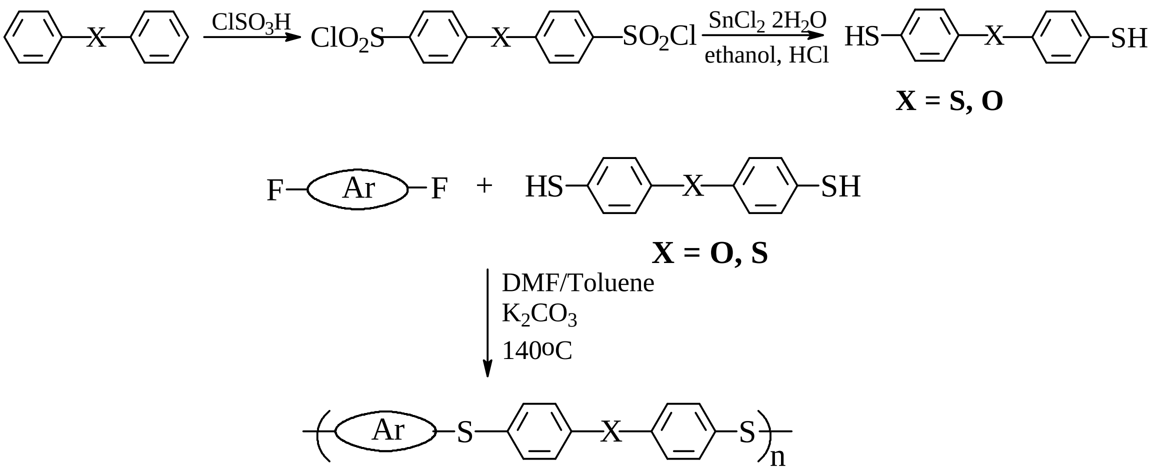
## 2.2.2  Poly(Thioether Ketone)s

Aromatic poly(ether ketone)s (PEKs) are a class of thermally stable engineering thermoplastics known for their excellent electrical and mechanical properties (104). Commercially investigated polymers were highly crystalline and exhibit excellent solvent resistance, much like poly(arylene ether ketone)s, PEEK, PEK, etc.. PEKs have been used as insulation materials, as matrices for composite materials (104), and in electronics applications (105).

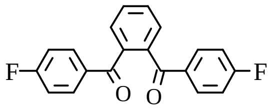
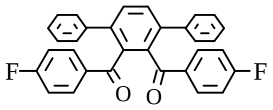
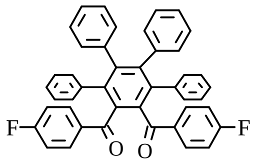
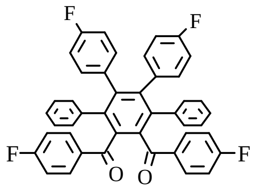
Bonner synthesized low molecular weight PEKs by an aluminum chloride mediated Friedel Crafts acylation of biphenyl ether with terephthaloyl chloride in nitrobenzene (106). The highly crystalline oligomers precipitated before high molecular weight polymer could form. Goodman et al. succeeded in synthesizing a high molecular weight PEK from isophthaloyl chloride and biphenyl ether using methylene chloride as the solvent (107). Polyacylation reactions have also be performed in highly acidic media, such as HF, using $BF_3$ as the Lewis acid (108).

The synthesis of PEKs by nucleophilic displacement polymerization was initially unsuccessful due to the insolubility of the highly crystalline product (109). Rose pioneered the use of diphenyl sulfone as a suitable reaction solvent and was able to synthesize high molecular weight semicrystalline PEKs by nucleophilic displacement polymerization (110). Several amorphous aromatic poly(ether ketone)s have been synthesized by using bisphenols such as 4,4′-(1-methylethylidene) bisphenol, and since these polymers are much more soluble, the reaction could be carried out at lower temperatures in an aprotic dipolar solvent (111).

The sulfur containing analogs to the aromatic poly(ether ketone)s, although important, have been greatly under-investigated. Only a few reports have been published on poly(thioarylene ketone)s, although conceptually their synthesis is similar to that of poly(arylene ether ketone)s. In 1997, Hay et al. reported the preparation of poly(thioether ketone)s from 4,4′-dimercaptodiphenyl ether and 4,4′-dimercaptodiphenyl thioether, by reaction with a series of ketone-activated aromatic fluoro compounds in DMF in the presence of anhydrous $K_2CO_3$ (Scheme 2.2.2.1) (112). The polymers formed were amorphous, as evidenced by WAXD measurements, and soluble in normal organic solvents. They had inherent viscosities of 0.3-0.88 dL/g in chloroform at $25^oC$. The glass transition temperatures of these poly(thioether ketone)s were in the range of 154 to $237^oC$. The 5% weight loss temperatures by TGA were in the range of 420 to $541^oC$ in nitrogen and 503 to $527^oC$ in air (112).

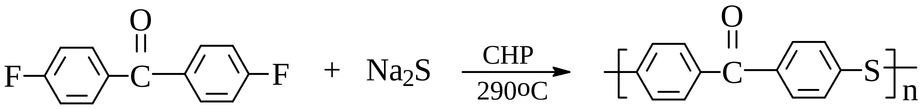


Scheme 2.2.2.1 Synthesis of aromatic poly(thioether ketone)s

|  | **X** | $M_n$ (g/mol) | $T_g$ (°C) |
|---|---|---|---|
|  | O | 68,000 | 161 |
| | S | 55,000 | 154 |
|  | O | 68,000 | 203 |
| | S | 90,000 | 192 |
|  | O | 69,000 | 237 |
| | S | 62,000 | 227 |
|  | O | 88,000 | 228 |
| | S | 92,000 | 232 |

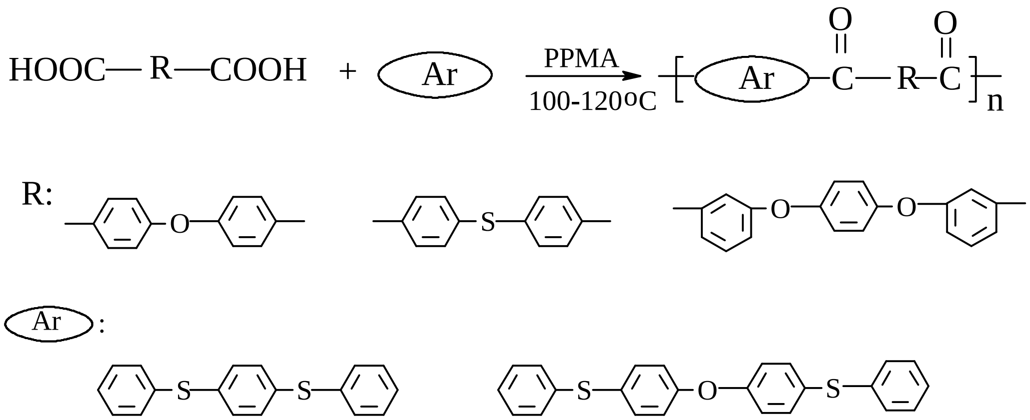
Researchers at Dow Chemical reported the preparation of poly(phenylene ketone sulfide) (PKS) from ketone-activated aromatic fluoro compounds by reaction with freshly crystallized anhydrous sodium hydrosulfide. (Scheme 2.2.2.2) (113). The polymerization occurs very rapidly in N-cyclohexyl-2-pyrrolidinone (CHP) at 290°C and in 0.5 hours high molecular weight PKS was obtained ($\eta_{inh}$ = 0.9 dL/g). In N-methyl-2-pyrrolidone (NMP), whose boiling point (202°C) is lower than CHP, only low molecular weight PKS was obtained ($\eta_{inh}$ = 0.23 dL/g). This indicates, along with the solvation effects, that a high temperature is essential in preventing premature crystallization of the polymer. Also in contrast to CHP, in diphenyl sulfone (DPS) after 3 h, the isolated PKS showed low molecular weight ($\eta_{inh}$ = 0.25 dL/g), which is a consequence of better solvation of sodium ions in CHP than in DPS (113).

In the reaction of 4,4′-difluorobenzophenone with anhydrous sodium sulfide, the purity of the sodium sulfide has an effect on the degree of polymerization. For example, when the polymerization was carried out with anhydrous sodium sulfide without prior purification, low molecular weight ($\eta_{inh}$ = 0.10 dL/g) PKS was obtained, which could be due to the presence of impurities, such as polysulfides, in the commercial sodium sulfide (113). Also, since sodium sulfide is hygroscopic, a slight excess (1%) was found to be necessary to obtain high molecular weight PKS. The DSC data indicated that the PKS had $T_g$ = 152°C and $T_m$ = 335°C (113).



Scheme 2.2.2.2 Synthesis of poly(phenylene ketone sulfide)

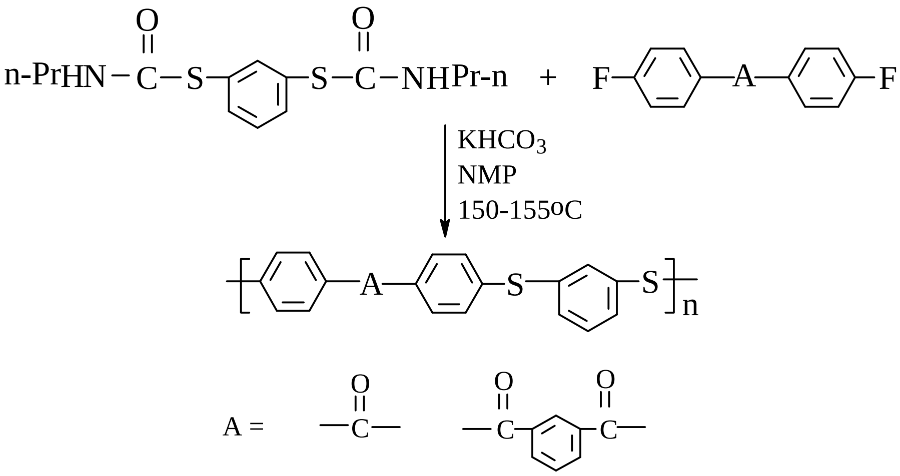
Ueda et al. synthesized a series of poly(thioether ketone)s by the direct polycondensation of aromatic dicarboxylic acids with aryl compounds containing sulfide structures, using phosphorous pentoxide/methanesulfonic acid (PPMA) as the condensing agent and solvent (Scheme 2.2.2.3) (114). The polycondensation, in general, proceeded in homogeneous solution and gave quantitative yields of polymers with moderate to high molecular weight. Under the optimum reaction conditions (120°C/24h), the highest molecular weight polymer with inherent viscosity up to 0.73 dL/g was obtained (114), and the synthesized poly(thioether ketone)s had glass transition temperatures ranging from 115-162°C (114).



Scheme 2.2.2.3 Synthesis of poly(thioether ketone)s by direct polycondensation

Poly(arylene ether ketone)s, such as PEEK, are conventionally synthesized by nucleophilic displacement of 4,4′-difluorobenzophenone with a bisphenol in NMP in the presence of potassium carbonate (115). Similarly, the sulfide polymers can be prepared from the corresponding bisthiophenols (116). In general poly(arylene sulfide)s have better thermal or thermooxidative stabilities than the ether analogues. However, they have not been extensively explored, which is partially due to problems associated with synthesizing and purifying the monomers and polymers. The bisthiophenol monomers, routinely prepared by reducing the arylsulphonyl chloride, are usually unstable in air and readily oxidize to disulfide. Recently, Wang and Hay (117) reported a new method for the synthesis of poly(thioether ketone)s from masked bisthiophenols in the presence of potassium bicarbonate.

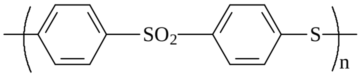
When the 1,3-dithiophenol was treated with a slight excess of *n*-propylisocyanate in ether, the corresponding biscarbamate was obtained in high yield. The monomer, recrystallized from toluene as a white crystalline solid, was polymerized with 4,4′-difluorobenzophenone and 1,3-bis(4-fluorobenzoyl) benzene, respectively, in the presence of potassium bicarbonate (2.2.2.4) (117). The polymerization reaction was carried out in NMP at 150-155°C, and high molecular weight polymers were readily obtained in 2 h. In comparison to the conventional two-stage procedure using bisthiophenol as a monomer, requiring a few hours to remove water azeotropically prior to polymerization, this new method offers a simple, rapid, one-stage polymerization.



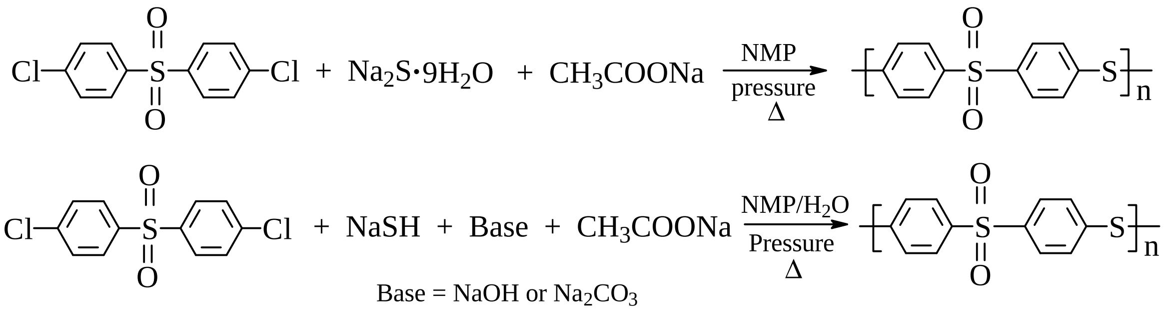
Scheme 2.2.2.4 Synthesis of poly(thioether ketone)s from a masked bisthiophenol

## 2.2.3 Poly(Phenylene Sulfide Sulfone)s (PPSS)

Considerable interest has been developed in the synthesis, characterization, and properties of poly(arylene ether)s. The sulfur containing analogs to the poly(arylene ether)s, although important, are much less well studied (14, 62, 77). By far and away the most important sulfur containing material in this classification is poly(phenylene sulfide)s (PPS). A related sulfide sulfone polymer, such as poly(phenylene sulfide sulfone) (PPSS),



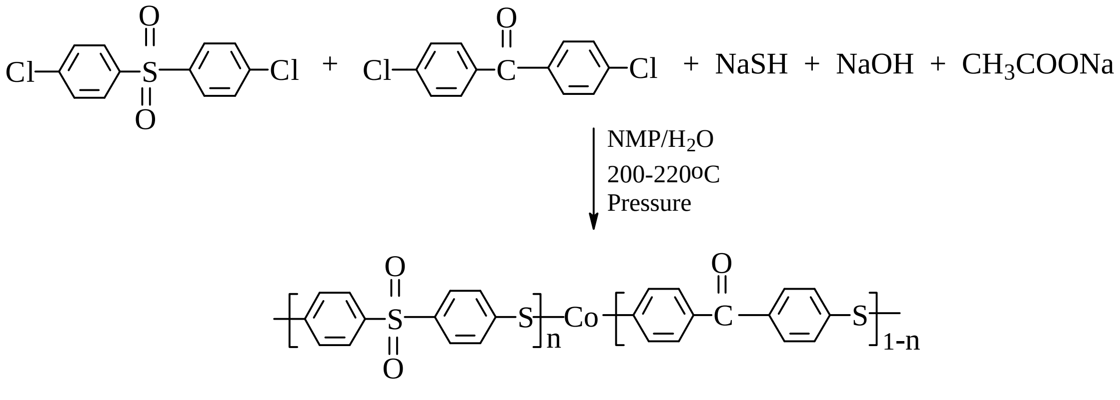
has been investigated relatively briefly in the literature and in commercial practice, references to it are mostly limited to either the patent literature or the commercial trade literature. PPSS has been described as an amorphous polymer with a $T_g$ around 212-217°C (118-119). The general preparation of PPSS involves reacting alkali metal sulfide with dihalo aromatic sulfone via a nucleophilic substitution reaction. Specifically, PPSS has been prepared through the reaction of 4,4′-dichlorodiphenyl sulfone (DCDPS) with sodium sulfide nonahydrate and sodium acetate in NMP (120-121). Another method utilized sodium hydrosulfide, plus either sodium hydroxide or sodium carbonate, along with sodium acetate in NMP, to which distilled water had been intentionally added (Scheme 2.2.3.1) (122-124). The polymerization reaction was conducted in a pressure reactor at a temperature of around 200°C for 3-5 h. High molecular weight PPSS was obtained when the molar ratios of NMP-to-sulfur and NMP-to-water utilized were 8-to-1 and 0.85-to-1, respectively (121, 124).



Base = NaOH or $Na_2CO_3$

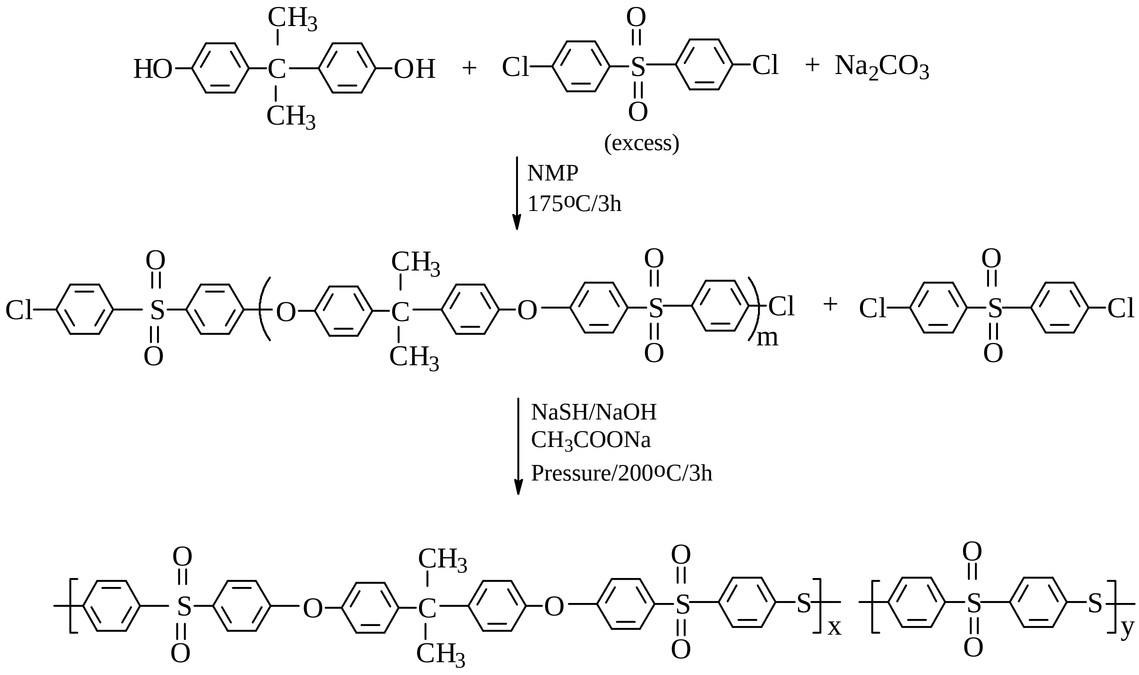
Scheme 2.2.3.1 Synthesis of poly(phenylene sulfide sulfone) (PPSS)

Recently, several new sulfide sulfone homo- or copolymers were developed. Senn (125) synthesized random copoly(*p*-phenylene sulfide sulfone/ketone)s (PPSS/K) in high yield by the polycondensation of sodium hydrosulfide with 4,4′-dichlorodiphenyl sulfone (DCDPS) and 4,4′-dichlorobenzophenone (DCBP) (Scheme 2.2.3.2). The polymerization was conducted in an autoclave between 200-220°C, depending on the composition of the copolymer, and in the presence of water and sodium acetate. The copolymers with sulfone/ketone molar ratios (S : K) > 25 : 75 were amorphous, while the copolymers with S : K ratios ≤ 25 : 75 were semicrystalline in nature. These materials formed tough, creaseable films and exhibited a linear increase in the glass transition temperature with increasing sulfone content. However, the melting point of the semicrystalline copolymers decreased from 345°C to 269°C with increasing sulfone content.



Scheme 2.2.3.2 Synthesis of random copoly(*p*-phenylene sulfide sulfone/ketone)s (125)

Poly(arylene sulfide sulfone) polymers containing ether groups were synthesized via a two-step process (Scheme 2.2.3.3) (126-129). In the first step, a prepolymer characterized as dihalo-terminated polyethersulfone oligomers was prepared by reacting an aromatic diphenol, such as bisphenol A, with a substantial excess of a dihalo aromatic sulfone, such as 4,4′-dichlorodiphenyl sulfone, in the presence of sodium carbonate in NMP. In the second step, sodium hydrosulfide, sodium acetate and water was subsequently added to the reaction mixture and the excess dihalo aromatic sulfone and the oligomers were copolymerized with sodium hydrosulfide, resulting in a modified poly(arylene sulfide sulfone) polymer containing ether linkages. These polymers exhibit improved softening temperature and glass transition temperature and are useful in high temperature applications.



Scheme 2.2.3.3 Synthesis of poly(arylene sulfide sulfone) containing ether groups

Other types of poly(arylene sulfide sulfone) copolymers have also been prepared and investigated. For example, Stone et al. (130) synthesized a new sulfide sulfone copolymer containing biphenyl groups by reacting sodium hydrosulfide with a mixture of 4,4′-dichlorodiphenyl sulfone and 4,4′-bis(*p*-chlorophenylsulfonyl) biphenyl, using a procedure similar to the one used to prepare traditional PPSS. The resulting copolymer had a glass transition temperature around 260$^{o}$C (130). Poly(arylene sulfide) polymers containing sulfone, ether and biphenyl groups were prepared by a two step process (131). In the first step, a diphenol was reacted with either dihaloaromatic sulfone monomer or a bis-(haloarylsulfonyl) biphenyl monomer, or both, in the presence of an alkali metal base in NMP. In the second step, the reaction mixture was reacted with sodium hydrosulfide, as well as with any monomer that was not employed in the first step (if any), in the presence of sodium acetate and sodium hydroxide at elevated temperature and pressure. The polymers exhibited increased glass transition temperatures over those of known poly(arylene sulfide) polymers (131). The structure of the repeat units of the polymer can be controlled by varying the sequence of addition of the monomers. In 1992, Bobsein developed a new poly(phenylene sulfide sulfone/sulfoxide) copolymer that is suitable for some applications requiring selective chemical degradation of arylene sulfide sulfone polymers, without sacrificing the ability of the polymer to withstand high use temperature (132). This copolymer was prepared by reacting sodium hydrosulfide with a mixture of 4,4′-dichlorodiphenyl sulfone and 4,4′-dichlorodiphenyl sulfoxide in the presence of sodium acetate, sodium carbonate, water and NMP.

Arylene sulfide sulfone polymers are engineering thermoplastics of potential commercial interest for film, fiber, molding, and composite applications because of their high glass transition temperatures, excellent thermal and chemical resistance, dimensional stability, and flame resistance. The physical and mechanical properties of injection molded specimens of poly(phenylene sulfide sulfone) (PPSS), compared with commercial products of polyethersulfone (PES) and polysulfone (PSF), are summarized in Table 2.2.3.1 (133). Table 2.2.3.1 shows that density, water absorption and refractive index of PPSS are higher than those of either PES or PSF. The mechanical properties of PPSS are also improved. Both the tensile strength and flexural strength increased in the order of PSF<PES<PPSS, while the elongation at rupture decreased in the order of PSF>PES>PPSS. The enthalpy relaxation behavior of PPSS was investigated using DSC in order to understand the reportedly brittle nature of PPSS. The rate of enthalpy relaxation of PPSS was found to be very high and the fast relaxation is probably responsible for the low elongation of PPSS (133).

Table 2.2.3.1 Physical and Mechanical Properties of PPSS, PES and PSF (133)

| | PPSS<br>(MFR = 25) | PES<br>Victrex® PES 200P | PSF<br>Udel® P-1700 |
|---|---|---|---|
| S content (%) | 25.8 | 13.8 | 7.2 |
| Density (g/cm$^{-3}$) | 1.40 | 1.37 | 1.24 |
| $T_g$ ($^oC$) | 217 | 223 | 187 |
| Refractive index | 1.71 | 1.65 | 1.63 |
| Water absorption (%) 24 h (equilibrium) | 0.61 (1.28) | 0.62 (1.24) | 0.30 (0.47) |
| Tensile strength (MPa) | 99 | 86 | 74 |
| Elongation at break (%) | 9.2 | 17 | 80 |
| Flexural strength (MPa) | 145 | 130 | 114 |
| Flexural modulus (MPa) | 3030 | 2810 | 2700 |

## *2.3 Flame Resistance in Polymeric Materials*

### 2.3.1 Modification of Polymers to Improve Flame Resistance

Organic polymers are one of the most versatile and widely utilized class of materials used today, and are used in many applications ranging from adhesives, aircraft interiors, and electronic components (134). However, except for a limited number of so-called inherently flame resistant polymers, such as polytetrafluoroethylene (Teflon), polyvinyl chloride, etc., thermoplastics are not generally flame resistant. However, the flame resistance of polymers has been improved using two different techniques: (1) by physically blending flame retardant additives such as $Sb_2O_3$ in combination with brominated aromatics (135-139) or various phosphates with the polymer, and (2) by incorporating flame retardant structures into a polymeric backbone (140-145). Flame retardant additives used in synthetic polymers include organic halogen and organic phosphorus compounds (146). A flame retardant additive interferes with one or more of the steps of the combustion cycle, including heating of the polymeric material, its subsequent degradation, and the further combustion of volatiles that may be generated (136-137, 142, 147-148).

While a flame retardant additive may function at one or more of these three steps, it is preferred that the additive function at more than one step. For example, it may inhibit combustion at Step 1 by forming a glass-like coating, which should preferably have low thermal conductivity on the surface of the material upon exposure to heat. The additive may also degrade endothermically, thereby absorbing energy from the polymer (135-137, 142-145). During the ignition stage, these flame retardant additives may also deactivate highly reactive radical propagating species that result from chain scission during the combustion process (149), as is illustrated below in Figure 2.3.1.1 (148). The flame retardant additives may function in a similar manner as in the second stage by reacting with radicals during the combustion of volatile to quench the propagating nature of the fire.

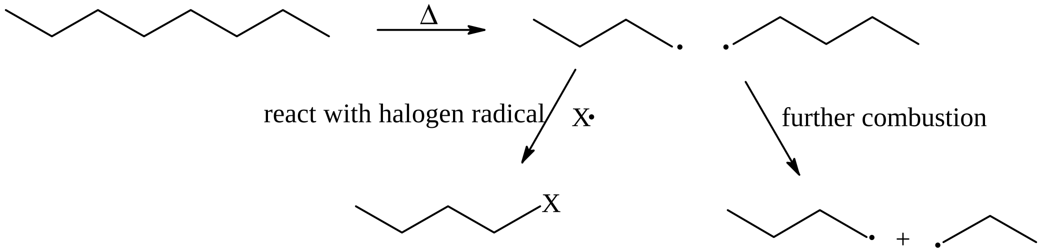


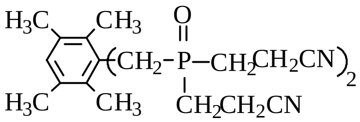
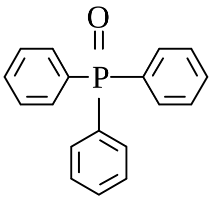
Figure 2.3.1.1 Illustration of how halogens can interrupt the combustion cycle

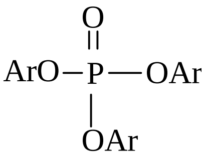
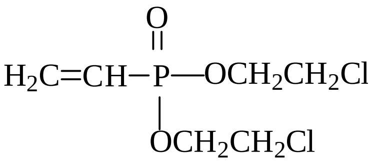
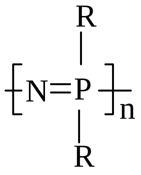
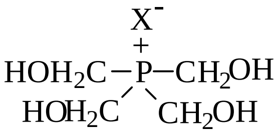
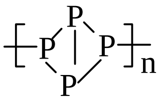
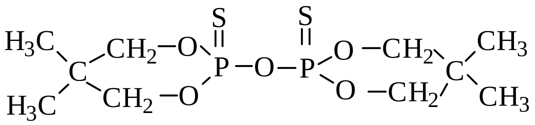
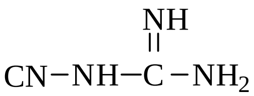
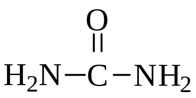
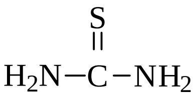
The effectiveness of the halogen depends on many factors, including the halogen used, the polymeric structure and the concentration of halogen. The effectiveness of the halogen follows the order Br>Cl>F, and generally large amounts of halogen (between 15-30 wt. %) are required (136, 150). Moreover, those halogens bonded to aliphatic carbons are better flame retardants than aromatic halogens (136). This is probably due to that fact that aliphatic halogens degrade at a lower temperature via a radical mechanism than aromatic halogens. However, there are problems associated with physically blended flame retardant additives. These drawbacks include compatibility issues, problem of the additive leaching out over time, and the fact that the decomposition temperature of the fire retardant needs to be appropriate for a specific polymeric material. Clough (150) studied the aging effects of ethylene-propylene rubber (EPR) containing various amounts of halogen-hydrocarbon additives combined with $Sb_2O_3$ and discovered a significant loss of both the halogen additive and the $Sb_2O_3$ due to aging.

In order to avoid the problem of aging, one may add halogens bonded to the backbone of the thermoplastic. This is particularly true for polyolefins (151) and epoxies (142, 152). This incorporation has resulted in an increased char yield and a higher limiting oxygen index, which is one of the often used measurement methodologies (142). Commercially, tetrabromobisphenol-A or its diglycidylether are often used to cure epoxies for use in printed circuit boards and other applications where fire resistance is needed (152).

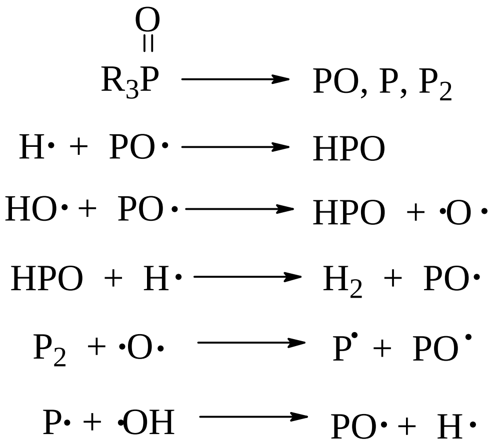
The disadvantage of halogen based flame retardants is the fact that toxic gases of the form HX are emitted upon combustion. Phosphorus or nitrogen containing additives, as well as others, are being investigated as a possible way to overcome this problem (139, 141, 135-137, 147). A survey of phosphorus and nitrogen containing flame retardant additives is listed in Table 2.3.1.1.

Table 2.3.1.1 Examples of Phosphorus and Nitrogen Containing
Flame Retardant Additives

| **Class of Additive** | **Structure** | **Reference** |
|---|---|---|
| Phosphine Oxide |  | 143, 153 |
| Triphenylphosphine oxide |  | 135 |

| | | |
|---|---|---|
| Triarylphosphates |  $\mathrm{ArO}-\underset{\underset{\mathrm{OAr}}{\vert}}{\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{P}}}-\mathrm{OAr}$ | 135 |
| Vinylphosphonates |  $H_2C{=}CH-\underset{\underset{\mathrm{OCH_2CH_2Cl}}{\vert}}{\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{P}}}-OCH_2CH_2Cl$ | 135 |
| Polyphosphazenes |  $\left[N{=}\underset{\underset{\mathrm{R}}{\vert}}{\overset{\overset{\mathrm{R}}{\vert}}{\mathrm{P}}}\right]_n$ | 135 |
| Phosphonium Salts |  | 135 |
| Red Phosphorus |  | 147 |
| Phosphine Sulfide |  | 154 |
| Cyanamide | $H_2N-CN$ | 135 |
| Dicyanamide |  $CN-NH-\overset{\overset{\mathrm{NH}}{\Vert}}{C}-NH_2$ | 135 |
| Urea |  $H_2N-\overset{\overset{\mathrm{O}}{\Vert}}{C}-NH_2$ | 135 |
| Thiourea |  $H_2N-\overset{\overset{\mathrm{S}}{\Vert}}{C}-NH_2$ | 135 |
| Ammonium Salt | $NH_4SCN$ | 135 |

Phosphorus containing flame retardants can be either gas phase or condensed phase active. For example, trimethylphosphate, triphenylphosphate, triphenylphosphine oxide, as well as the halogens previously discussed, exhibit vapor phase inhibition. A proposed mechanism for the vapor phase inhibition of phosphine oxide flame retardant additives is provided in Figure 2.3.1.2 (155). This mechanism produces two radical scavengers; a hydrogen radical and an oxygen radical. These radicals can combine with radicals produced during chain scission and inhibit the propagation of the flame front. A similar idea is shown in Figure 2.3.1.1.



$$R_3\overset{\overset{\displaystyle O}{\|}}{P} \longrightarrow PO,\ P,\ P_2$$
$$H\cdot + PO\cdot \longrightarrow HPO$$
$$HO\cdot + PO\cdot \longrightarrow HPO + \cdot O\cdot$$
$$HPO + H\cdot \longrightarrow H_2 + PO\cdot$$
$$P_2 + \cdot O\cdot \longrightarrow P^{\bullet} + PO^{\bullet}$$
$$P\cdot + \cdot OH \longrightarrow PO\cdot + H\cdot$$

Figure 2.3.1.2 Illustration of the vapor phase inhibition mechanism of phosphorus containing flame retardants

Inagaki et al. (156) have shown that there is a linear correlation between the weight percent phosphorus and the limiting oxygen index (LOI) for cotton samples treated with phosphorus containing flame retardants. The LOI is an empirical technique developed to estimate the amount of oxygen in an oxygen/nitrogen atmosphere that is required to sustain a flame. Thus, the higher the LOI value, the more flame resistant the material is. (151). In general, these studies show that as the amount of phosphorus is increased, the LOI increased linearly within the range tested.

Phosphorus containing fire retardants may also behave as condensed phase inhibitors (142, 155). Condensed phase inhibition involves changes in the polymer substrate to promote crosslinking and the formation of a char, serving two purposes. Firstly, it behaves as an insulating layer protecting the underlying polymer from the heat and flame. Secondly, it can act as a barrier preventing oxygen from reaching the uncombusted polymer, therefore inhibiting further combustion. Figure 2.3.1.3 below illustrates how phosphorus can behave as a condensed phase flame retardant (155). Organophosphorus compounds containing P-O-C bonds can thermally or hydrolytically degrade to phosphorus acids. These acids then react with cellulose to form a phosphorus ester. The phosphorus acid can also catalyze dehydration of an organic species, leading to increased unsaturation and increased char formation. When a phosphorus aryl compound is incorporated into the backbone of a polymer, the phosphorus forms a char consisting of a phosphorus anhydride type structure, which inhibits combustion via a condensed phase mechanism (143). The condensed mechanism is preferred because it offers the advantages of a material with lower flammability without the release of toxic gases, such as HX, and does not require as large a loading as is needed for the vapor phase mechanism. Table 2.3.1.2 shows a variety of polymers that have phosphorus incorporated within their backbones.

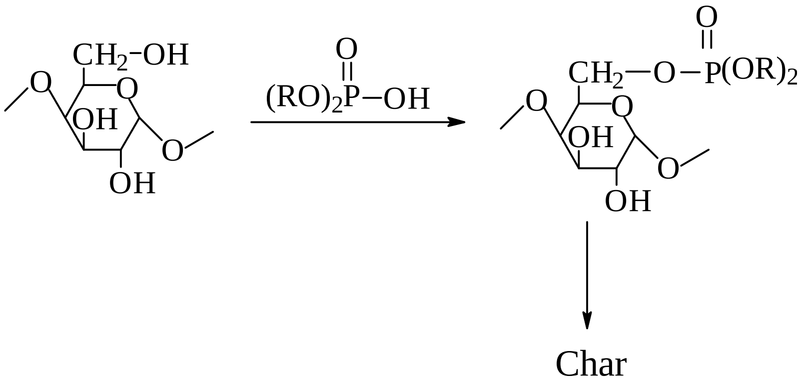
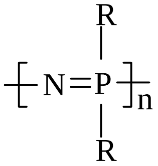
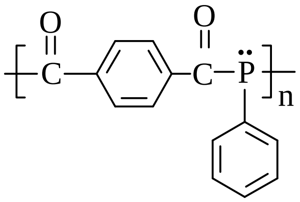
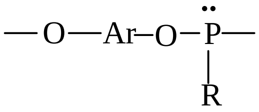
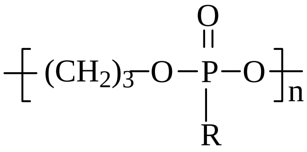
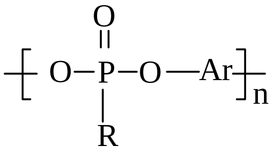
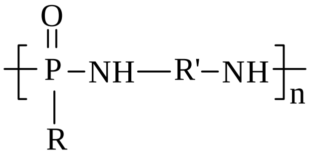
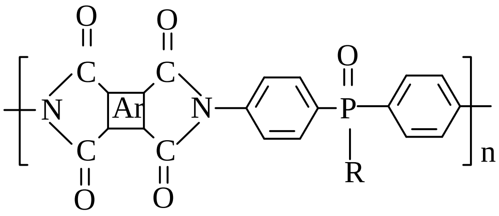
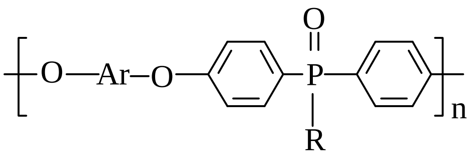
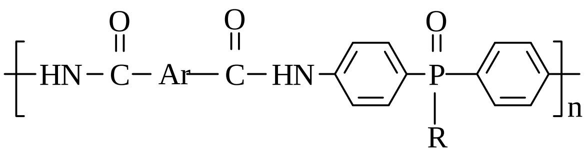
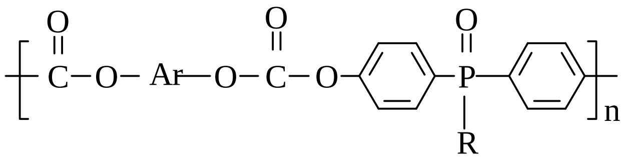
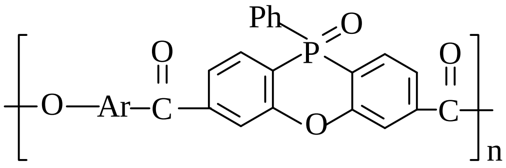


Figure 2.3.1.3 Illustration of how a phosphorus flame retardant may induce char

Table 2.3.1.2 Illustration of the Variety of Polymers Containing Phosphorus

| Polymer Class | Polymer Structure | Reference |
|---|---|---|
| Polyphosphazines |  $\left[ N = P(R)_2 \right]_n$ | 157-162 |

| | | |
|---|---|---|
| Polyphosphine |  | 163 |
| Polyphosphonite |  | 164-166 |
| Polyphosphonate |  | 164 |
| Polyphosphonate |  | 167-169 |
| Phosphorus Amide |  | 170-174 |
| Polyimide |  | 175-176 |
| Poly(arylene ether) |  | 139, 141, |
| Polyamide |  | 177 |

| | | |
|---|---|---|
| Polycarbonate |  | 178 |
| Polyester |  | 179 |

Another area of interest is the actual mechanism of char formation and how to induce high char yields in polymers to enhance flame resistance (139). Figure 2.3.1.4 illustrates a proposed mechanism for char formation (180), wherein a polymer is thermally decomposed *via* chain scission. After this initial decomposition step, the polymer may either undergo further decomposition or react with another polymer chain to form a crosslinked network. If the polymer undergoes further decomposition, it may form small molecular weight volatile by-products that do not form char and, in fact, may actually feed the combustion process. However, if after initial decomposition the polymer radical reacts with another polymer chain, the polymer may form a crosslinked char. This mechanism would help explain why the char of many highly aromatic polymers contain graphitic structures on the surface.

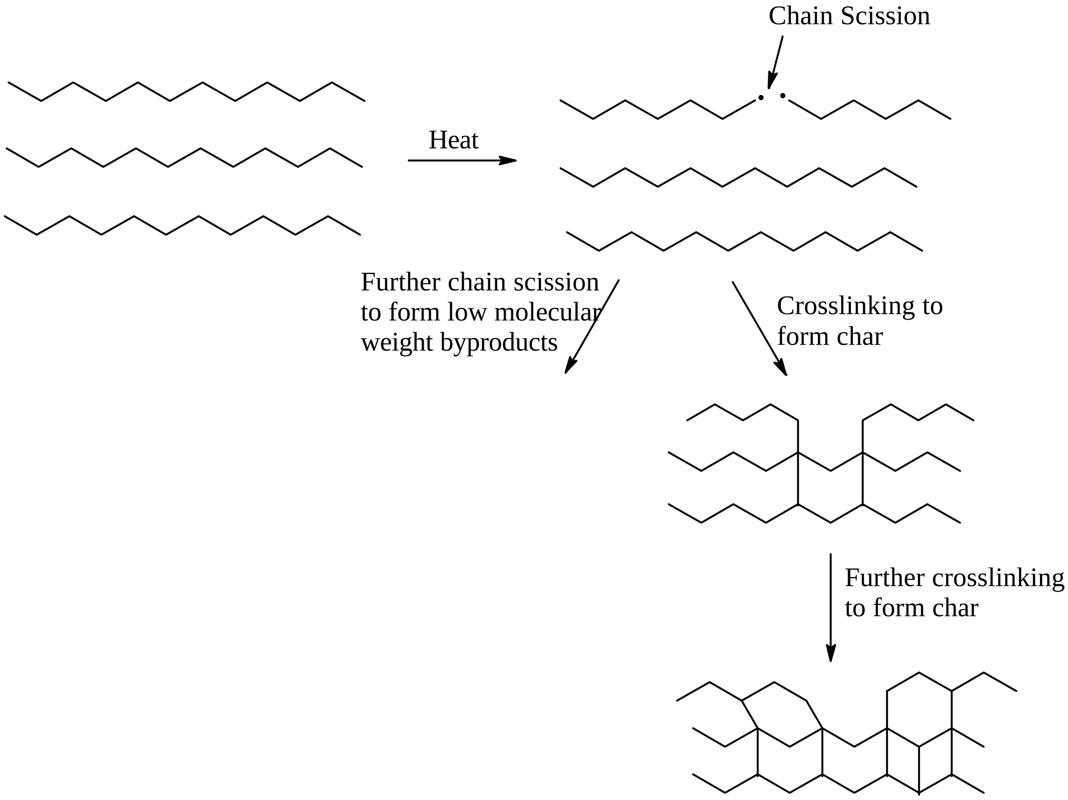
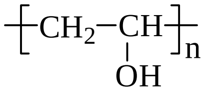
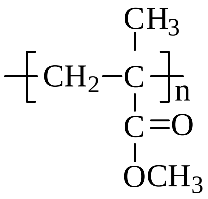
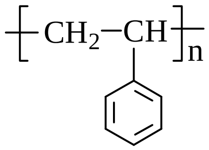
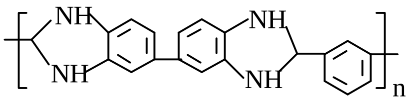
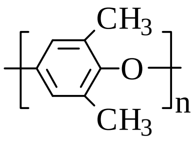
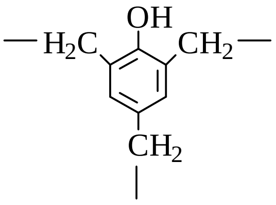


Figure 2.3.1.4  Possible mechanism for char formation

These char forming condensed phase reactions are important in fire resistant polymers, such as poly 2,6-dimethyl-1,4-phenylene oxide (PPO) and phenolic resins. Fenimore and Martin (181) illustrated that the high limiting oxygen index of PPO was due to its ability to form char residue upon heating.  Table 2.3.1.3 illustrates the effect of aromatic rings upon char formation in non-halogenated polymers (137).  It is evident from this data that as the char yield increases, so does the LOI.

Table 2.3.1.3 Effect of Aromatic Rings upon the Char Yield

| Polymer | Structure | Oxygen Index | Char Yield |
|---|---|---|---|
| Poly(vinyl alcohol) |  $\left[ CH_2-CH(OH) \right]_n$ | 22 | 0 |
| Poly(methyl methacrylate) |  $\left[ CH_2-C(CH_3)(C{=}O)(OCH_3) \right]_n$ | 17 | 0 |
| Polystyrene |  | 18 | 0 |
| Poly(benzimidazole) |  | — | 58 |
| Poly(phenylene oxide) |  | 28 | 40 |
| Phenolic Resin |  | 35 | 60 |

## 2.3.2 Methods for Testing Flammability

The combustion of polymeric materials is a complex process that includes environment, ignition, flame growth, fire retardants, and “burn out” to name a few. A single flammability test, therefore, is only a partial indicator of how the material may behave in a “real” fire. Many tests have been developed to characterize each aspect of a material’s combustion behavior. The areas of combustion behavior of interest to researchers include: ease of ignition, flame spread, ease of extinction, smoke obscuration, smoke toxicity and heat release rate (142, 180, 182).

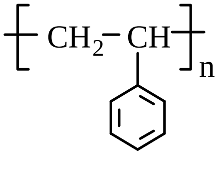
Ease of ignition may be measured by subjecting a specimen to an ignition source for a specified amount of time (142, 180). The ignition source may be at a specific temperature or heat flux and if the material ignites it fails the test. The angle at which the sample is exposed to the ignition source and the heat flux of the source are the two main variables in this test. For materials that have low melting or softening points, the surface melt may flow away from the ignition source (180). If the softening temperature is below the ignition temperature, the material may simply flow away from the ignition source and avoid ignition. Significant differences in horizontal *vs.* vertical tests have been observed. If a material can withstand exposure to a heat source without ignition the fire will not occur and combustion is prevented; thus ease of ignition is extremely important. However, this resistance to ignition generally coincides with an increased emission of smoke and toxic gases such as carbon monoxide (180). This is to be expected since most flame retardants work by inhibiting the combustion process, resulting in partially burned or combusted products.

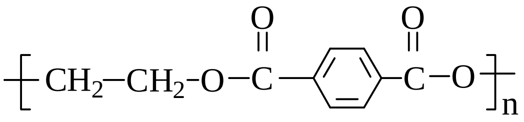
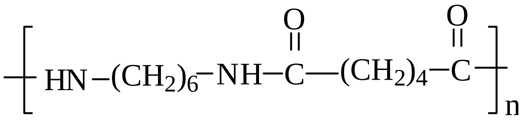
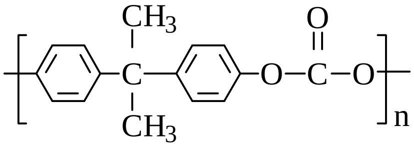
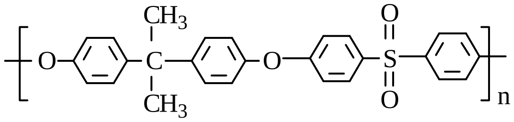
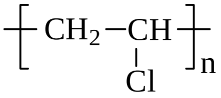
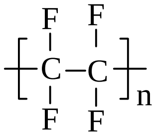
The characteristics of the flame after ignition are also important, including how fast the flame spreads. This is especially critical in materials that may be used in aircraft interiors (142, 180). In general, if a material ignites easily, then its flame will spread rapidly. This is easy to understand if one views the propagating flame front as an advancing ignition, and there are many types of analyses to characterize how a flame spreads. They consist of igniting a specimen with a specific orientation to the product exhaust (i.e. product exhaust carried into specimen flames) and analyzing visually how the flame spreads over the surface of the test specimen. Flame spread depends upon ignition temperature, orientation, thermal properties of the polymer, and flame heat flux (180). The orientation of the sample is an extremely important variable in a flame spreading experiment. For example, a flame will spread up to an order of magnitude faster up a vertically oriented sample ignited at the bottom than it will when same sample is ignited at the top. This is because the heat is transferred more efficiently ahead of the burning zone if the flame propagation occurs in an upwards direction (180).

The heat release rate, regarded by many as the most important variable in fire resistance, is another factor characterizing the flammability of polymeric materials. Beause most deaths in a fire occur due to inhalation of toxic gases, the heat release rate is a critical predictor of fire hazard (182). Heat release rate is usually analyzed utilizing cone calorimetry. The cone calorimeter applies a specific heat to a sample and measures the ignitability, heat release rate, and toxic gases emitted (182). The ignitability is measured by determining how long a sample can withstand exposure to a specific heat flux before ignition occurs. After ignition, the heat release rate is measured as a function of time using an oxygen compensation method. The oxygen compensation method involves calculating the heat release rate from the amount of oxygen consumed by the polymer during combustion (182). Using this method, it is also possible to monitor the heat release behavior throughout the combustion cycle, from ignition to burn out.

Another important issue in determining the flammability of a material is how quickly it extinguishes after ignition. This is generally analyzed by determining a materials limiting oxygen index (142). The limiting oxygen index (LOI) is the minimum percentage of oxygen in an oxygen/nitrogen environment that is required to sustain combustion (151). Thus, a material with a high LOI value is considered easier to extinguish than a material with a low LOI. One should note that a material is considered flammable if its LOI is <27 (151). The limiting oxygen indices for some commercially important polymers are listed below in Table 2.3.2.1 (151).

Table 2.3.2.1 Effect of Polymer Structure upon Its Limiting Oxygen Index

| **Polymer** | **Structure** | **Oxygen Index** |
|---|---|---|
| Polyethylene | $-\!\left[CH_2-CH_2\right]\!-_n$ | 18 |
| Polystyrene |  | 19 |

| | | |
|---|---|---|
| Poly(ethylene terephthalate) |  | 21 |
| Nylon 6,6 |  | 23 |
| Polycarbonate |  | 27 |
| Polysulfone |  | 30 |
| Poly(vinyl chloride) |  $-\!\!\left[CH_2-\underset{\underset{Cl}{\vert}}{CH}\right]_n\!\!-$ | 42 |
| Poly(tetrafluoroethylene) |  $-\!\!\left[\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}\right]_n\!\!-$ | 95 |

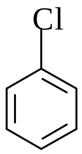
In addition to how a material behaves thermally when exposed to heat, it is also important to determine the amount of smoke that is emitted upon combustion. Obviously, in a fire it is desirable to have as little smoke as possible. Smoke can cause loss of visibility, loss of breath and panic among people trapped in a fire. The structure-property relationships between a thermoplastics and smoke are not well understood. It appears to be extremely dependent upon the conditions of combustion (180).

# Chapter 3.0 Experimental

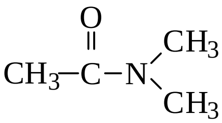
## *3.1 Materials*

### 3.1.1 Solvents

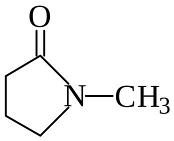
Chlorobenzene (Fisher Scientific) was dried over calcium hydride for at least 12 hours and distilled under reduced pressure. (b.p. 132°C/760mmHg)



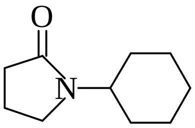
N,N-Dimethylacetamide (DMAc, Fisher Scientific) was dried over calcium hydride for at least 12 hours and distilled under reduced pressure. (b.p. 163-165°C/760mmHg)



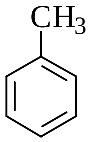
1-Methyl-2-Pyrrolidone (NMP, Fisher Scientific) was dried over phosphorus pentoxide for at least 12 hours and distilled under reduced pressure. (b.p. 205°C/760mmHg, 82°C/10mmHg)



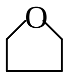
1-Cyclohexyl-2-Pyrrolidone (CHP, Fisher Scientific) was dried over calcium hydride for 24 hours and distilled under reduced pressure. (b.p. 154°C/7mmHg)



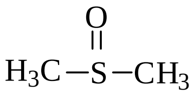
Toluene (Fisher Scientific) was used as received. (b.p. 110.6°C/760mmHg)



Tetrahydrofuran (THF, Fisher Scientific) was purified by distillation over sodium and benzophenone. (b.p. 67°C/760mmHg)

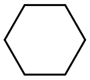


Dimethyl Sulfoxide (DMSO, Fisher Scientific) was used as received. (b.p. 190°C/760mmHg)



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

Cyclohexane (Fisher Scientific) was used as received. (b.p. 80°C/760mmHg)



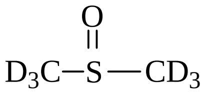
Chloroform (Fisher Scientific) was received as a HPLC grade solvent and used without purification. (b.p. 61-62°C/760mmHg)

Diethyl Ether (Mallinckrodt) was used as received. (b.p. 34.6°C/760mmHg)

Methanol (Fisher Scientific) was received as HPLC grade solvent and used without purification. (b.p. 64.7°C/760mmHg)

Deuterated Chloroform ($CDCl_3$, Cambridge Isotope Laboratories) was used as received. (b.p. 61°C/760mmHg)

Deuterated Dimethyl Sulfoxide (DMSO-$d_6$, Cambridge Isotope Laboratories) was used as received. (b.p. 55°C/5mmHg)



$$D_3C-\overset{O}{\overset{\|}{S}}-CD_3$$

## 3.1.2 Commercially Available Monomers

4,4′-Dichlorodiphenyl Sulfone (DCDPS)

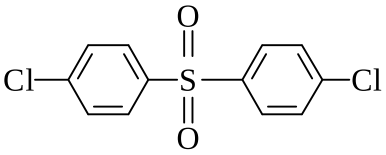
Supplier: Amoco Chemical Company

Empirical Formula: $C_{12}H_8C_{l2}O_2S$

Molecular Weight: 287.16

Melting Point: 147°C

Structure:



Purification: DCDPS is a monomer grade material and used as received.

4,4′-Difluorobenzophenone (DFBP)

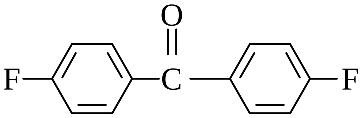
Supplier: Aldrich Chemical Company

Empirical Formula: $C_{13}H_8\,F_2O$

Molecular Weight: 218.20

Melting Point: 105°C

Structure:



Purification: DFBP is a monomer grade material and used as received.

4,4′-Dichlorobenzophenone (DCBP)

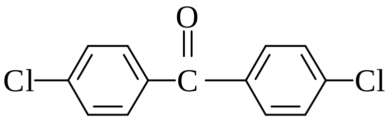
Supplier: Aldrich Chemical Company

Empirical Formula: $C_{13}H_8Cl_2O$

Molecular Weight: 251.11

Melting Point: 144-146°C

Structure:



Purification: DCBP is a monomer grade material and used as received.

4-tert-Butylphenol (TBP)

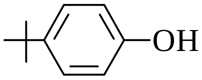
Supplier: Aldrich Chemical Company

Empirical Formula: $C_{10}H_{14}O$

Molecular Weight: 150.22

Melting Point: 98-101°C

Structure:



Purification: TBP is a monomer grade material and used as received.

## 3.1.3 Monomer Synthesis

### 3.1.3.1 Reagents Used

Benzenesulfonyl Chloride

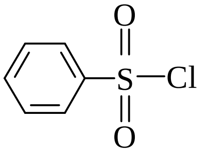
Supplier: Aldrich, 99%

Empirical Formula: $C_6H_5ClO_2S$

Molecular Weight: 176.62

Boiling Point: 251-252°C

Structure:



Purification: used as received.

1-Bromo-4-Fluorobenzene

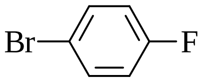
Supplier: Aldrich, 99%

Empirical Formula: $C_6H_4FBr$

Molecular Weight: 175.01

Melting Point: 150°C

Structure:



Purification: used as received.

Sodium Hydroxide

Supplier: Mallinckrodt, Pellets, AR, 99.4%,

Empirical Formula: NaOH

Molecular Weight: 40.00

Purification: used as received.

Phenylphosphonic Dichloride

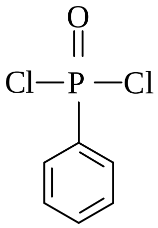
Supplier: Aldrich, 97%

Empirical Formula: $C_6H_5Cl_2OP$

Molecular Weight: 194.99

Boiling Point: 258°C

Structure:



Purification: used as received.

Magnesium Turnings

Supplier: Aldrich, 99%

Empirical Formula: Mg

Purification: used as received.

Sulfuric Acid

Supplier: Mallinckrodt, AR, 96.2%, d=1.84,

Empirical Formula: $H_2SO_4$

Molecular Weight: 98.07

Purification: used as received.

### Sodium Hydrosulfide

Supplier: Aldrich, 70.6%

Empirical Formula: $NaSH$

Molecular Weight: 56.06

Purification: used as received.

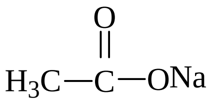
### Sodium Acetate

Supplier: Aldrich, 99%

Empirical Formula: $NaC_2H_3O_2$

Molecular Weight: 82.03

Structure:



$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-ONa$

Purification: used as received.

### Anhydrous Potassium Carbonate

Supplier: Aldrich, 99.9%

Empirical Formula: $K_2CO_3$

Molecular Weight: 138.21

Purification: used as received.

### Anhydrous Aluminum Chloride

Supplier: Aldrich, 99.99%

Empirical Formula: $AlCl_3$

Molecular Weight: 133.34

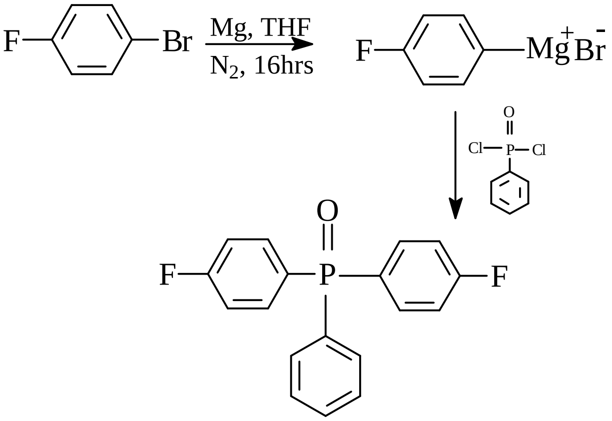
Purification: used as received.

Hydrochloric Acid
Supplier: Aldrich, 36.5-38.0%
Empirical Formula: HCl
Molecular Weight: 36.46
Purification: used as received.

Anhydrous Magnesium Sulfate
Supplier: Aldrich, 99.99%
Empirical Formula: $MgSO_4$
Molecular Weight: 120.37
Purification: used as received.

#### 3.1.3.2 Synthesis of Bis-(4-fluorophenyl)phenyl Phosphine Oxide (BFPPO)

BFPPO was synthesized by reacting 2.1 equivalents of 1-bromo-4-fluorobenzene with 1 equivalent of phenylphosphonic dichloride via Grignard chemistry (141). For example, 12.1g (0.5 moles) of magnesium turnings (Aldrich 99%) and 450 mL of freshly distilled THF (Aldrich 99+%) were added to a 1000 mL 3-neck flask equipped with a mechanical stirrer, addition funnel, nitrogen inlet, and condenser. To the solution 86.6g (0.49 moles) of 1-bromo-4-fluorobenzene (Aldrich 99%) was added dropwise at room temperature over a period of 1-2 hours. The mixture was stirred at room temperature overnight. Next, 48.2g (0.24 moles) of phenylphosphonic dichloride (Aldrich 97%) was added dropwise at room temperature. The reaction was stirred overnight to give a yellow solution. Aqueous sulfuric acid (10 vol.%) was added until the solution was acidic. Water (180 mL) and diethyl ether (25 mL) was added to the reaction mixture and the THF layer was decanted. The water layer was washed well with diethyl ether and all organic layers were combined. The organic layer was then dried over anhydrous magnesium sulfate, filtered, and the filtrate evaporated to afford a light yellow solid. The material was purified by distillation utilizing a Kugelrohr apparatus and subsequent recrystallization from a 1 : 6 THF/cyclohexane mixture. The resulting material was monomer grade with a melting point of 130-131°C (lit. 124-126°C) (141). The yield of the reaction was 80-85% after purification. Elemental analysis for $C_{18}H_{13}F_2OP$: C, 68.8%; H, 4.2%. Found: C, 68.6%; H, 4.0%.



Scheme 3.1.1 Synthesis of bis-(4-fluorophenyl)phenyl phosphine oxide (BFPPO)

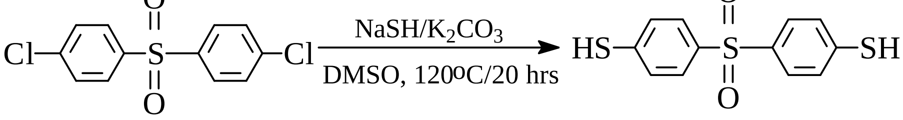
### 3.1.3.3 Synthesis of 4-Chlorophenylphenyl Sulfone (CPPS)

CPPS was synthesized via an aromatic electrophilic substitution reaction of benzenesulfonyl chloride with chlorobenzene in the presence of $ACl_3$ as the catalyst (177, 183). For example, 15g (0.0849 moles) of benzenesulfonyl chloride (Aldrich 99%) and chlorobenzene (Fisher, HPLC grade) were charged into a 3-neck flask equipped with a nitrogen inlet, a condenser and a mechanical stirrer. 6g (0.045 moles) of anhydrous $AlCl_3$ (Aldrich, 99.99%) was added to the mixture in two aliquots and refluxed for 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 recrystallized from toluene. The overall yield of the expected product, 4-chlorophenylphenyl sulfone (CPPS), was 76% and the melting point was 106°C - 107°C (lit. 93.5-94.5°C) (183). Elemental analysis for $C_{12}H_9ClO_2S$: C, 57.03%; H, 3.56%; S, 12.67%. Found: C, 57.17%; H, 3.60%; S, 12.78%.

Scheme 3.1.2 Synthesis of 4-chlorophenylphenyl sulfone (CPPS)

### 3.1.3.4 Synthesis of Bis-(4-mercaptophenyl) Sulfone (BMPS)

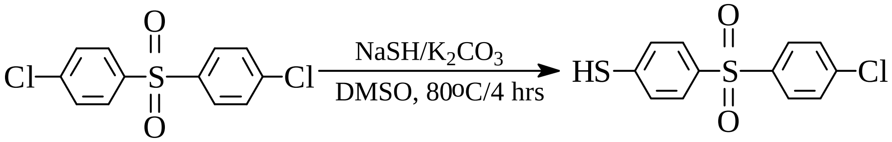
The A-A type dithiol monomer, BMPS, was synthesized by reacting 4,4′-dichlorodiphenyl sulfone (DCDPS) with a large excess of sodium hydrosulfide via an aromatic nucleophilic substitution reaction. For example, 43.1g (0.150 moles) of DCDPS (Amoco, monomer grade) and 100 mL of methyl sulfoxide (DMSO) (Fisher, 99.9%) were charged into a 500 mL 3-neck round-bottom flask fitted with an overhead mechanical stirrer, condenser, and nitrogen inlet. The mixture was stirred at 60°C for about 2 hours. After the DCDPS was completely dissolved in the DMSO, 35.7 g (0.450 moles) of sodium hydrosulfide (Aldrich, 70.6%) and 31.1 g (0.225 moles) of anhydrous potassium carbonate (Aldrich, 99.9%) were added into the flask, and the resulting mixture was allowed to stir at 120°C for 20 hours under an atmosphere of nitrogen. The dark brown reaction mixture was cooled, added to ice water, filtered, and slowly acidified with concentrated hydrochloric acid to a pH~3. An off-white precipitate was formed immediately upon acidification. The crude product was dissolved in 600 mL of 5% $K_2CO_3$ aqueous solution and precipitated by adding concentrated HCl. The white granular product was collected, washed well with deionized water, and vacuum dried at 80°C for 24 hours. The overall yield of the expected product, bis-(4-mercaptophenyl) sulfone (BMPS), was about 66% and the melting point was 144-145°C (lit. 138-140°C) (184). Elemental analysis for $C_{12}H_{10}O_2S_3$: C, 51.03%; H, 3.56%; S, 34.06%. Found: C, 50.96%; H, 3.49%, S, 34.56%.



Scheme 3.1.3 Synthesis of bis-(4-mercaptophenyl) sulfone (BMPS)

### 3.1.3.5 Synthesis of 4-Chloro-4′-Mercaptodiphenyl Sulfone (CMDPS)

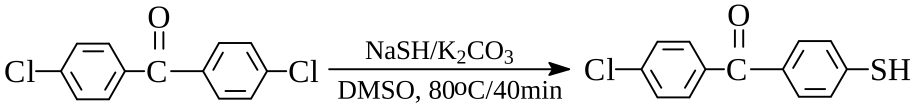
CMDPS was prepared by reacting 1.2 moles of 4,4′-dichlorodiphenyl sulfone (DCPS) with 1.0 mole of sodium hydrosulfide via an aromatic nucleophilic substitution reaction. For example, 57.5g (0.20 moles) of DCDPS (Amoco, monomer grade) and 100 mL of DMSO (Fisher, 99.9%) were added to a 500 mL 3-neck flask equipped with a mechanical stirrer, nitrogen inlet, and a condenser. After the DCDPS was completely dissolved in the DMSO at 60°C, 14.3g (0.18 moles) of sodium hydrosulfide (Aldrich, 70.6%) and 12.4g (0.09 moles) of anhydrous potassium carbonate (Aldrich, 99.9%) were added to the solution. The solution was then raised to 80°C and allowed to react for 4 hours under nitrogen. The solution was cooled, added to ice water, filtered, and slowly acidified with concentrated hydrochloric acid to a pH~3. An off-white precipitate was formed immediately upon acidification. The crude product was dissolved in 600 mL of 5% $K_2CO_3$ aqueous solution and precipitated by adding concentrated HCl. The white granular product was collected, washed well with deionized water, and vacuum dried at 70°C for 24 hours. The overall yield of the expected product, 4-chloro-4′-mercaptodiphenyl sulfone (CMDPS), was about 56% and the melting point was 139-140°C (lit. 136-137°C) (185). Elemental analysis for $C_{12}H_9ClO_2S_2$: C, 50.60%; H, 3.19%; S, 22.52%. Found: C, 50.56%; H, 3.19%, S, 22.84%.



Scheme 3.1.4 Synthesis of 4-chloro-4′-mercaptodiphenyl sulfone (CMDPS)

### 3.1.3.6 Synthesis of 4-Chloro-4′-Mercapto Benzophenone (CMBP)

CMBP was prepared by the similar method as described for the CMDPS preparation. 4,4′-dichlorobenzophenone (DCBP) (Aldrich, 99.0%) (50.2g, 0.20 moles) and DMSO (Fisher, 99.9%) (100 mL) were heated to 60°C for 2 hours. Then, sodium hydrosulfide ( Aldrich, 70.6%) (14.3g, 0.18 moles) and potassium carbonate (Aldrich, 99.9%) (12.4g, 0.09 moles) were added into this clear solution, and the temperature was maintained at 60°C for one hour. At the end of the reaction, the reaction solution was treated by the same method as discussed previously. The overall yield of the CMBP was 48% and the melting point was 158-159°C. Elemental analysis for $C_{13}H_9ClOS$: C, 62.77%; H, 3.62%; S, 12.89%. Found: C, 62.48%; H, 3.45%, S, 13.19%.



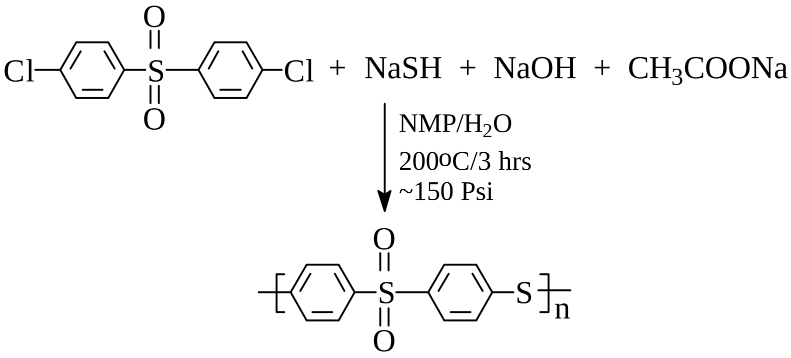
Scheme 3.1.5 Synthesis of 4-chloro-4′-mercapto benzophenone (CMBP)

# *3.2 Polymer Synthesis*

## 3.2.1 Poly(Phenylene Sulfide Sulfone) (PPSS)

### 3.2.1.1 High Pressure Method

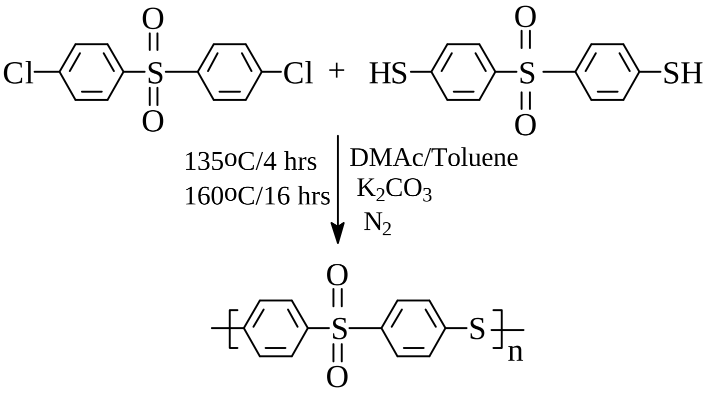
High molecular weight PPSS was synthesized by the aromatic nucleophilic substitution reaction of 4,4′-dichlorodiphenyl sulfone (DCDPS) with sodium hydrosulfide at elevated reaction temperature and pressure (122-124). Polymerization reactions were conducted in a 250 mL stainless steel pressure reactor equipped with a reflux condenser, mechanical stirrer, and temperature and pressure indicator. A typical example is given below. To the pressure reactor were added 7.0081g (0.08830 moles) of sodium hydrosulfide (Aldrich, 70.6%), 25.6092g ( 0.08918 moles) of DCDPS (Amoco, monomer grade), 7.2435g ( 0.08830 moles) of sodium acetate (Aldrich, 99.0%), 3.5318g (0.008830 moles) of sodium hydroxide (Mallinckrodt, 99.4%), 70 mL of NMP (Fisher, 99.0%), and 12.9 mL ( 0.717 moles) of deionized water. The pressure reactor was closed, flushed with argon gas and heated to 200°C with stirring over a 30-min period. The temperature was maintained at 200°C for 3 hours. After the reactor was cooled and opened, the solid product was dissolved in 200 mL of NMP at 150°C, and precipitated into an 75:25 (by volume) water/methanol mixture using a Waring blender. The fibrous polymer was filtered, washed well with hot water, and dried in a vacuum oven at 170°C for 20 hours, redissolved in NMP (20% solid), precipitated into methanol and again dried under the same conditions.



Scheme 3.2.1 Synthesis of PPSS by high pressure reaction

### 3.2.1.2 New Simplified Method Using an A-A Type Dithiol Monomer

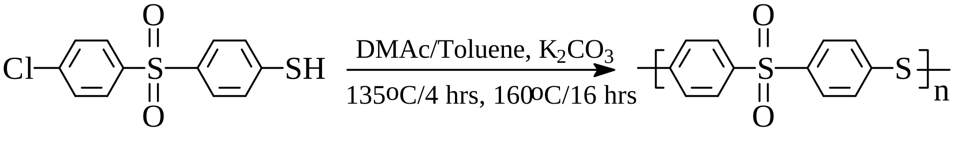
PPSS was synthesized via a new simplified nucleophilic substitution step (condensation) polymerization by using a new A-A type dithiol monomer. A typical example is given below. To a 100 mL 3-neck flask equipped with a nitrogen inlet, thermometer, Dean-Stark trap and condenser were added equal molar amounts (8.0 mmoles) of bis-(4-mercaptophenyl) sulfone (BMPS) and 4,4′-dichlorodiphenyl sulfone (DCDPS) (Amoco, monomer grade) followed by potassium carbonate (Aldrich, 99.9%) (8.7 mmoles). Freshly distilled DMAc (Fisher, 99.0%) was introduced to afford a concentration of 15% solids. Toluene (Fisher, 99.4%) (20 mL) was added as an azeotroping agent and the reaction temperature was raised to 135-140°C to give a reflux. After four hours, the solution temperature was raised to 160°C by removing the toluene and the reaction was maintained at that temperature for 16 hours. The reaction mixture was cooled, diluted with DMAc (15-20 mL), and several drops of a weak acid (e. g., acetic acid) were added to neutralize the thiophenoxide end groups. The polymer solution was added to vigorously stirred 500 mL of a 75:25 (by volume) methanol/water mixture and filtered, redissolved in DMAc and filtered hot through a medium pore size sintered glass funnel. The clear DMAc solution was coagulated in methanol (300 mL). The white fibrous polymer was recovered by filtration and dried under vacuum at 150°C for 24 hours.



Scheme 3.2.2  Synthesis of PPSS via an A-A type dithiol monomer

### 3.2.1.3  Self-Polycondensation of an A-B monomer

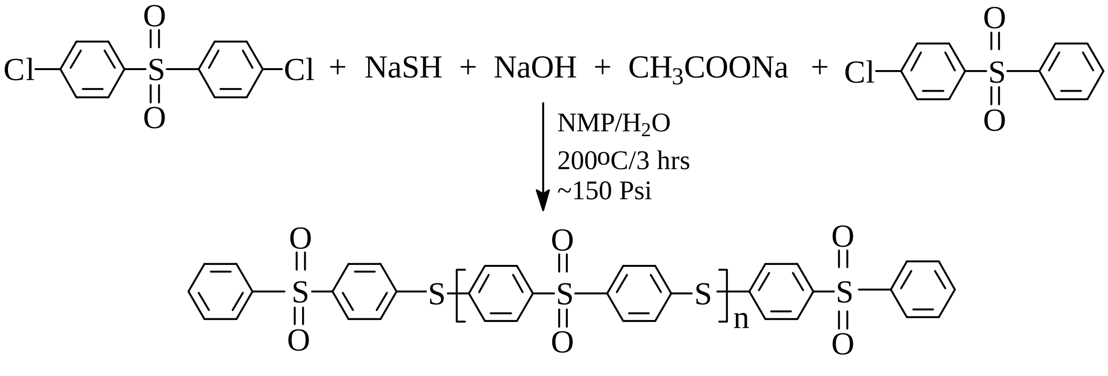
PPSS can also be synthesized by a simple self-polycondensation of an A-B monomer. For example, the A-B monomer, 4-chloro-4′-mercaptodiphenyl sulfone (CMDPS) (15.0 mmoles), and DMAc (Fisher, 99.0%) (30 mL) were charged into a 100 mL 3-neck flask fitted with a mechanical stirrer, thermometer, Dean-Stark trap and condenser. Toluene (Fisher, 99.4%) (20 mL) was added, followed by potassium carbonate (Aldrich, 99.9%) (8.6 mmoles). The reaction was initially conducted at 135-140°C for approximately 4 hours under nitrogen purge to azeotrope off the water and after removing the toluene the temperature was raised to 160°C for an additional 16 hours. The reaction flask was then cooled and 10 mL of DMAc was added to the flask and the salts were filtered off. After adding several drops of acetic acid the polymer was precipitated into a mixture of water/methanol and dried in a vacuum oven at 150°C overnight. The fibrous polymer was redissolved in DMAc, precipitated into methanol, and dried in a vacuum oven at 150°C for 24 hours.



Scheme 3.2.3  Synthesis of PPSS via an A-B monomer

### 3.2.2 Diphenyl Sulfone Endcapped Poly(Phenylene Sulfide Sulfone) (1a)

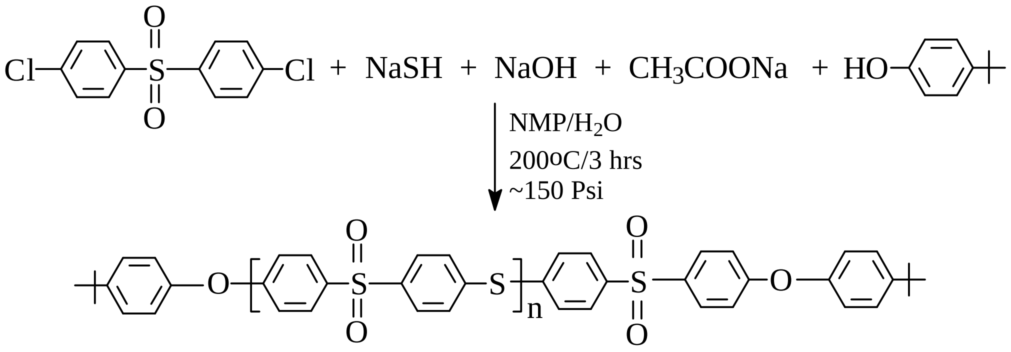
Diphenyl sulfone endcapped PPSS was synthesized by reacting 4,4′-dichlorodiphenyl sulfone (DCDPS) with 2 mol% excess of sodium hydrosulfide at elevated reaction temperature and pressure, and 4 mol% of the monofunctional compound, 4-chlorophenylphenyl sulfone (CPPS), was used as the endcapper. A typical example is given as follows. To a 250 mL autoclave equipped with a reflux condenser, mechanical stirrer, and temperature and pressure indicator were added 7.0036g (0.08824 moles) of sodium hydrosulfide (Aldrich, 70.6%), 24.8331g (0.08648 moles) of DCDPS (Amoco, monomer grade), 0.8920g (0.00352 mol) of CPPS, followed by sodium acetate (Aldrich, 99.0%) (7.2390g, 0.08824 moles), sodium hydroxide (Mallinckrodt, 99.4%) (3.5296g, 0.08824 moles), NMP (Fisher, 99.0%) (70 mL), and deionized water (12.9 mL, 0.7170 moles). The pressure reactor was closed, flushed with argon gas and heated to 200$^{o}$C with stirring over a 30-min period. The temperature was maintained at 200$^{o}$C for 3 hours. After the reactor was cooled and opened, the solid product was dissolved in 200 mL of NMP at 150$^{o}$C, and precipitated into a vigorously stirred 75:25 (by volume) water/methanol mixture, filtered, washed several times with hot water, and dried in a vacuum oven at 170$^{o}$C overnight. The fibrous polymer was redissolved in NMP and precipitated into methanol and dried in a vacuum oven at 170$^{o}$C for 24 hours. Spectroscopic analysis ($^{13}$C NMR) confirmed the endgroups as is given in section 4.2.



Scheme 3.2.4 Synthesis of diphenyl sulfone endcapped PPSS

## 3.2.3 T-Butylphenoxide Endcapped Poly(Phenylene Sulfide Sulfone) (1b)

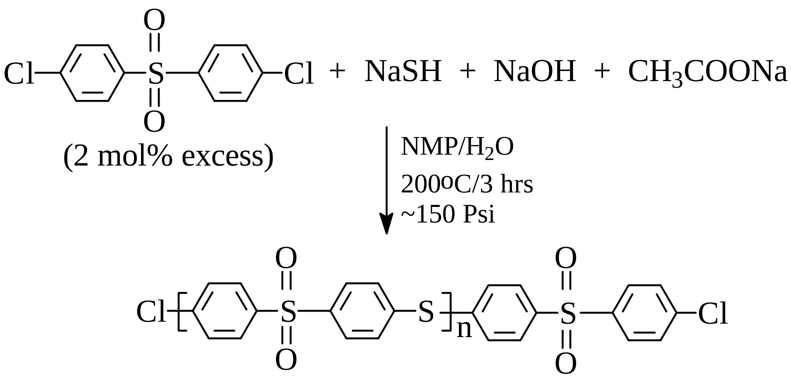
Similar conditions were used as described in the synthesis of diphenyl sulfone endcapped PPSS via a high pressure reaction. The only exception was that 2 mol% excess of 4,4′-dichlorodiphenyl sulfone (DCDPS) was used related to sodium hydrosulfide, and 4 mol% of 4-tert-butylphenol (TBP) was utilized as the endcapper. The endgroup structure was confirmed by spectroscopic analyses ($^1$H NMR and $^{13}$C NMR) that are given in Section 4.2.



Scheme 3.2.5 Synthesis of t-butylphenoxide endcapped PPSS

## 3.2.4 4-Chlorophenylphenyl Sulfone Endcapped Poly(Phenylene Sulfide Sulfone) (1c)

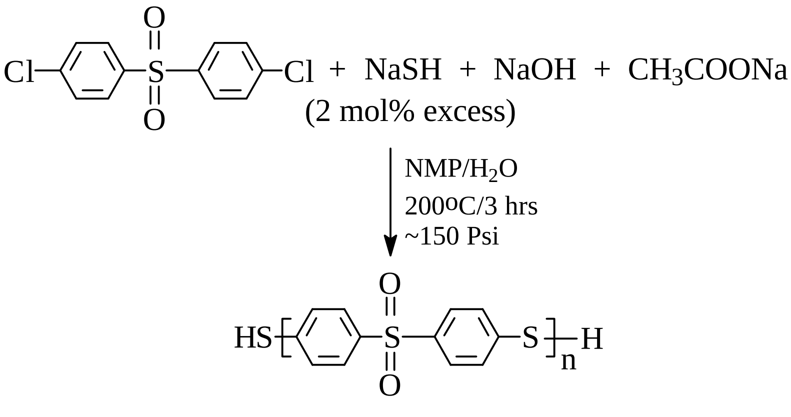
Similar conditions were used as described in the synthesis of PPSS via a high pressure reaction. The only exception was that 2 mol% excess of 4,4′-dichlorodiphenyl sulfone (DCDPS) was employed related to that of sodium hydrosulfide to control the endgroups. The $^{13}$C NMR spectroscopic analysis of the endgroups is given in Section 4.2.



Scheme 3.2.6 Synthesis of 4-chlorophenylphenyl sulfone endcapped PPSS

## 3.2.5 Thiophenol Endcapped Poly(Phenylene Sulfide Sulfone) (1d)

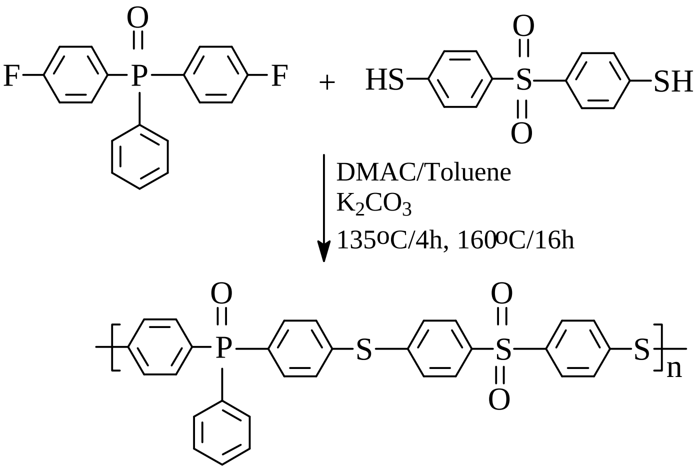
Similar conditions were used as described in the synthesis of PPSS via a high pressure reaction. The only exception was that 2 mol% excess of sodium hydrosulfide was employed related to 4,4′-dichlorodiphenyl sulfone (DCDPS) to ensure the thiophenol endcapped PPSS. The $^{13}$C NMR spectroscopy was utilized to confirm the thiophenol endgroups that is given in Section 4.2.



Scheme 3.2.7 Synthesis of thiophenol endcapped PPSS

### 3.2.6 Poly(Thioarylene Sulfone Phosphine Oxide) (2a)

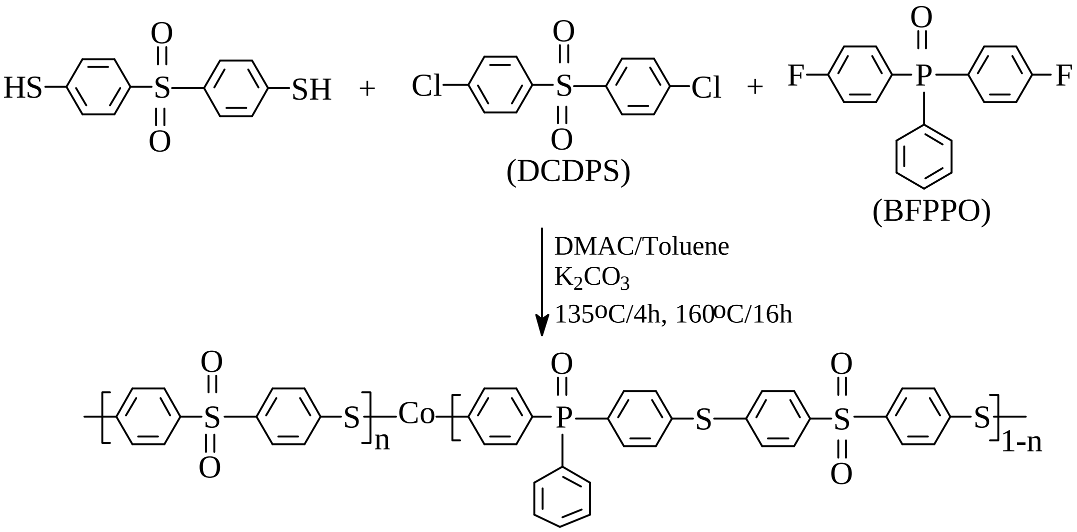
High molecular weight poly(thioarylene sulfone phosphine oxide) homopolymer based on bis-(4-fluorophenyl)phenyl phosphine oxide (BFPPO) was synthesized as follows. To a 3-neck 100 mL flask equipped with a nitrogen inlet, mechanical stirrer, Dean-Stark trap and reflux condenser were added equal molar amounts (0.012 moles) of bis-(4-mercaptophenyl) sulfone (BMPS) and BFPPO, followed by potassium carbonate (Aldrich, 99.9%) (0.0138 moles), DMAc (Aldrich, 99.0%) (30 mL), and toluene (Aldrich, 99.4) (20 mL). The reaction mixture was blanketed with dry nitrogen and quickly heated to reflux temperature (132-135°C) with a high temperature silicone oil bath and a water/toluene azeotrope formed. After four hours, toluene was gradually removed, and the reaction mixture was raised to 155-160°C and kept at that temperature for 16 hours to yield a very viscous solution. The reaction mixture was cooled and diluted with 15-20 mL of DMAc, and several drops of acetic acid were added to neutralize the thiophenoxide end groups. The polymer solution was then added to vigorously stirred 500 mL of a 75:25 (by volume) methanol/water mixture, filtered, redissolved in DMAc, and filtered through a medium pore size sintered glass funnel. The clear solution was coagulated in methanol. The fibrous polymer was recovered by filtration and dried under vacuum at 150°C for 20 hours. Spectroscopic analyses ($^{1}$H NMR and $^{31}$P NMR) confirmed the structure as are given in Section 4.3.



Scheme 3.2.8 Synthesis of poly(thioarylene sulfone phosphine oxide) homopolymer

### 3.2.7 Poly(Thioarylene Sulfone/Phosphine Oxide) Copolymers (2b-2d)

High molecular weight random copoly(thioarylene sulfone/phosphine oxide)s with various aryl phosphine oxide compositions were prepared by a method similar to that described for the poly(thioarylene sulfone phosphine oxide) homopolymer. The only exception was that both bis-(4-fluorophenyl)phenyl phosphine oxide (BFPPO) and 4,4′-dichlorodiphenyl sulfone (DCDPS) were used as the activated dihalides.

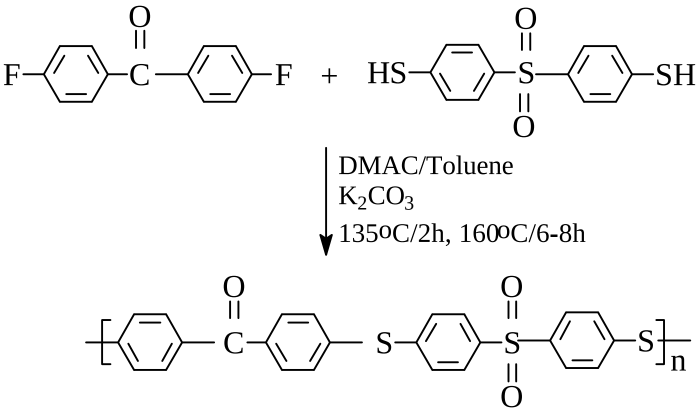


| Polymers | **2b** | **2c** | **2d** |
|---|---|---|---|
| DCDPS/BFPPO | 75/25 | 50/50 | 25/75 |

Scheme 3.2.9 Synthesis of poly(thioarylene sulfone/phosphine oxide) copolymers

### 3.2.8 Poly(Thioarylene Sulfone Ketone) (3a)

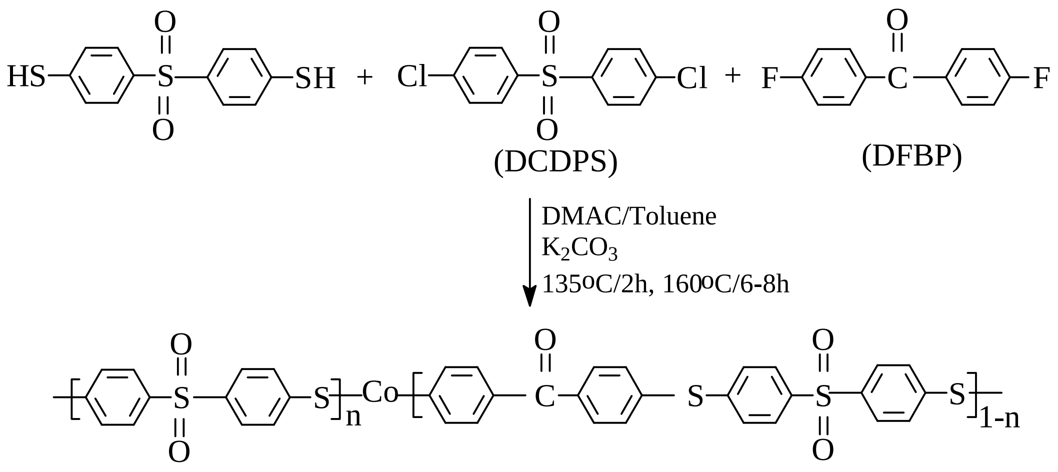
An amorphous poly(thioarylene sulfone ketone) homopolymer was synthesized based on bis-(4-mercaptophenyl) sulfone (BMPS) and 4,4′-difluorobenzophenone (DFBP) as follows. The polymerization reaction was conducted in a 3-neck flask that was equipped with a nitrogen inlet, thermometer, Dean-Stark trap and condenser. The flask was charged with 3.4182g (0.012 moles) of BMPS, 2.6668g (0.012 moles) of DCDPS (Amoco, monomer grade), and 30 mL of DMAc (Aldrich, 99.0%). Toluene (Aldrich, 99.4%) (20 mL) was added, followed by potassium carbonate (Aldrich, 99.9%) (1.208 g, 0.0087 moles). The reaction mixture was then heated until the toluene began to reflux. An optimum reflux temperature range was achieved between 132°C-135°C. The reaction mixture was maintained at this temperature range until the presence of water was no longer observed in the Dean-Stark trap, which took approximately 2 hours. Upon dehydration and slow removal of toluene from the reaction mixture, the temperature was gradually increased to 160°C. The reaction was discontinued when the solution viscosity increased dramatically (6-8h). The reaction mixture was cooled and diluted with DMAc (15-20 mL), and several drops of acetic acid were added to neutralize the thiophenoxide end groups. The polymer solution was precipitated into a methanol/water mixture. The polymer was then redissolved in DMAc, precipitated into methanol and dried under vacuum at 150°C for 20 hours. The $^1$H NMR spectroscopic analysis is given in Section 4.4.



Scheme 3.2.10 Synthesis of poly(thioarylene sulfone ketone) homopolymer

### 3.2.9 Poly(Thioarylene Sulfone/Ketone) Copolymers (3b-3d)

High molecular weight poly(thioarylene sulfone/ketone) random copolymers with various ketone contents were prepared by reacting bis-(4-mercaptophenyl) sulfone (BMPS) with a mixture of 4,4′-dichlorodiphenyl sulfone (DCDPS) and 4,4′-difluorobenzophenone (DFBP) using similar conditions employed in the synthesis of poly(thioarylene sulfone ketone) homopolymer.

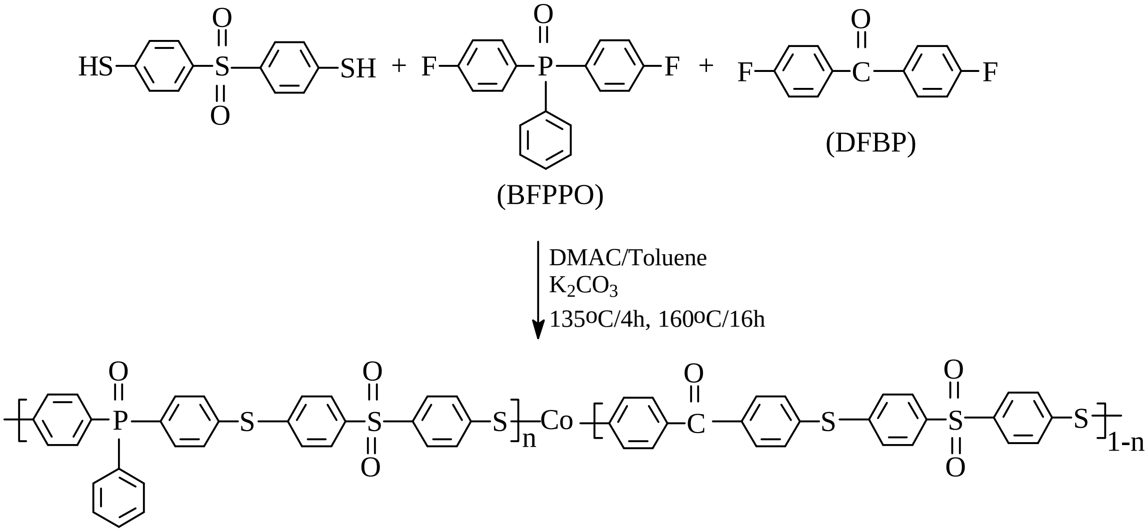


| polymers<br>DCDPS/DFBP | **3b** | **3c** | **3d** |
|---|---|---|---|
|  | 75/25 | 50/50 | 25/75 |

Scheme 3.2.11  Synthesis of poly(thioarylene sulfone/ketone) copolymers

### 3.2.10  Poly(Thioarylene Sulfone Ketone/Phosphine Oxide) Copolymers (4a-4c)

A series of new engineering thermoplastics containing sulfone, ketone and aryl phosphine oxide groups was synthesized by reacting bis-(4-mercaptophenyl) sulfone (BMPS) with a mixture of 4,4′-difluorobenzophenone (DFBP) and bis-(4-fluorophenyl) phenyl phosphine oxide (BFPPO) via aromatic nucleophilic substitution polycondensation reactions. Similar reaction conditions were used as described in the preparation of poly(thioarylene sulfone phosphine oxide) homopolymer. The only exception was that the activated dihalides utilized here were both DFBP and BFPPO.  The $^1$H NMR spectroscopic analysis is given in Section 4.5.

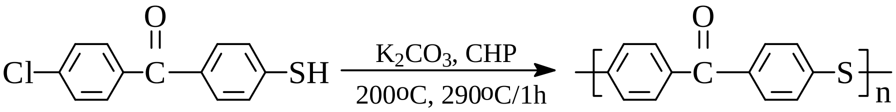


| polymers | **4a** | **4b** | **4c** |
|---|---|---|---|
| BFPPO/DFBP | 75/25 | 50/50 | 25/75 |

Scheme 3.2.12  Synthesis of poly(thioarylene sulfone ketone/phosphine oxide) copolymers

### 3.2.11  Semi-Crystalline Poly(Phenylene Sulfide Ketone) (PPSK)

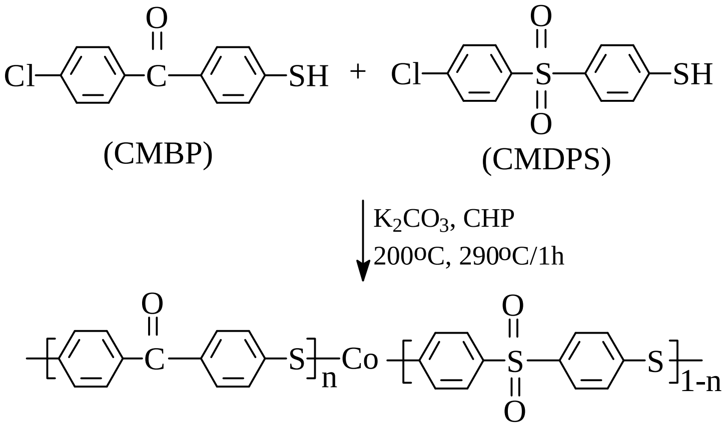
The semi-crystalline poly(pheylene sulfide ketone) homopolymer was synthesized by the self-polycondensation reaction of the new A-B monomer, 4-chloro-4′-mercapto benzophenone (CMBP). For example, A 100 mL resin flask provided with a three-necked head equipped with a mechanical stirrer, a thermometer, and a condenser was charged with 7.4550g (0.0300 moles) of CMBP, 4.7682g (0.0345 moles) of anhydrous potassium carbonate (Aldrich, 99.9%) and 30 mL of 1-cyclohexyl-2-pyrrolidone (CHP) (Fisher, 99.0%). The reaction mixture, with stirring under a blanket of nitrogen, was heated with a salt bath. The top part of the reaction flask was kept hot with an infrared lamp. After the reaction temperature reached 200$^{o}$C, the nitrogen purge was increased to drive out the water formed in the reaction through one of the necks of the flask (by removing the condenser). After the reaction mixture reached 285-290$^{o}$C, it was maintained at this temperature for 1 hour. The viscous reaction mixture was cooled to 50-60$^{o}$C, diluted with 40 mL of methanol, heated to reflux, and filtered. The isolated polymer was boiled with 60 mL of water and filtered and the operation was repeated. The polymer was dried in a vacuum oven at 120°C for overnight yielding an off-white powder.



Scheme 3.2.13 Synthesis of poly(phenylene sulfide ketone) homopolymer

## 3.2.12 Semi-Crystalline Poly(Phenylene Sulfide Sulfone/Ketone) Copolymers (5a-5b)

Semi-crystalline poly(pheylene sulfide sulfone/ketone) compolymers with 75 mol% or 85 mol% of ketone compositions were prepared via a similar method described in the synthesis of poly(phenylene sulfide ketone). The only exception was that using 15 mol% or 25 mol% of 4-chloro-4′-mercaptodiphenyl sulfone (CMDPS) replaced the CMBP.

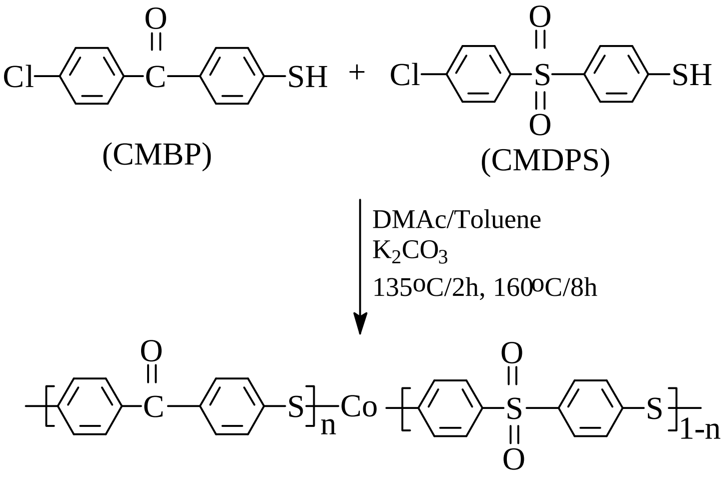


Molar Ratio of CMBP/CMDPS: **5a**, 85/15; **5b**, 75/25.

Scheme 3.2.14 Synthesis of semicrystalline copoly(phenylene sulfide sulfone/ketone)s

## 3.2.13 Amorphous Poly(Phenylene Sulfide Sulfone/Ketone) Copolymers (5c-5e)

Amorphous poly(phenylene sulfide sulfone/ketone) copolymers with ketone compositions ranged from 15 mol% to 50 mol% were prepared by the reaction of a mixture of the two A-B monomers, CMBP and CMDPS, in DMAc and potassium carbonate used as the base. The reaction conditions are similar to that described for the preparation of poly(thioarylene sulfone ketone) homopolymer.



CMBP/CMDPS: **5c**, 50/50; **5d**, 25/75; **5e**, 15/85

Scheme 3.2.15 Synthesis of amorphous copoly(phenylene sulfide sulfone/ketone)s

## *3.3 Characterization Methods*

### 3.3.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

Proton ($^1$H), carbon ($^{13}$C) and phosphorus ($^{31}$P) NMR spectra were measured on a Varian 400 Hz instrument in $CDCl_3$ or DMSO-$d_6$, depending on the solubility of the material being analyzed. $^1$H and $^{13}$C NMR spectra were referred to tetramethylsilane (TMS) at 0 ppm and $^{31}$P NMR spectra were referred to $H_3PO_4$ at 0 ppm. NMR spectra were used to determine purity, chemical composition, and incorporation of monomers and polymers synthesized. The endgroups of poly(phenylene sulfide sulfone)s were analysized by $^1$H and $^{13}$C NMR using a 10 mm NMR tude at a polymer concentration of 20 wt.% in DMSO-$d_6$ at 140°C.

### 3.3.2 Melting Point of Monomers by Capillary Methods

The melting points of purified compounds were determined in a capillary tube with a Lab devices Melt-Temp II at a heating rate of no greater than 1°C/min. Samples were ground before measuring and the formation of a meniscus was identified as the beginning of the melt.

### 3.3.3 Intrinsic Viscosity

Intrinsic viscosities were determined to obtain the molecular weight information of polymers. The measurements were conducted at 25°C in NMP solvent for amorphous polymers and concentrated sulfuric acid was used as the solvent for semi-crystalline polymers, using a Cannon-Ubbelodhe viscometer. The intrinsic viscosity value $[\eta]$ was obtained by measuring specific viscosity $\eta_{sp} = \eta/\eta_0-1$ and reduced viscosity $\eta_{red} = \ln(\eta/\eta_0)$ at four concentrations and extrapolating $(\eta_{sp}/c)$ and $(\eta_{red}/c)$ to zero concentration.

### 3.3.4 Gel Permeation Chromatography (GPC)

GPC measurements were used to determine molecular weight and molecular weight distribution information. Chromatographs were obtained on a Waters 150C ALC/GPC instrument equipped with a differential refractive index detector and a Viscotek® Model 100 viscosity detector connected in parallel. NMP (HPLC grade), containing ~0.02M $P_2O_5$ and filtered through 0.5μm Teflon filter, served as mobile phase. The stationary phase was crosslinked polystyrene gel (Waters μstyragel HT $10^2$ Å, $10^3$ Å and $10^4$ Å, mean particle diameter 10 μm) packed in three (7.8 mm I. D. × 30cm) stainless steel columns. Samples prepared to known concentrations (~4 mg/mL) were dissolved in the mobile phase and filtered through 0.2μm PTFE disposable filter prior to analysis. The injected sample volume was 200 μL and the flow rate of the mobile phase was 1.0 mL/min. The column compartment, lines and detectors were kept at a temperature of 60°C during the measurements. Number average molecular weight ($\overline{M_n}$), weight average molecular weight ($\overline{M_w}$) and polydispersity ($\overline{M_w}$ / $\overline{M_n}$) were determined by universal calibration generated with narrow molecular weight distribution polystyrene standards (186).

### 3.3.5 Differential Scanning Calorimetry (DSC)

DSC was used to determine glass transition temperatures, melting points, and recrystallization temperatures of polymers. DSC was conducted on a Perkin-Elmer DSC 7 instrument. Scans were run in nitrogen at a heating rate of 10°C/min. $T_g$ values were identified as the midpoint of the change in endothermic baseline from the second heat after a quench cool from the first run.

### 3.3.6 Thermogravimetric Analysis (TGA)

Dynamic TGA was performed to access the relative thermal stability of polymers. Thermograms were obtained using a Perkin Elmer TGA 7 thermogravimetric analyzer. Thin film or powder samples of ~10 mg were placed in a platinum pan connected to an electric microbalance. The samples were heated at a rate of 10°C/min. in air or nitrogen. Weight loss of the samples was measured as a function of temperature.

### 3.3.7 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was carried out on a Perkin-Elmer DMA apparatus using extension mode. Frequency was 1 Hz and heating rate was 5°C/min. The samples analyzed from pressed films had approximate dimensions of 0.6 x 5 x 6 mm.

### 3.3.8 Stress-Strain Behavior

The stress-stain behavior was analyzed at room temperature using an Instron 1123 instrument equipped with a strain gauge extensiometer (Instron 2630-013). The dog-bone shape samples (ASTM D-638 #5) were cut out of a compression molded film with thickness of ~0.5 mm. The samples were tested at an average cross head speed of 1.0 mm/min. (ASTM D-638). Approximately 8 samples were tested and the results were averaged.

### 3.3.9 Cone Calorimetry

Polymer samples with dimensions of 10 cm x 10 cm x 3 mm were compression molded 50$^{o}$C above their $T_g$ and measured at the Fire Research Laboratory of the National

Institute of Standards and Technology (NIST), under the supervision of Dr. T. Kashiwagi, where they were evaluated in air using cone calorimetry at a constant flux of 70 KW/m$^2$. The instrument was run in the standard mode of ASTM E 1354.

Micro calorimetry analyses were performed by Dr. Richard Lyon and Dr. Richard Walters at FAA Fire Safety Laboratory. This new technique required small amount of samples (1-1.5 g) which were compression molded into dimensions of 1 cm x 1 cm x 1 mm. Micro calorimetry measured the peak heat release rates and total amount of heat release at a constant interface temperature of 475$^o$C and a constant heat flux of 50 kW/m$^2$ in a nitrogen atmosphere.

### 3.3.10 Refractive Index Measurements

The refractive indices of solution cast films were measured using a Metricon Model 2010 Prism Coupler. The laser used was a low power (0.5 mW nominal) He-Ne (632.8 nm) laser.

### 3.3.11 X-Ray Photoelectron Spectroscopy (XPS)

XPS analysis was performed on a Perkin-Elmer PHI 5400 spectrometer employing a MgK$\alpha$ (1253.6 eV) achromatic X-ray source operated at 14 KeV with a total power of 300 watts. Typical operation pressure was $<1\times10^{-7}$ torr and the surface area analyzed was a 1x3 mm$^2$ spot. The spectrometer was calibrated to the 4f$_{7/2}$ photopeak of gold at 83.8 eV and the 2p$_{3/2}$ photopeak of copper at 932.4 eV, and all binding energies were referenced to the main C1s photopeak at 285.0 eV.

### 3.3.12 Rheology Measurements

Samples for melt viscosity measurements were prepared by compression molding at a temperature 50$^o$C above T$_g$. Vacuum dried polymers were used to prepare 2.5 cm diameter samples of about 0.2 cm thickness. Samples were kept under vacuum prior to measurement. Parallel plate scans were performed using a Bohlin Rheometer in air. Tests were conducted using parallel plates at a frequency of 1 Hz and a constant temperature (300$^o$C) for 60 minutes.

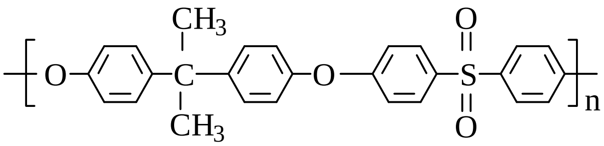
# Chapter 4.0 RESULTS AND DISCUSSION

## *4.1 Influence of Polymerization Conditions on Poly (Phenylene Sulfide Sulfone) Molecular Structure and Physical Behavior*

### 4.1.1 Introduction

Thermoplastic materials possess many attractive characteristics, such as rapid processibility injection molding, film extrusion and fiber spinning. In addition, the likelihood recycling these materials appears to be more straightforward than for the other material systems, e.g., thermosetting network systems. Much research has been carried out in recent years toward developing new or improved thermoplastic resins. In particular, poly(arylene ether)s, such as Udel and Victrex, have been extensively studied because of their excellent mechanical and thermal properties.

The sulfur containing analogs to the poly(arylene ether)s, although important, are much less well studied (14, 62, 77). By far and away, the most important sulfur containing material in this classification is poly(phenylene sulfide) (PPS), which is a semicrystalline polymer with $T_g$ around 85$^o$C and a $T_m$ of about 285$^o$C. PPS is considered to possess inherent fire resistance and excellent chemical resistance. A related sulfide sulfone, poly(phenylene sulfide sulfone) (PPSS), has been investigated much less extensively. In fact, references to it are somewhat limited to either the patent literature or the commercial trade literature, where it has been described as an amorphous polymer with a $T_g$ around 217$^o$C (119). Poly(phenylene sulfide sulfone)s have been prepared by nucleophilic aromatic substitution step polymerization, which involves utilizing sodium sulfide as the nucleophile, and 4,4′-dichlorodiphenyl sulfone as the activated aromatic halide. Although there have been several reports in the patent literature about the effect of reaction conditions on molecular weights of PPSS (119-120), a detailed study has not yet been reported. This section examines the effects of reaction temperature, reaction time, and the use of water as an additive, on molecular structure, as well as the relationship of molecular weight to thermal and mechanical properties.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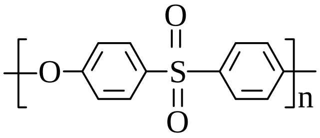
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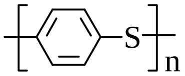
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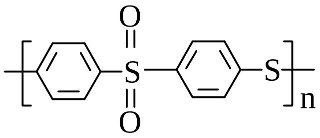

**PPSS**

### 4.1.2 Effect of Reaction Temperatures and Time on Molecular Weights

The synthesis of the poly(phenylene sulfide sulfone)s (PPSS) is shown in Scheme 3.2.1. These conditions were largely developed on the basis of the patent literature, as indicated in references 120 and 124. These reactions were conducted in a pressure reactor at 100-150 psi to contain the solvent and reactants. Formation of PPSS proceeds by the nucleophilic aromatic substitution step polymerization. Specifically, 4,4′-dichlorodiphenyl sulfone (DCDPS) was reacted with sodium hydrosulfide, plus either sodium hydroxide or sodium carbonate, along with sodium acetate in NMP, to which deionized water had been intentionally added. 1 mole percent excess of the DCDPS was utilized in order to ensure that the endgroups in the polymer chain would be mostly derived for the relatively stable chlorophenyl groups. According to our previous study (122), high molecular weight PPSS could also be prepared from the DCDPS by reaction with sodium sulfide nonahydrate and sodium acetate in NMP. The synthetic variables studied here include reaction temperature, reaction time, and the water content in the reaction medium. In order to investigate the effect of reaction conditions on molecular weight, gel permeation chromatography (GPC) equipped with an online viscosity detector along with universal calibration was used to determine absolute molecular weights. In addition, intrinsic viscosity measurements were also performed in NMP at 30°C to confirm the GPC analyses.

Reaction temperatures were varied from 165°C to 245°C while maintaining the ratio of water to NaSH as 9 : 1 mol/mol. Other reaction conditions were held constant with a NaSH/DCDPS molar ratio of 1:1.01, a NaSH/NMP molar ratio of 1:8, a NaSH/NaOH/NaAc molar ratio of 1:1:1, and a reaction time of 3 hours. As expected, the reaction temperature had a significant effect on the molecular weight of the resulting PPSS as shown in Table 4.1.2.1 and Figure 4.1.2.1. A maximum molecular weight of around 39,000 g/mole was obtained at the optimum polymerization temperatures from 185°C to 200°C. Conversely, a relatively low molecular weight material ($M_n$ = 25,100) was obtained at the relatively low reaction temperature of 165°C, which is understandable due to kinetic and/or thermodynamic factors. The dramatic decrease of molecular weight above 230°C was considered to be a result of side reactions, including degradation.

Based on dynamic thermogravimetric analysis, PPSS was found to be quite thermally stable. In fact, no degradation occurred even as temperatures approached 480°C in both air and nitrogen atmospheres. When the PPSS was dissolved in NMP and heated to 245°C/180 Psi for 3 hours, the molecular weight ($M_n$ = 38,000) did not change and no obvious degradation was observed (Scheme 4.1.2.1). Degradation of PPSS, however, did occur when the PPSS in NMP solution was heated to 245°C/180 psi in the presence of water and sodium acetate (Scheme 4.1.2.2). After 3 hours, the number average molecular weight decreased from 38,000 to 10,800. To better understand the degradation mechanism, $^{13}$C NMR was utilized to analyze the endgroup structures of the PPSS before and after decomposition. It was found that the polymer solution in DMSO-$d_6$ was not stable and the PPSS was observed to crystallize out of the solution at room temperature. Therefore, $^{13}$C NMR analyses were performed at 140°C to maintain the polymer in solution. As can been seen in Figure 4.1.2.2, once the PPSS degraded, the signals corresponding to the mercaptide and hydroxide endgroups increased significantly in comparison with that of the polymer prior to degradation. This phenomenon suggests that the degradation was due to chemical attack at the S-C bonds in the polymer chain by nucleophiles, such as hydroxide or acetate anions. This no doubt reflects the weaker bond strength of a sulfide-carbon covalent bond relative to sulfone-carbon and aromatic carbon-carbon bond.

Table 4.1.2.1 Effect of Reaction Temperatures on Molecular Weights of PPSS[a]

| Run# | Rxn. Temp. ($^oC$) | <Mn> by GPC (g/mol) | Mw/Mn by GPC | [η][b] (dL/g) |
|---|---|---|---|---|
| 1 | 165 | 25,100 | 2.0 | 0.36 |
| 2 | 175 | 38,000 | 1.8 | 0.59 |
| 3 | 185 | 38,600 | 1.7 | 0.59 |
| 4 | 200 | 39,000 | 1.9 | 0.61 |
| 5 | 215 | 30,200 | 1.8 | 0.44 |
| 6 | 230 | 15,400 | 1.7 | 0.35 |
| 7 | 245 | 7,200 | 1.9 | 0.15 |

[a]reaction conditions: NMP/$H_2O$=0.85/1, NaSH/DCDPS=1/1.01, time: 3h.

[c]in NMP solution at 30$^o$C.

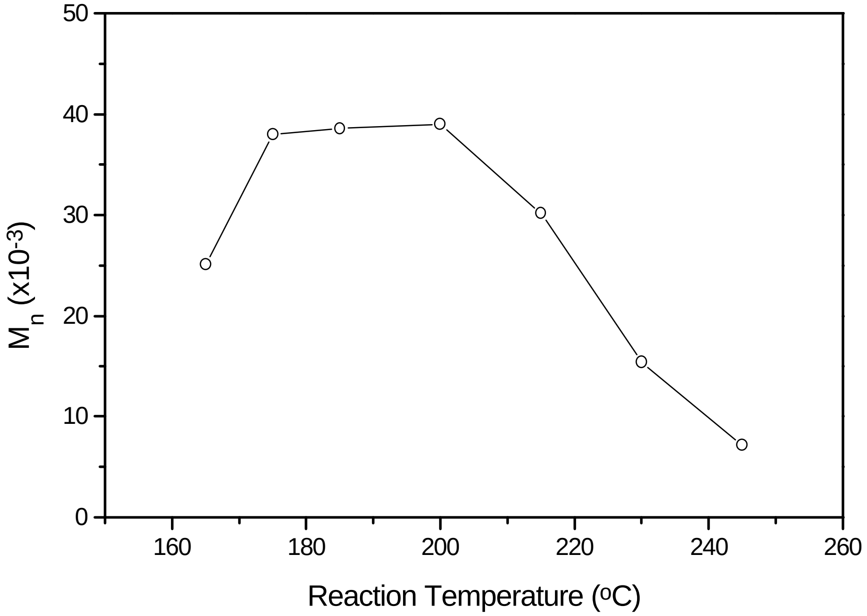
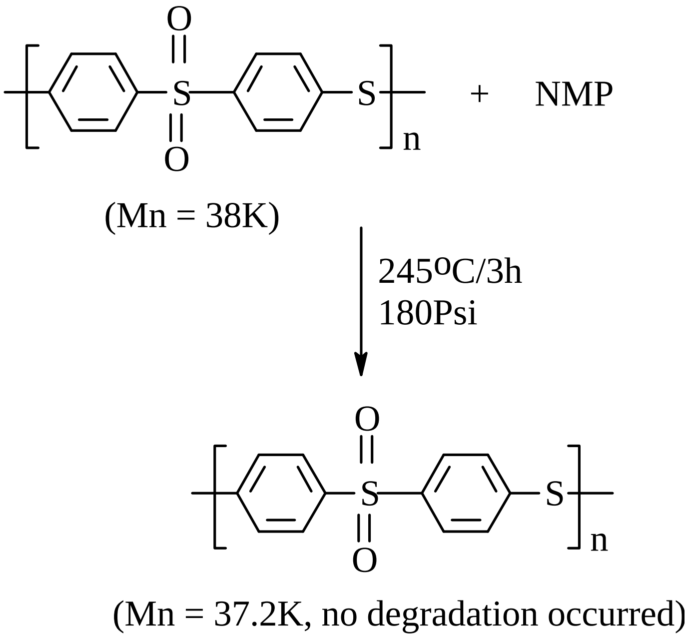
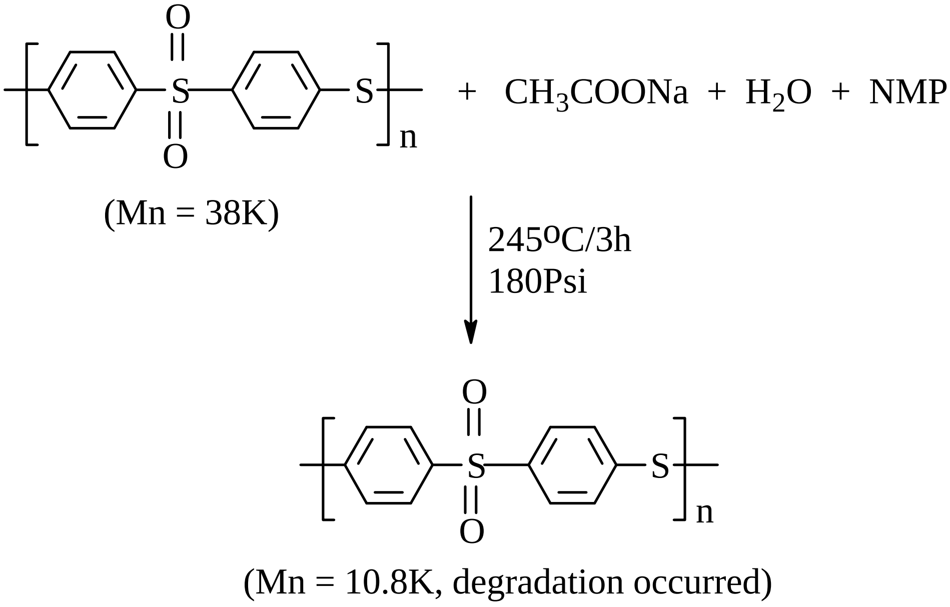


Figure 4.1.2.1 Effect of reaction temperatures on the $M_n$ of PPSS



Scheme 4.1.2.1 Stability of PPSS in NMP solution at 245$^{o}$C after 3h



Scheme 4.1.2.2 Degradation of PPSS in NMP/$H_2O$/$CH_3COONa$ solution at 245$^{o}$C

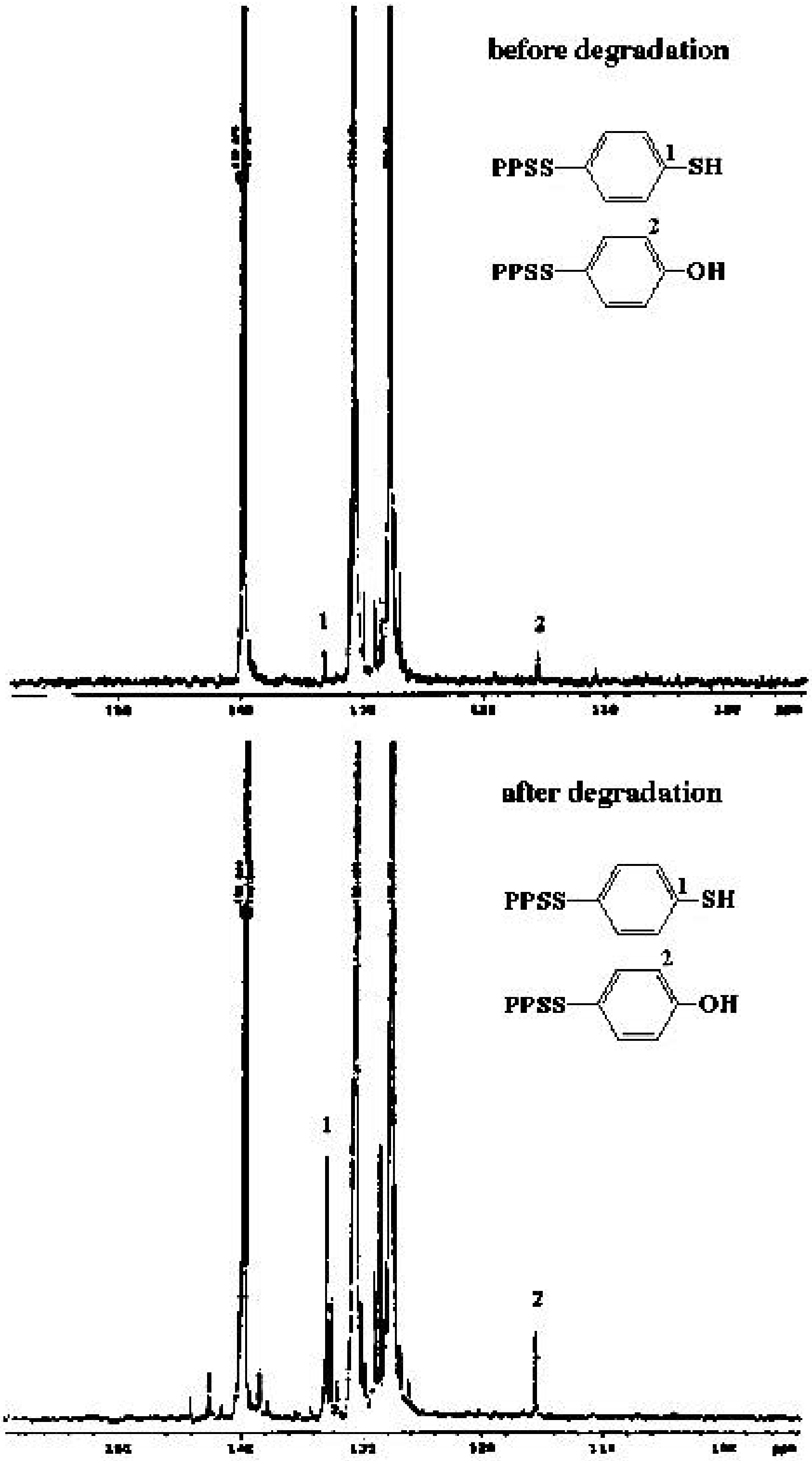


Figure 4.1.2.2 $^{13}$C NMR spectra of PPSS before and after degradation at 245°C

The effect of reaction time on molecular weight was also examined from 20 minutes to 10 hours, while keeping the following reaction conditions constant: NaSH/DCDPS molar ratio of 1:1.01, NaSH/NaOH/NaAc molar ratio of 1:1:1, NaSH/NMP molar ratio of 1:8, NaSH/$H_2O$ molar ratio of 1:9, and reaction temperature of 200°C. The indications from data are that the polymerization occurs very rapidly and is essentially complete after 1.5 hours at 200°C for the stoichiometry utilized (Table 4.1.2.2 and Figure 4.1.2.3). Longer reaction times, such as 8 or 10 hours, resulted in low molecular weight materials. As was the case using higher reaction temperatures discussed above, the resulting low molecular weight polymers were likely due to the chemical degradation that occurred at the long reaction time at 200°C in the presence of water, sodium hydroxide, and sodium acetate.

Table 4.1.2.2 Effect of Reaction Time on Molecular Weights of PPSS[a]

| Run# | Rxn Time | $<M_n>$ by GPC (g/mol) | $M_w/M_n$ (GPC) | $[\eta]$[b] (dL/g) |
|---|---|---|---|---|
| 1 | 20 min | 21,100 | 1.7 | 0.30 |
| 2 | 40 min | 28,200 | 1.8 | 0.43 |
| 3 | 1.0 hr | 34,000 | 1.8 | 0.49 |
| 4 | 1.5 hrs | 40,200 | 1.9 | 0.58 |
| 5 | 2.0 hrs | 43,100 | 1.9 | 0.59 |
| 6 | 3.0 hrs | 42,800 | 1.9 | 0.59 |
| 7 | 4.0 hrs | 38,300 | 1.9 | 0.50 |
| 8 | 6.0 hrs | 30,100 | 1.9 | 0.45 |
| 9 | 8.0 hrs | 20,200 | 1.8 | 0.29 |
| 10 | 10.0 hrs | 12,800 | 2.0 | 0.24 |

[a] reaction conditions: NMP/$H_2O$=0.85/1, NaSH/DCDPS=1/1.01, temp.: 200°C.

[b] in NMP solution at 30°C.

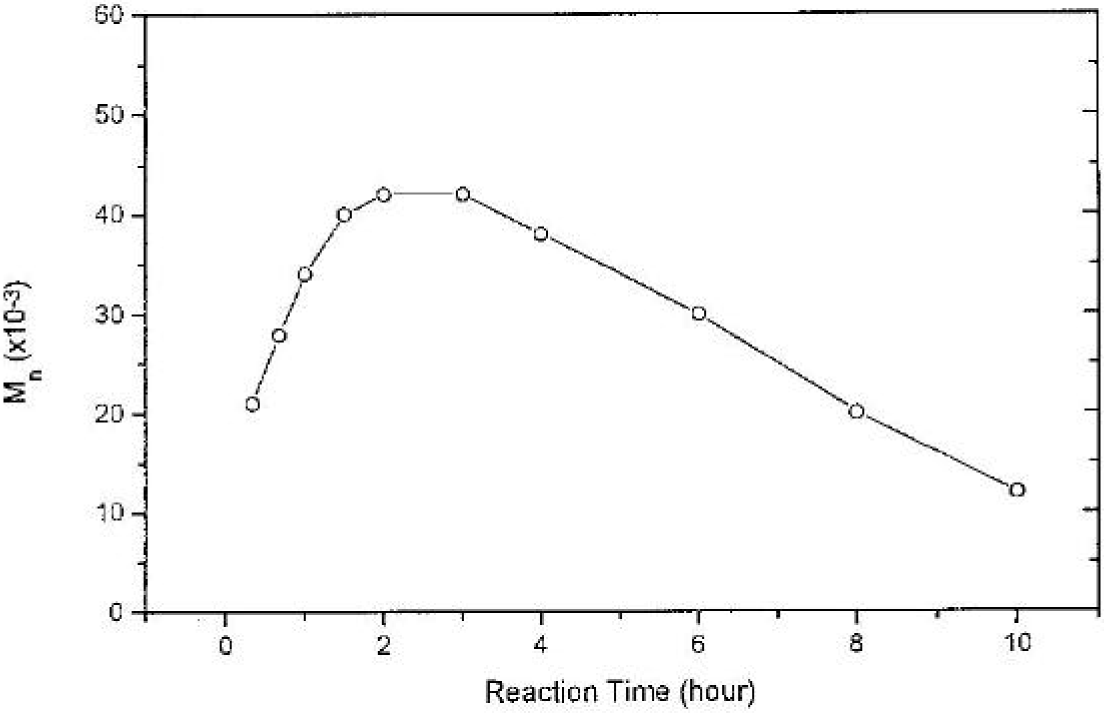


Figure 4.1.2.3 Effect of reaction time on the $M_n$ of PPSS

### 4.1.3 Effect of the Molar Ratios of $H_2O$/NaSH or $H_2O$/NMP on the Molecular Weight

As reported in the patent literature (120, 124), optimum molar ratios of $H_2O$-to-NaSH and NMP-to-$H_2O$ are critical for obtaining high molecular weight materials. Specifically, maximum molecular weight was achieved with molar ratios of 9.4:1 and 0.85:1 for $H_2O$-to-NaSH and NMP-to-$H_2O$, respectively. Regretably, these authors did not explain why the water in the reaction medium was important and how it influenced molecular weights. In this study, the molar ratio of total water to NaSH was varied from 1.3:1 (the water came from $NaSH \cdot xH_2O$, no additional water was added) to 20:1, and the corresponding NMP-to-$H_2O$ ratio was simultaneously changed from 6.2:1 to 0.4:1, since the amount of NMP utilized was fixed. The other reaction conditions were held constant with a NaSH/DCDPS molar ratio of 1:1.01, a NaSH/NaOH/NaAc molar ratio of 1:1:1, a NaSH/NMP molar ratio of 1:8, a reaction temperature of 200°C, and a reaction time of 3 h.

Table 4.1.3.1 The Effect of Water on the Molecular Weight of PPSS[a]

| Run# | Molar Ratio $H_2O$/NaSH | Molar Ratio NMP/$H_2O$ | $\langle M_n \rangle$ by GPC (g/mol) | $M_w/M_n$ by GPC | $[\eta]^b$ (dL/g) |
|---|---|---|---|---|---|
| 1 | 1.3/1 | 6.2/1 | 12,200 | 1.8 | 0.21 |
| 2 | 3.0/1 | 2.7/1 | 28,100 | 1.9 | 0.44 |
| 3 | 6.0/1 | 1.3/1 | 30,200 | 1.8 | 0.43 |
| 4 | 9.4/1 | 0.85/1 | 38,500 | 2.0 | 0.59 |
| 5 | 12.0/1 | 0.67/1 | 35,800 | 1.9 | 0.52 |
| 6 | 15.0/1 | 0.53/1 | 34,800 | 1.9 | 0.49 |
| 7 | 20.0/1 | 0.40/1 | 19,200 | 1.9 | 0.31 |

[a] reaction conditions: NaSH/DCDPS=1/1.01, reaction temp.: 200°C, time: 3h;

[b] in NMP solution at 30°C.

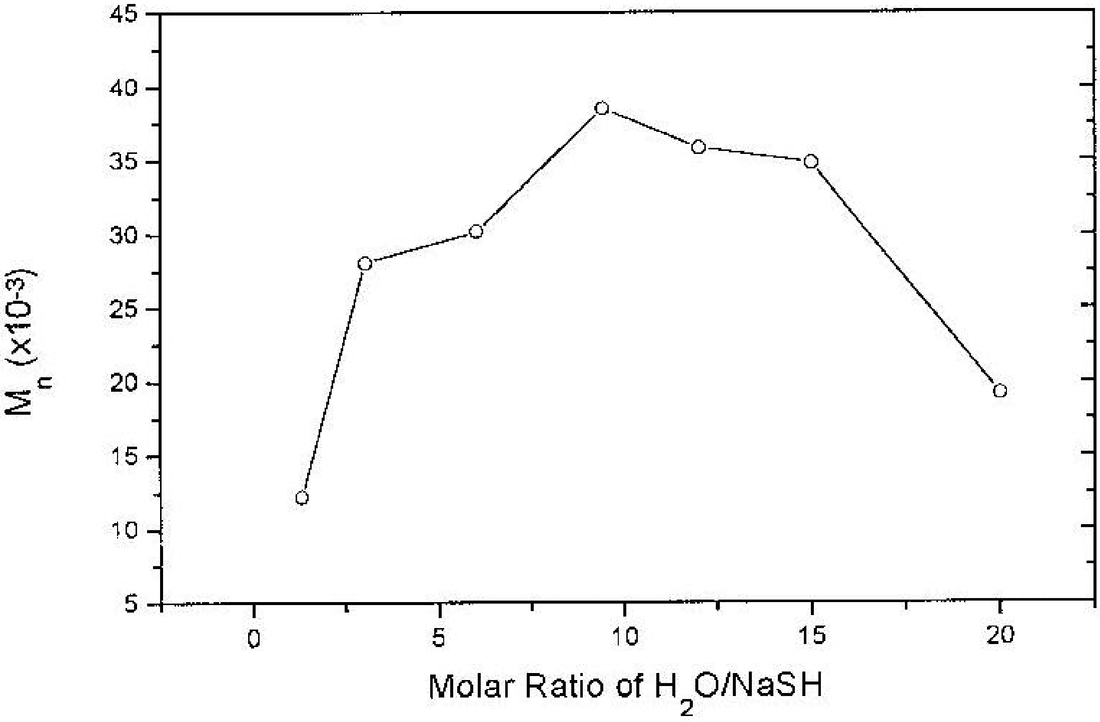


Figure 4.1.3.1 Effect of the water content on the $M_n$ of PPSS

As shown in Table 4.1.3.1 and Figure 4.1.3.1, high molecular weight PPSS was obtained using $H_2O$-to-NaSH ratio ranging from 6.0:1 to 15:1. The existence of a maximum molecular weight in Figure 4.1.3.1 may be explained by the increased solubility of growing polymer chains in the reaction medium. It should be noted that the premature precipitation of polymer chains has been cited as one of the reasons for the low molecular weight of PPS and similar PPS copolymers (97).

### 4.1.4 Solubility and Refractive Index Results

PPSS exhibited interesting solubility characteristics. The solubility of PPSS has been examined in various solvents (Table 4.1.4.1). Interestingly, PPSS is resistant to many solvents that will dissolve polyether sulfones, such as Udel and Victrix. This is true both at ambient and elevated temperatures.

Table 4.1.4.1. Solubility Behavior of Poly(Phenylene Sulfide Sulfone)

| SOLVENT | RT | HOT |
|---|---|---|
| Chloroform | no | no |
| THF | no | no |
| Chlorobenzene | no | no |
| 1,2-Dichlorobenzene | no | no |
| DMSO | yes* | --- |
| DMAc | yes* | --- |
| DMF | yes* | --- |
| NMP | yes* | --- |

*soluble initially, precipitated out of solution upon standing.

Although PPSS was soluble in several polar solvents, an interesting phenomenon was noted. After the materials were dissolved and allowed to stand for a few hours, the materials precipitated out of solution. This phenomenon could be very important to the susceptibility of molded PPSS films to environmental stress-cracking and crazing (ESC). As detailed in Table 4.1.4.2, for this test, the materials were placed under a constant stress in a test jig, which was conducted in the laboratories of Prof. D.A. Dillard. The films were examined for cracking and crazing and, surprisingly, the sulfide-sulfones showed a remarkable degree of resistance to these important organic liquids, which may be a result of crystallization on the surface. Researchers in Russia studied solutions of PPSS in NMP and found that the formation of spherulite-shaped PPSS-NMP solvates is responsible for the unstable polymer solution (187). These solvates were found to possess crystalline structures as seen by X-ray diffraction, and had a melting point at around 200$^o$C (187). As evidenced by elemental analysis, the crystals contained 3.75% nitrogen, which should result from NMP. In fact, extracting the NMP from the crystal solvates with benzene at room temperature resulted in a decrease of NMP content in the crystals and the sample becoming almost completely amorphous (187). In addition, our research showed that PPSS cast films exhibited a very high refractive index value of around 1.70.

Table 4.1.4.2. Susceptibility of PPSS Films to ESC

| SOLVENT | CRAZING | CRACKING |
|---|---|---|
| Acetone | no | no |
| MEK | no | no |
| Diglyme | no | no |
| Ethylene Glycol | no | no |
| Jet Fuel | no | no |
| Hydraulic Fuel | no | no |
| Toluene | no | no |

### 4.1.5 Influence of Molecular Weight on Thermal and Mechanical Properties of PPSS

The glass transition temperatures ($T_g$s) of the polymers were measured by DSC at a heating rate of 10$^o$C/min. under an atmosphere of nitrogen (Table 4.1.5.1). DSC analyses of these polymers showed that they all had glass transition temperatures ($T_g$) > 200$^o$C (2nd heat) and no melting in the first heat. Furthermore, as the number average molecular weight increased from 15,000 to 43,000, the value of $T_g$ increased only slightly from 207°C to 222°C.

Thermogravimetric analysis (TGA) results indicated that the PPSS samples were quite thermally stable as judged by the 5% weight loss temperatures (Figure 4.1.5.1 and Table 4.1.5.1), which ranged from 477°C to 490°C in air and 482°C-487°C in nitrogen. The values of char yields at 700°C were observed to range from 7.8% to 12.0% in air and from 35.6% to 37.4% in nitrogen, respectively.

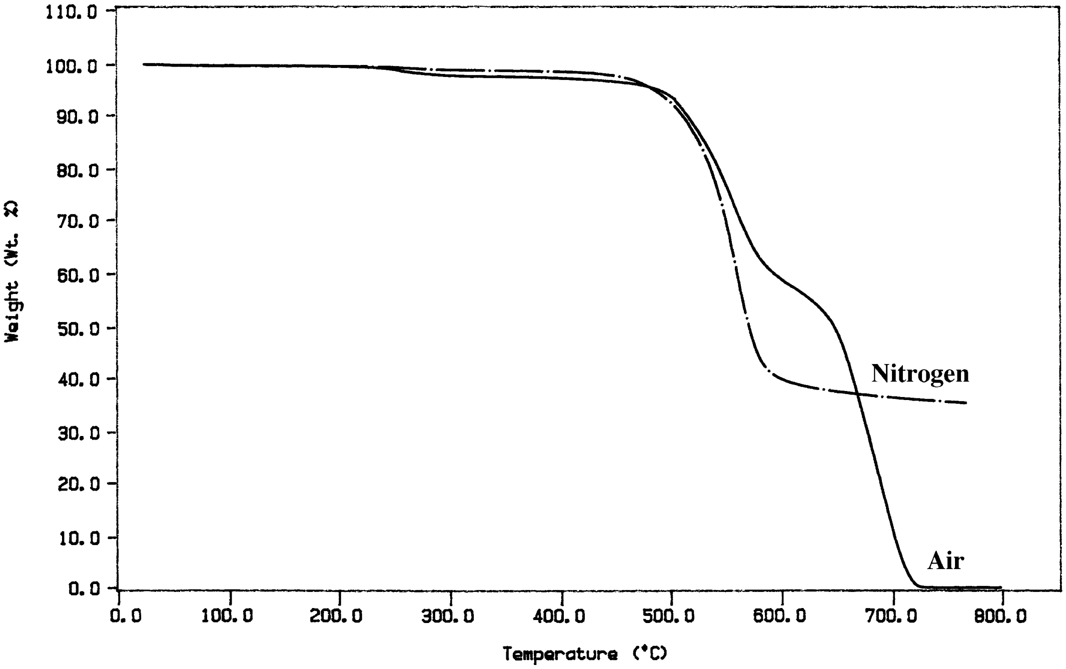


Figure 4.1.5.1 TGA curves of PPSS (Mn=43,000) at a heating rate of 10°C/min.

Table 4.1.5.1 Thermal Properties of PPSS

| $M_n$ (g/mol) | $T_g$[a] (°C) | TGA, °C[b] (5% weight loss) |  | TGA, %[b] Char yield at 700°C |  |
|---|---|---|---|---|---|
|  |  | $N_2$ | air | $N_2$ | air |
| 15,000 | 207 | 482 | 477 | 35.6 | 7.8 |
| 20,000 | 217 | 485 | 487 | 36.0 | 9.2 |
| 25,000 | 218 | 485 | 485 | 35.8 | 10.7 |
| 30,000 | 220 | 489 | 490 | 35.9 | 12.0 |
| 39,000 | 220 | 487 | 490 | 37.4 | 12.0 |
| 43,000 | 222 | 486 | 489 | 37.1 | 11.5 |

[a] second heat, heating rate of 10°C/minute under $N_2$;

[b] heating rate of 10°C/minute.

The materials also showed what appears to be two-step degradation behavior in air as seen in Figure 4.1.5.1. The XPS analysis of the PPSS, as shown in Figure 4.1.5.2, illustrated that the sulfur peak at 168.0 eV, due to the sulfone moiety in the polymer backbone, disappeared after TGA degradation at 580°C (the 2nd degradation temperature) in air, whereas the other sulfur peak at 163.9 eV, due to the sulfide moiety, remained. Table 4.1.5.2, which summarizes the XPS surface atomic concentrations of carbon, sulfur, and oxygen for the PPSS before and after exposure to 580°C in air atmosphere, indicates that both sulfur and oxygen concentrations decreased after the polymer was exposed to 580°C. These results suggest that the sulfide moiety in the polymer backbone may form some kinds of layers, such as crosslinked sulfide chars (75), on the polymer surface to protect the material from further degradation at that temperature, which would partially explain the two-step degradation phenomenon.

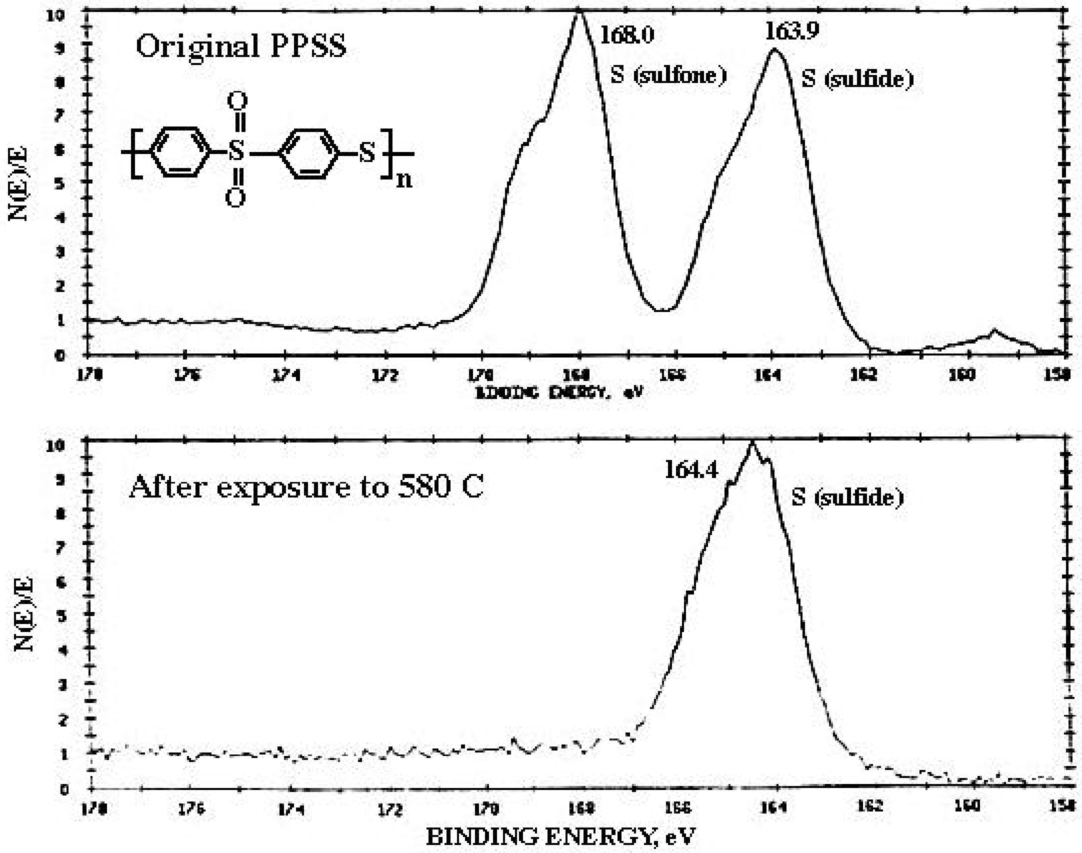


Figure 4.1.5.2 XPS Analysis of sulfur for PPSS

Table 4.1.5.2 Comparison of XPS Surface[a] Atomic Concentrations of C, S, O for the PPSS Before and After Exposure to 580°C in Air Atmosphere

| Element | Carbon (C) (%) | Sulfur (S) (%) | Oxygen (O) (%) |
|---|---|---|---|
| Theoretical Value | 75.0 | 12.5 | 12.5 |
| PPSS before exposure to 500°C | 72.9 | 12.3 | 14.9 |
| PPSS after exposure to 580°C | 83.3 | 5.5 | 11.1 |

[a] angle of 45°, depth of 50 angstrom.

The dynamic mechanical behavior (DMA) of the compression molded PPSS films has been investigated, as is shown in Figure 4.1.5.3. These materials showed a high modulus up to temperatures approaching the glass transition temperature of 215$^{o}$C, and exhibited a secondary relaxation at –100$^{o}$C, indicative of molecular motion well below $T_g$ and often tied to enhanced ductility (188). Mechanical tests were performed to measure the tensile properties of the PPSS with different molecular weights (Mn=20,000-43,000 g/mole) at room temperature using an Instron equipped with a strain gauge extensiometer. The compression molded samples were tested at an average cross head speed of 1.0 mm/min. and the results are shown in Figure 4.1.5.4 and Table 4.1.5.3. The properties these films, including tensile strength and elongation, are in the range of the polyarylene ether sulfones and thus would be considered to represent ductile behavior.

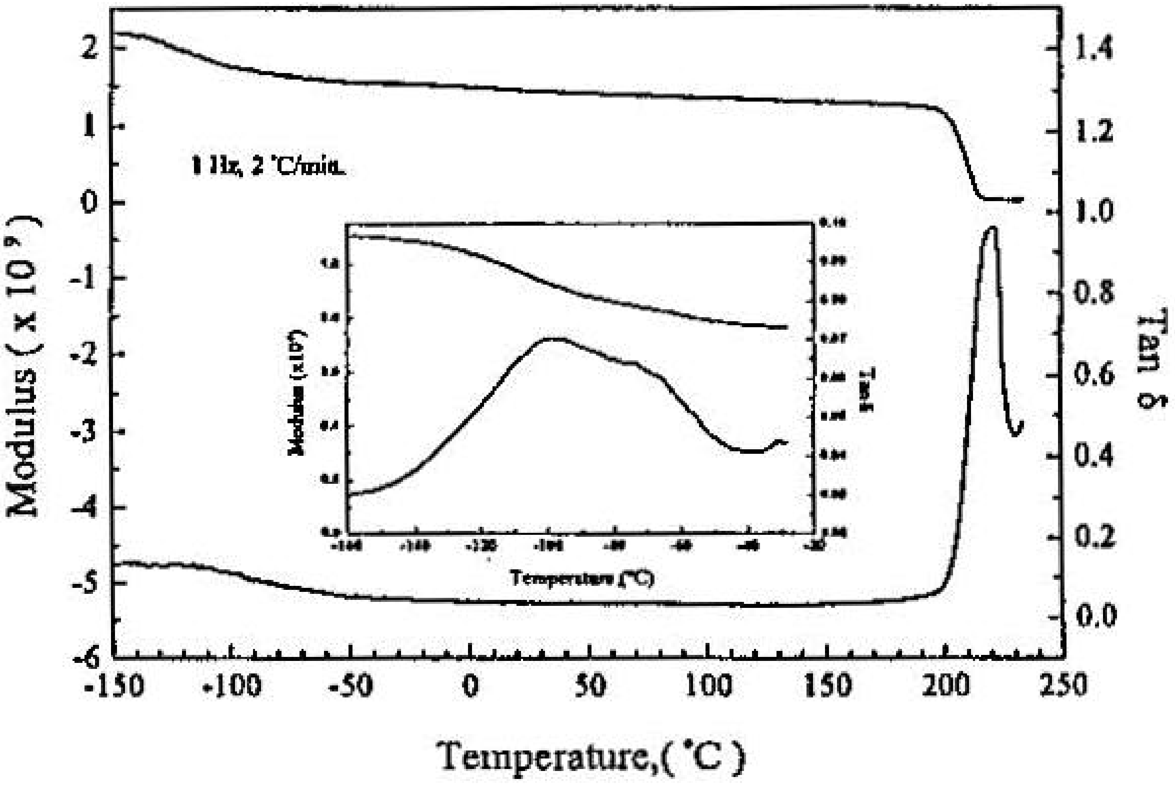


Figure 4.1.5.3 Dynamic mechanical analysis of PPSS

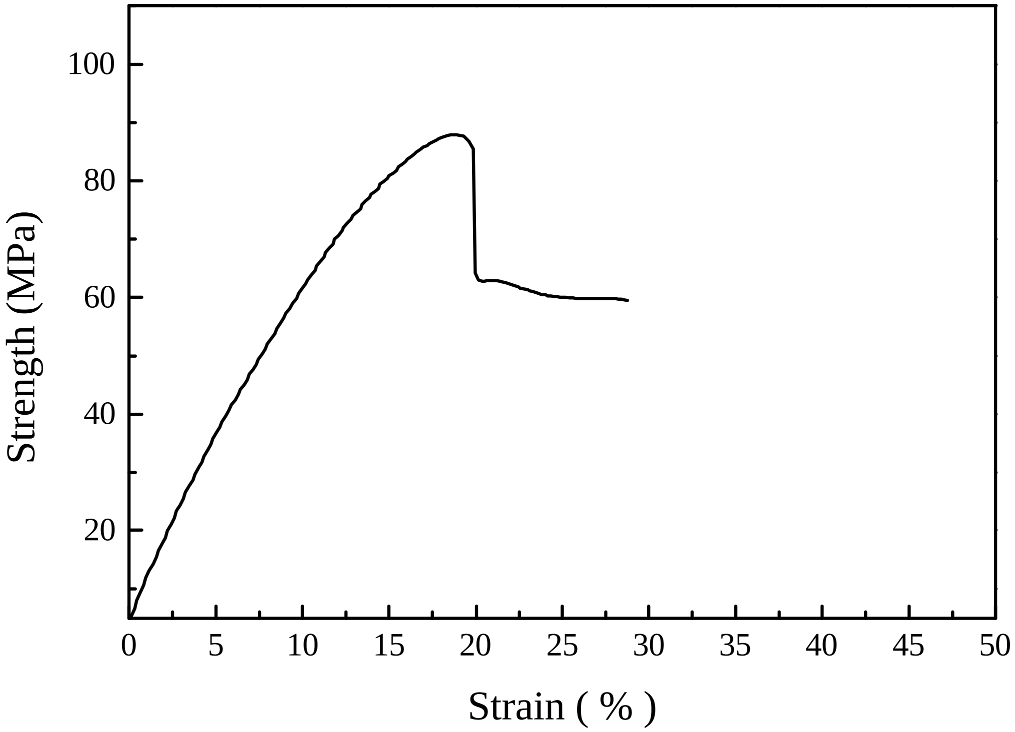


Figure 4.1.5.4 Tensile stress-strain behavior of PPSS ($M_n$=43,000 g/mole) at a cross head speed of 1.0 mm/min. (rom temperature).

Table 4.1.5.3. Room Temperature Stress-Strain Behavior of Compression Molded PPSS

| $M_n$ (g/mol) | Tensile Strength[a] (MPa) | Elongation at Break[a] (%) |
|---|---|---|
| 20,000 | 74.5 ± 71 | 12.5 ± 3.1 |
| 25,000 | 88.5 ± 0.5 | 17.4 ± 0.8 |
| 30,000 | 92.8 ± 0.7 | 22.2 ± 3.1 |
| 39,000 | 92.9 ± 0.6 | 22.0 ± 3.7 |
| 43,000 | 93.9 ± 0.7 | 22.3 ± 4.1 |
| Udel | 70.0 ± 6.9 | >40 |
| Victrex[b] | 86 | 17 |

[a] ASTM D638 (1.0 mm/min), average value of eight samples

[b] Encyclopedia of polymer Science and Engineering 2nd ed.; H. Tamada, et al., Polym. J., 25(4), 339, (1993).

The flammability behavior of PPSS was examined by cone calorimetry in corporation with Dr. T. Kashiwagi of the NIST Fire Laboratories, with the commercial Udel and Victrex polyarylene ether sulfones and poly(phenylene sulfide) (PPS) used as controls. Cone calorimetry is an important measurement of the heat release rate and the amount of heat released by a polymer due to combustion under a specific applied heat flux. These results are summarized in Figure 4.1.5.5 and Table 4.1.5.4. The Udel control had the highest heat release rate of the samples analyzed, which may be due to the partially aliphatic bisphenol-A structure. It should be noted in Figure 4.1.5.5 and Table 4.1.5.4 that the poly(phenylene sulfide sulfone) displayed a much lower heat release rate in comparison with Udel, Victrix, and PPS, indicating good fire resistance.

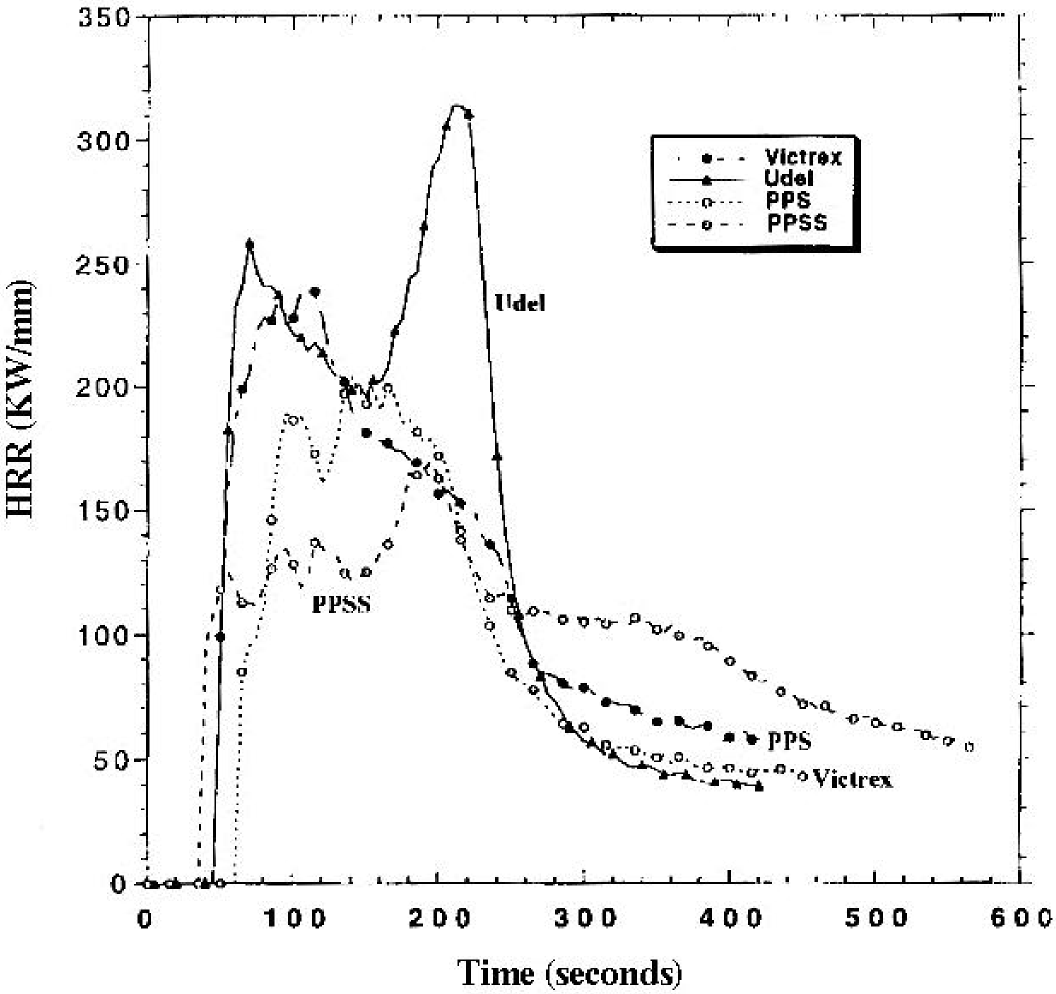
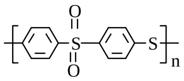
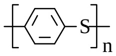
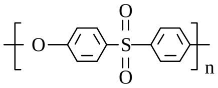
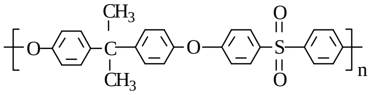


Figure 4.1.5.5 Cone calorimetry results (70 KW/m$^2$)

Another way to analyze the heat release rate is to average the heat release rate over time, e.g. 180 seconds. An average heat release rate allows one to generate a combustion time cycle. For example, in a "real-life" fire not every portion of the burning item is undergoing its peak burning. Indeed, some portions could be barely igniting while others are decaying. Therefore, to better analyze how a material behaves in a "real-life" fire, it is necessary to determine the average heat release rate over a period of time. Statistical consideration developed at NIST led to 3 minutes being utilized as the averaging period (182). When considering the 3 minute averaging period, the change in heat release rate of the PPSS with respect to the three commercial materials, PPS, Udel, and Victrex, is dramatic. Not only did the PPSS show a lower peak heat release rate, but it also demonstrated an improved average heat release rate under the conditions tested.

Table 4.1.5.4 Comparison of Peak Heat Release Rate (HRR) of Various Polymers

| Polymer | Structure | Heat Release Rate* ($kW/m^2$) |
|---|---|---|
| PPSS |  | 165 |
| PPS |  | 198 |
| Victrex |  | 235 |
| Udel |  | 310 |

* Samples tested using cone calorimetry at a flux of 70 $kW/m^2$

## 4.1.6 Conclusions

High molecular weight poly(phenylene sulfide sulfone)s (PPSS) have been successfully synthesized under the following optimum reaction conditions: reaction temperature of 175°C - 200°C, reaction time of 3 – 5 hours, and water-to-NaSH molar ratio of 9.4:1 to 15:1. In addition, these materials could be compression molded to produce tough, solvent resistant films that showed good thermal stability in air and degraded via a two-step mechanism. Other attractive properties include good fire resistance and very high refractive index values.

## *4.2 Synthesis and Characterization of Poly(Phenylene Sulfide Sulfone)s with Well Designed Endgroups*

### 4.2.1 Introduction

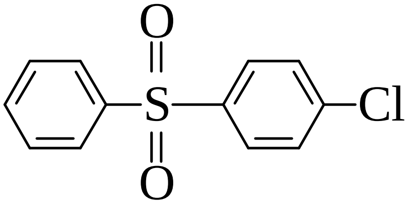
In recent years, a wide variety of high performance polymers has been prepared, many of which are currently being produced and marketed on a large scale. In particular, thermoplastic polymers can be molded rapidly and efficiently into almost any desired shape, and are thus good candidates for mass production.

Poly(phenylene sulfide sulfone)s (PPSS) are engineering thermoplastics of commercial interest for films, molding and composite applications because of their high glass transition temperatures, good mechanical and electrical properties, and good chemical resistance. The most common process for producing poly(phenylene sulfide sulfone)s involves reacting a dichlorodiphenyl sulfone with an alkali metal sulfide in NMP at elevated temperature and pressure via an aromatic nucleophilic substitution reaction (120, 124).

Despite the advantages noted above, poly(phenylene sulfide sulfone)s have in the past is exhibited relatively low melt stability and were not very processable, possibly due to the presence of mercaptans or metal sulfides as end groups on polymer chains (189-191). However, the patent literature describes a method of producing PPSS with increased melt stability, which involes treating the polymer with a zinc source, thereby incorporating zinc cations into the polymer (192-193). For certain poly(phenylene sulfide sulfone) applications, however, including the production of injection molded parts, the polymer must exhibit a high degree of clarity. This requires that the polymer be relatively free of impurities, such as salt by-products and metal ions. Unfortunately, the process by which the melt stability of PPSS is increased is likely to introduce impurities into the polymer, which affect the clarity of molded parts (190-191). For other applications using PPSS, such as the production of composites, it is also desirable to have a polymer of increased purity to aid in the interfacial bonding of the resin and fiber used in the composite. Again, impurities in the polymer could interfere with the resin/fiber interfacial bonding and are undesirable.

Therefore, the objective of this study was to provide a method for preparing PPSS with increased melt stability, while not adversely affecting the purity and clarity of the polymer. This section describes the synthesis of the poly(phenylene sulfide sulfone)s with three different thermally stable end groups, diphenyl sulfone, t-butylphenoxide, and 4-chlorophenylphenyl sulfone. Their chemical structures and thermal properties were characterized and evaluated, in comparison with the mercaptide endcapped PPSS control.

### 4.2.2 Synthesis of Monofunctional 4-Chlorophenylphenyl Sulfone End Capper



The monofunctional compound, 4-chlorophenylphenyl sulfone (CPPS), was applied as a reactive endcapper and was successfully synthesized using a modified procedure based on reference (177). This synthetic approach utilized for preparing CPPS is outlined in Scheme 3.1.2, in which benzenesulfonyl chloride is reacted with chlorobenzene in the presence of anhydrous $AlCl_3$ as the catalyst, via the Friedel-Aldrich reaction. This reaction was complete after refluxing for 6 hours and afforded yields of 75-80% after recrystallization from toluene (melting point: 106-107$^{o}$C). The molecular structure of this material was confirmed using $^{1}$H and $^{13}$C NMR in $CDCl_3$. These spectra are shown below in Figures 4.2.2.1and 4.2.2.2. The $^{1}$H NMR spectrum reveals the appearance of three different aromatic protons shown as $H_a$ (7.86-7.94 ppm), $H_b$ (7.50-7.58 ppm), and $H_c$ (7.45 ppm), all exhibiting proper integration. The $^{13}$C NMR spectrum shows eight different peaks in the range of 127.8-141.0 ppm, which correspond to the eight different aromatic carbons in this compound. Elemental analysis of this compound is in good agreement with the designed chemical structure.

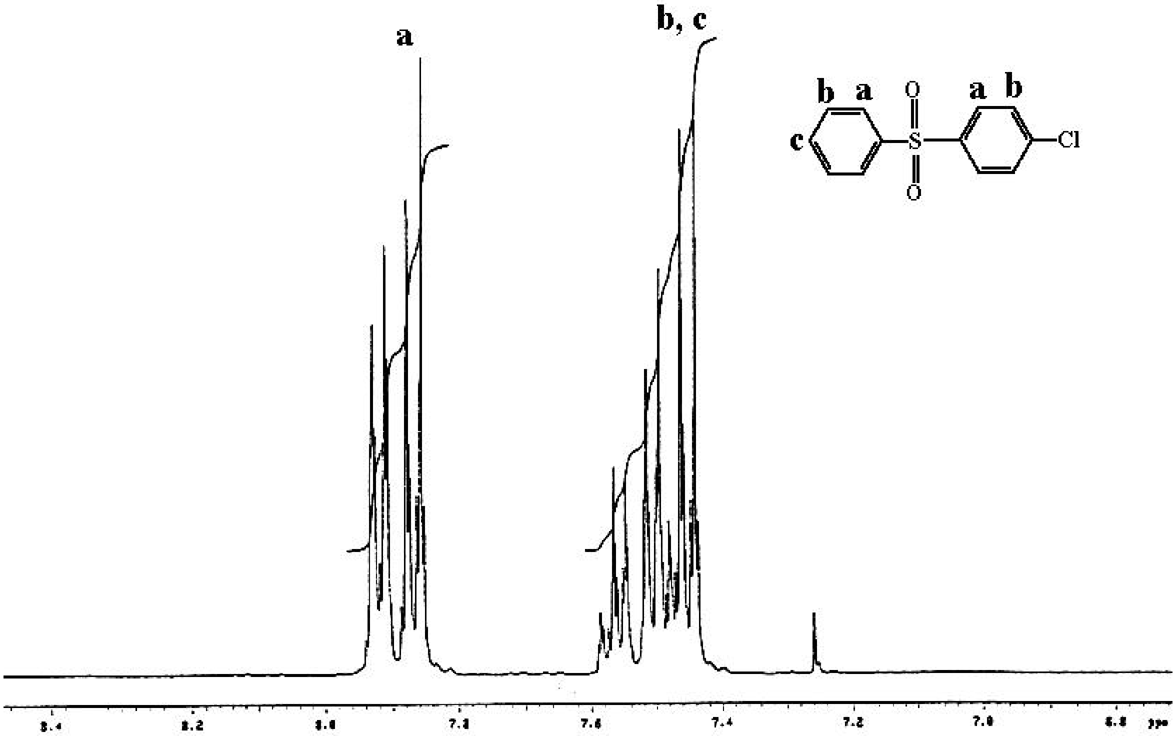


Figure 4.2.2.1 $^1$H NMR spectrum of 4-chlorophenylphenyl sulfone (CPPS) in CDCl$_3$

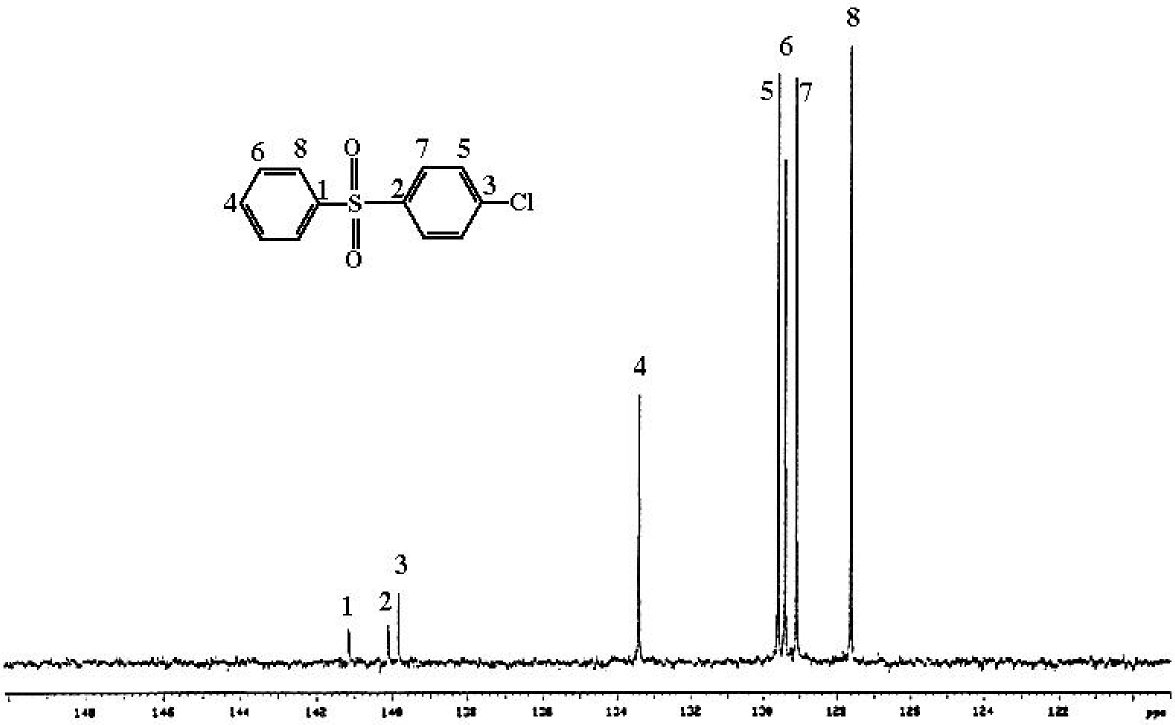
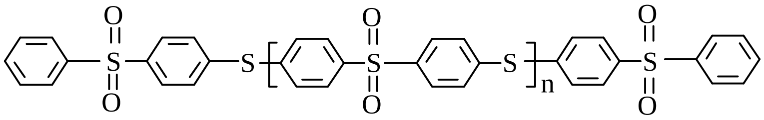
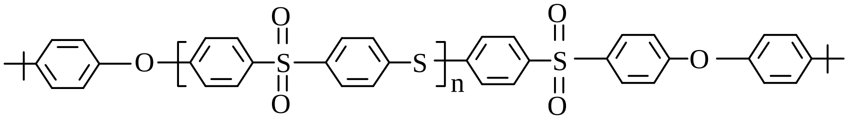
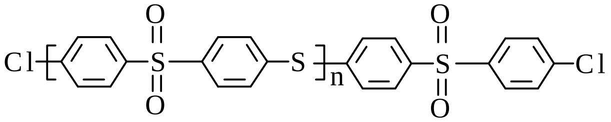


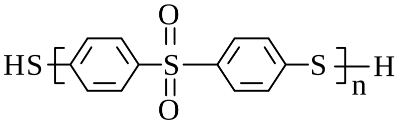
Figure 4.2.2.2 $^{13}$C NMR spectrum of 4-chlorophenylphenyl sulfone (CPPS) in CDCl$_3$

### 4.2.3 Synthesis of PPSS with Well Designed Endgroups


**1a**


**1b**


**1c**


**1d**

To a great extent, the thermal properties of poly(phenylene sulfide sulfone)s are dependent on the nature of their endgroups. It has been found that the mercaptide-type endgroups, as well as the presence of impurities such as inorganic salts and metal ions, will deteriorate their melt stability and result in dark and brittle melt molded films (190-191). In order to investigate the structure/melt stability relationship, and improve the thermal properties of PPSS, three types of PPSS with thermally stable endgroups, (diphenyl sulfone, 4-chlorophenylphenyl sulfone, and t-butylphenoxide), have been prepared. In addition, mercaptide endcapped PPSS was also synthesized and used as a control. Scheme 3.2.4-3.2.7 shows the synthesis of these polymers, which was conducted in a pressure reactor at 100 - 150 Psi and 200$^{o}$C for 3 hours. The formation of PPSS proceeded by nucleophilic aromatic substitution step polymerization. 4,4′-dichloro-diphenyl sulfone (DCDPS) was reacted with sodium hydrosulfide in the presence of sodium hydroxide, sodium acetate, and deionized water in NMP. The NMP-to-water and NMP-to-sulfur molar ratios utilized were about 0.85-to-1 and 8-to-1, respectively. The diphenyl sulfone endcapped PPSS (**1a**) and t-butylphenoxide endcapped PPSS (**1b**) were prepared utilizing 4 mole percent of monofunctional compounds of 4-chlorophenylphenyl sulfone (CPPS) and t-butylphenol (BP), respectively. The PPSS with 4-chlorophenylphenyl sulfone endgroups (**1c**) was synthesized using 2 mole percent excess of DCDPS relative to sodium hydrosulfide. The control sample, mercaptide endcapped PPSS (**1d**), was obtained by using 2 mole percent excess of sodium hydrosulfide relative to DCDPS in the stoichiometry. The chemical structures of these endgroups were analyzed via 10 mm $^{13}$C and $^{1}$H NMR in DMSO-$d_6$ at 140°C, using high temperature to maintain the polymers in solution. The resulting spectra are shown in Figures 4.2.3.1-4.2.3.5. The diphenyl sulfone endgroups in polymer **1a** were observed in Figure 4.2.3.1 and appear at 133.4 ppm. The t-butyl endgroups in polymer **1b** were observed by both $^{13}$C NMR (31 ppm) and $^{1}$H NMR (1.32 ppm) in Figures 4.2.3.2 and 4.2.3.3, respectively. As seen in Figure 4.2.3.4, the peak corresponding to the mercaptide endgroups in the control sample (**1d**) was observed at ~133.2 ppm and is quite large. Although the peak corresponding to the 4-chlorophenylphenyl sulfone endgroup in Figure 4.2.3.5 was overlapped by one of the major peaks of the polymer backbone at 139.9 ppm, it can be seen that the peak of the mercaptide endgroups was very small, which suggests that the predominant end group in polymer **1c** is the 4-chlorophenylphenyl sulfone, as expected. After examining these spectra, it was found that the ether linkages or hydroxide endgroups were also present in all of the synthesized polymers (115.1 ppm in $^{13}$C NMR spectra), which could be derived from a hydrolysis side-reaction during the polymerization.

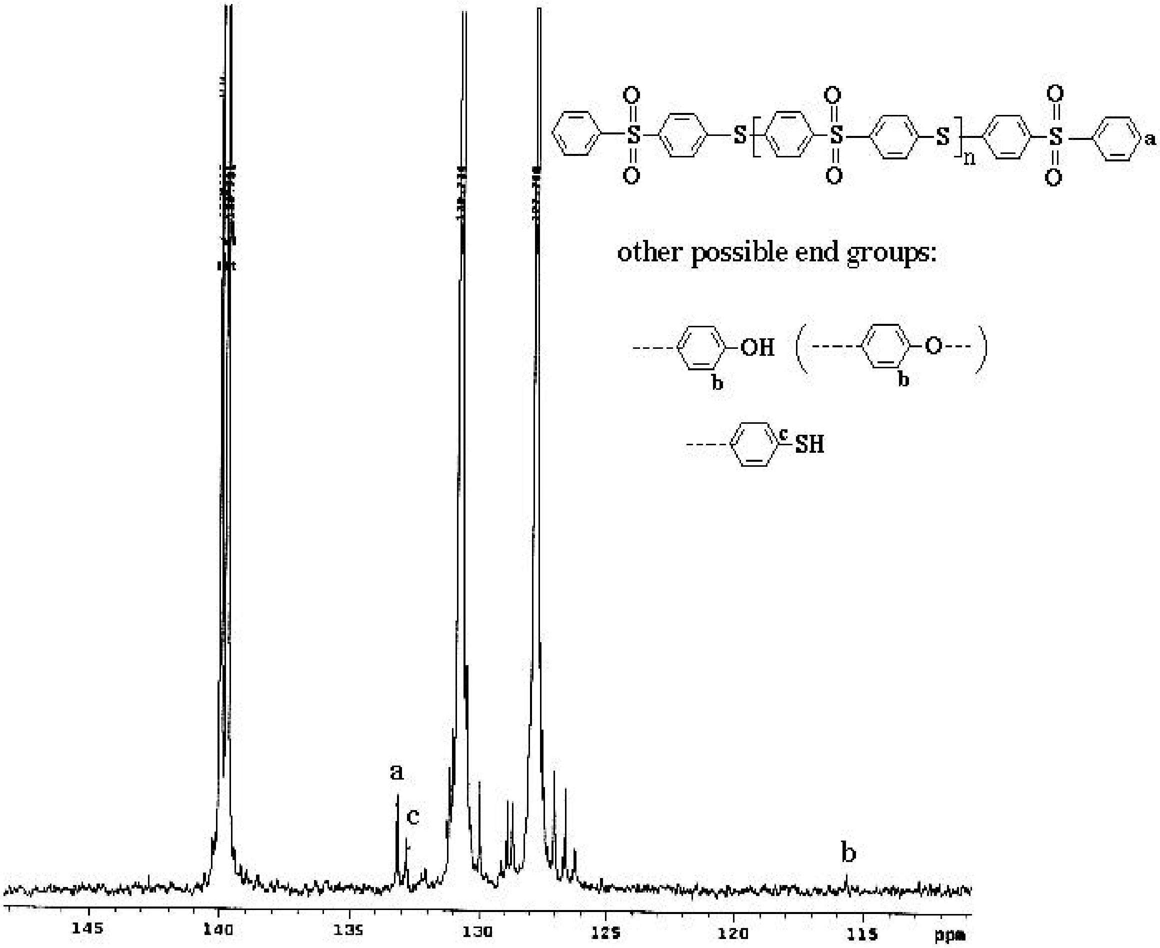


Figure 4.2.3.1 $^{13}$C NMR spectrum of polymer **1a** in DMSO-$d_6$ at 140°C

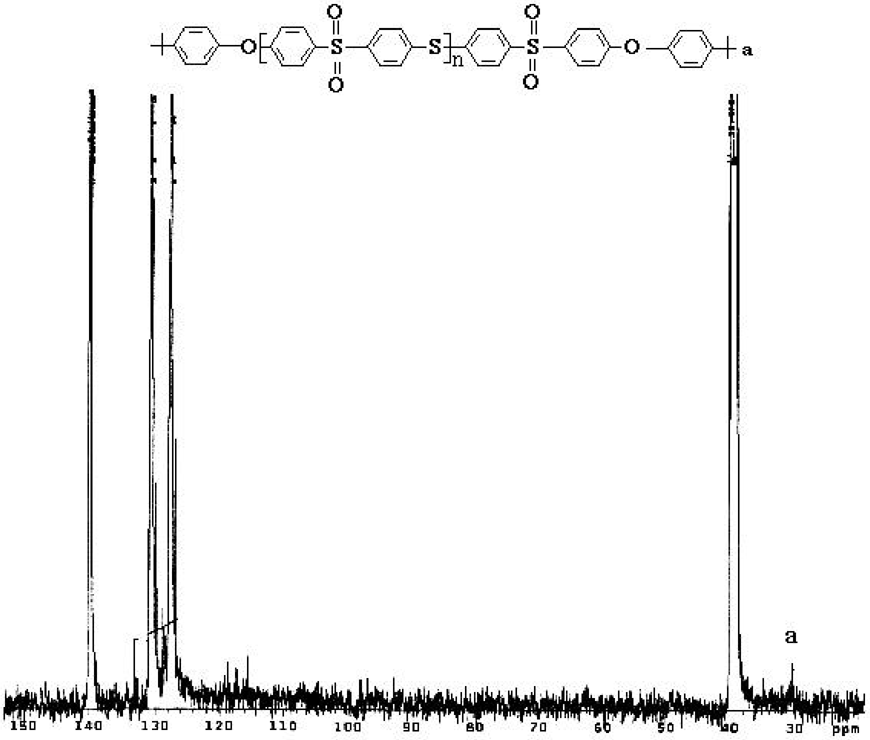


Figure 4.2.3.2 $^{13}$C NMR spectrum of polymer **1b** in DMSO-$d_6$ at 140$^{o}$C

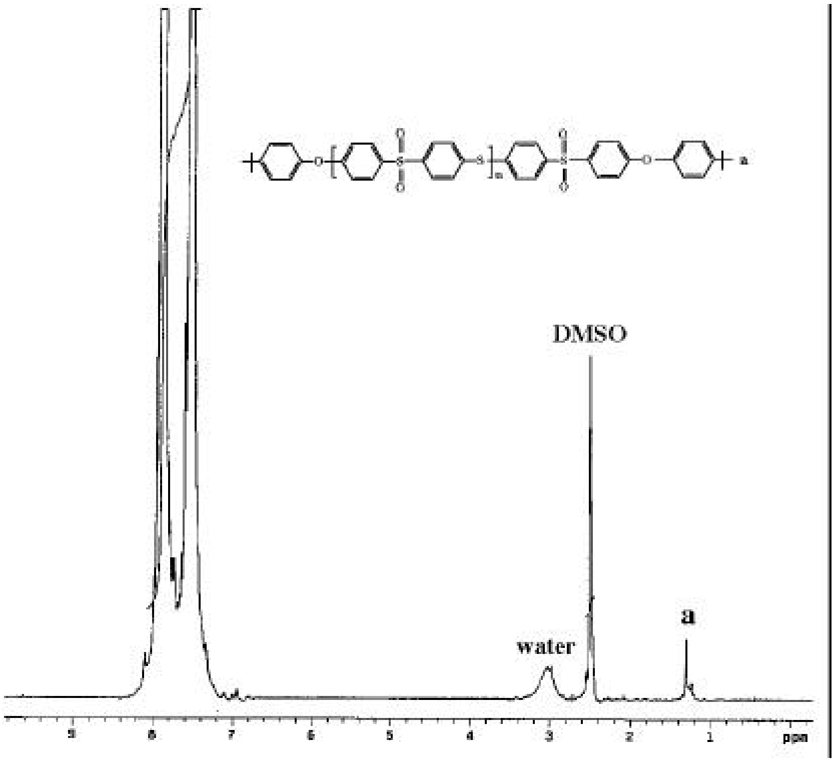


Figure 4.2.3.3 $^{1}$H NMR spectrum of polymer **1b** in DMSO-$d_6$ at 140$^{o}$C

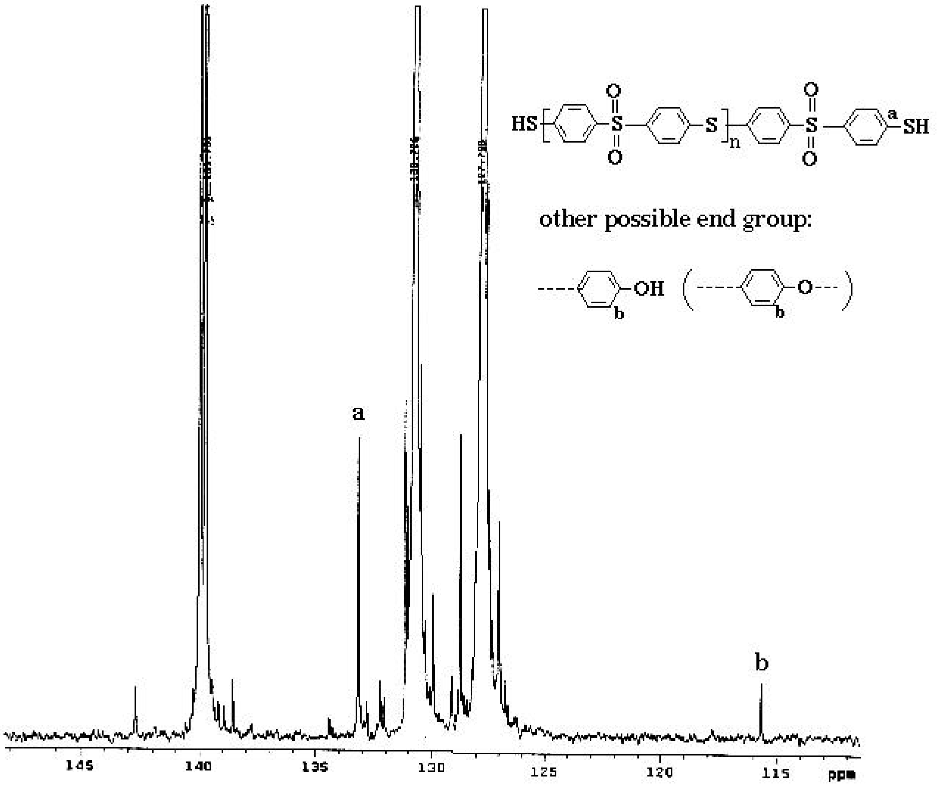


Figure 4.2.3.4 $^{13}$C NMR spectrum of polymer **1d** in DMSO-$d_6$ at 140$^{\circ}$C

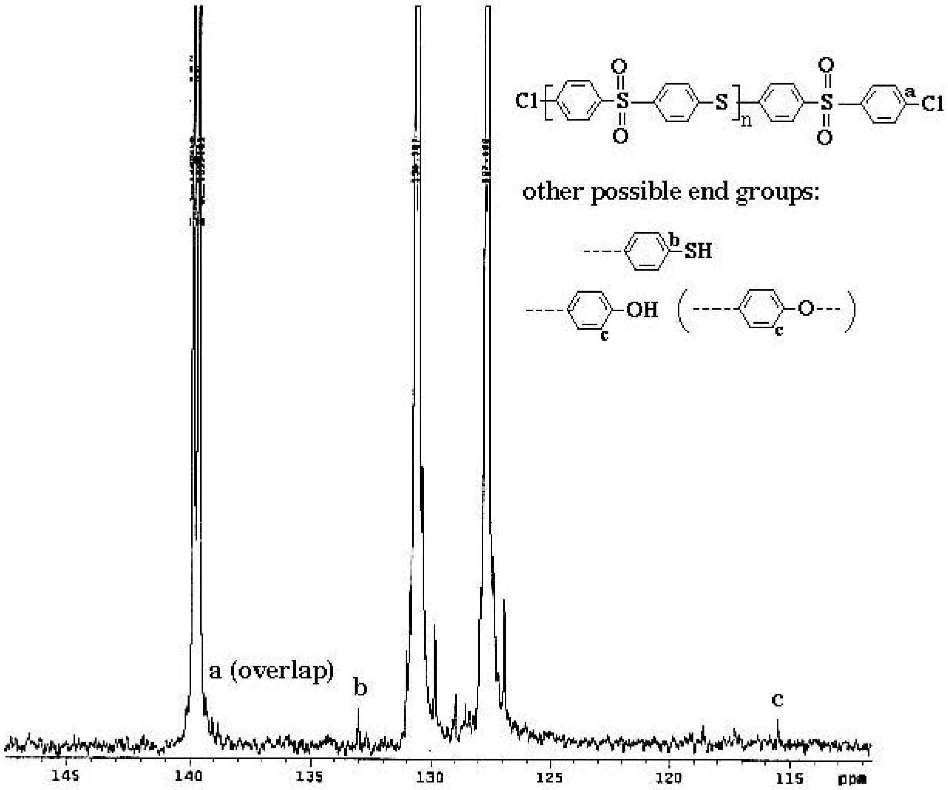


Figure 4.2.3.5 $^{13}$C NMR spectrum of polymer **1c** in DMSO-$d_6$ at 140$^{\circ}$C

### 4.2.4 Molecular Weight and Thermal Transition Characterization by GPC, Intrinsic Viscosity and DSC

Determining absolute molecular weight averages and distribution of the polymer samples was accomplished using a universal calibration GPC (186). Eighteen different polystyrene standards with low polydispersity indices were used to construct a calibration curve. The results for the molecular weight characterization, along with intrinsic viscosity data for the poly(phenylene sulfide sulfone)s with different endgroups are listed in Table 4.2.4.1. The molecular weight control could be achieved by offsetting the stoichiometry and the target molecular weight calculated from the Carothers equation is 25,000 g/mole in all of the cases. As demonstrated in Table 4.2.4.1, however, the experimental molecular weights obtained from GPC analysis were in the range of 21,000 - 31,000, but only polymer **1d** corresponded well with the theoretical molecular weight. The molecular weights of the remaining polymers **(1a**, **1b**, and **1c)** varied from the target value, possibly due to side reactions such as hydrolysis, which deteriorate the stoichiometry utilized. The relatively narrow molecular weight distribution may be due to the fact that these polymers were purified by being precipitated twice. It is thought that the low molecular weight fraction may have remained in the methanol precipitation medium, which would produce a polydispersity index ($M_w/M_n$) less than the theoretical value of 2.0. Intrinsic viscosities were measured in NMP solution at 30$^o$C and increased with increasing molecular weight (Table 4.2.4.1). The thermal transition behavior of the polymers was analyzed by differential scanning calorimetry (DSC) at a heating rate of 10$^o$C/min. under a nitrogen atmosphere. The glass transition temperatures ($T_g$s) of polymers **1a-d** were observed to be in the range of 211$^o$C-217$^o$C (Table 4.2.4.1and Figure 4.2.4.1) from the second scans. It should be noted that endgroup structure did not appear to have a significant effect on $T_g$s.

Table 4.2.4.1 GPC, Intrinsic Viscosity and DSC Characterization Data

| Polymer | Target $M_n$ (g/mol) | $M_n$ (g/mol) by GPC | $M_w/M_n$ by GPC | $[\eta]^a$ (dL/g) | $T_g^b$ (°C) |
|---|---|---|---|---|---|
| **1a** | 25,000 | 21,000 | 1.8 | 0.32 | 215 |
| **1b** | 25,000 | 31,000 | 1.7 | 0.46 | 217 |
| **1c** | 25,000 | 29,000 | 1.9 | 0.44 | 217 |
| **1d** | 25,000 | 25,000 | 1.8 | 0.37 | 211 |

[a] in NMP solution, 30°C,

[b] measured by DSC in $N_2$, heating rate of 10°C/min., 2nd heat.

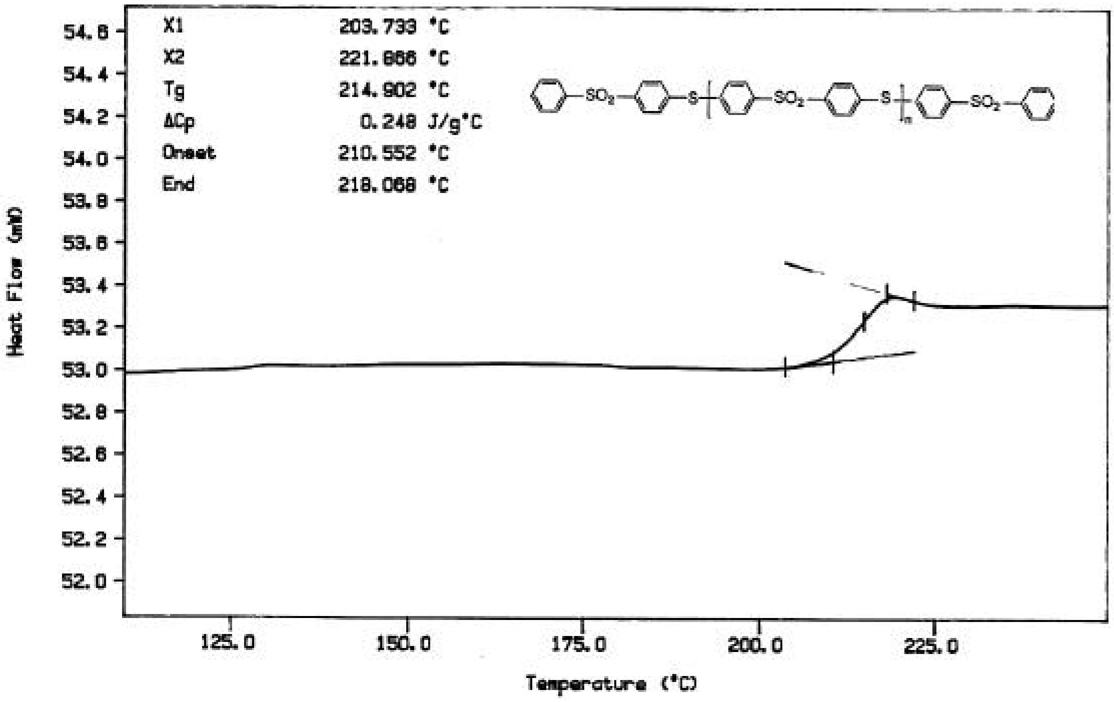


Figure 4.2.4.1 DSC thermogram of polymer **1a** (10°C/minute in $N_2$, 2nd heat)

### 4.2.5 Influence of Molecular Structures on Melt Rheology and Thermal Stability

Thermogravimetric analysis (TGA) was used to determine weight loss and, by implication, the thermal stability of these polymers in an air atmosphere. Table 4.2.5.1 and Figure 4.2.5.1 illustrates the effect of the endgroups upon the TGA char yields and initial degradation temperatures of the polymers **1a**-**1d**. As shown, the 2% weight loss temperatures in air ranged from 458°C-464°C for polymers **1a-c**, whereas the control sample (**1d**) showed an initial degradation temperature of 429°C. Furthermore, polymers **1a**-**1c** have ~10 wt.% increase in char yields at 650°C in air, compared to the mercaptide endcapped PPSS control. Clearly, TGA analysis indicates that the PPSS with thermally stable endgroups, such as diphenyl sulfone (**1a**), t-butylphenoxide (**1b**), and 4-chlorophenyl phenyl sulfone (**1c**), have much higher thermal stability than the mercaptide endcapped PPSS (**1d**).

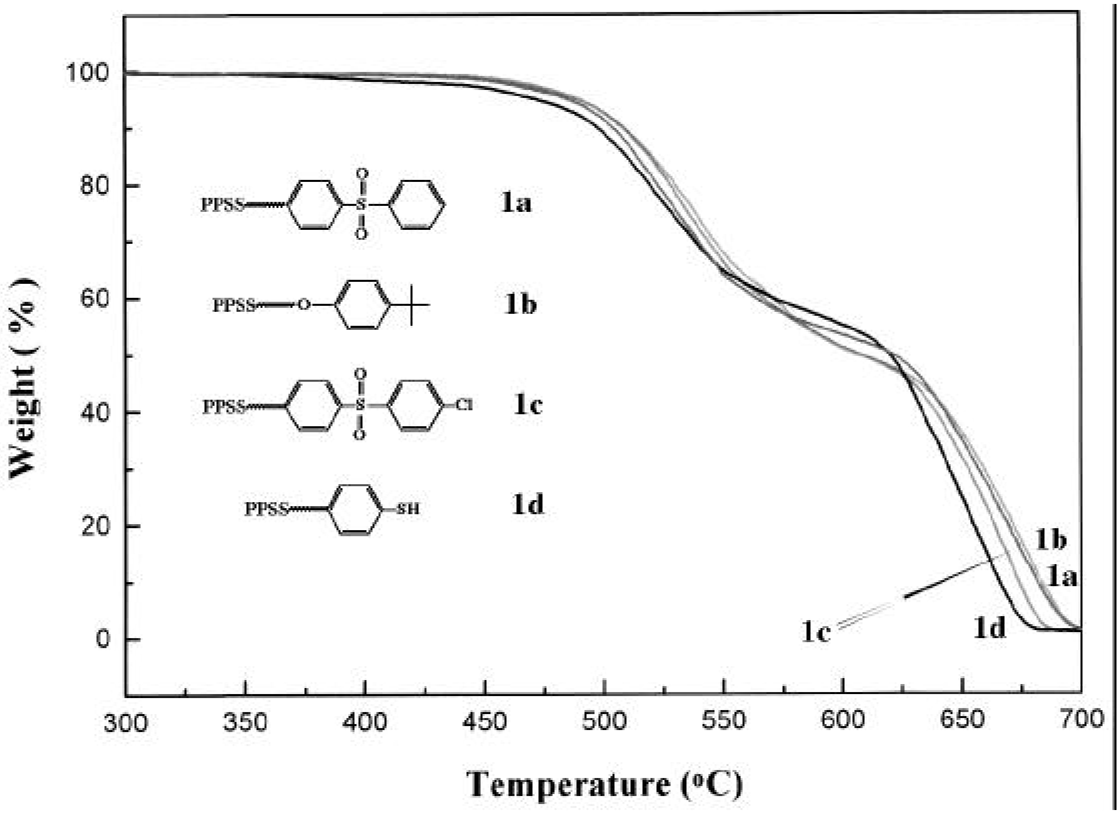
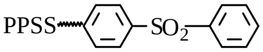
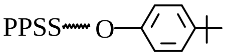
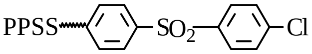
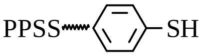


Figure 4.2.5.1 The effect of endgroups on the TGA behavior of PPSS in air (10°C/min.)

Table 4.2.5.1 The Effect of Endgroup Structures on TGA Weight Loss Behavior of PPSS

| Polymer | Structure | 2% Wt. Loss Temp. (°C)[a] | 5% Wt. Loss Temp. (°C)[a] | % Char Yield[a] at 650°C |
|---|---|---|---|---|
| **1a** |  | 462 | 490 | 34.6 |
| **1b** |  | 458 | 486 | 35.5 |
| **1c** |  | 464 | 488 | 32.2 |
| **1d** |  | 429 | 473 | 24.2 |

[a]heating rate of 10°C/minute in air.

The melt stability of polymers **1a-1d** was characterized using a Bohlin Rheometer. Melt viscosity measurements were conducted using rheological parallel plates at a frequency of 1 Hz and a constant temperature of 300°C. As can be seen in Figure 4.2.5.2, the viscosity *vs*. time results for polymers **1a-c** indicate that their melt viscosities were almost constant for one hour at 300°C. On the other hand, the melt viscosity of the control sample (**1d)** increased with time and almost doubled after 1 hour, suggesting that some grafting and/or crosslinking reactions occurred, since the mercaptide is a reactive endgroup. These results clearly demonstrate that the poly(phenylene sulfide sulfone)s containing thermally stable end groups of diphenyl sulfone, 4-chlorophenylphenyl sulfone, or t-butylphenoxide, have significantly improved melt stability and processibility in comparison to the mercaptide endcapped PPSS control sample.

The resulting compression molded films produced from polymer **1a-1c** were transparent and ductile, whereas the film from polymer **1d**, the mercaptide endcapped PPSS, was dark in color. The dynamic mechanical behavior (DMA) of the films using polymers **1a** and **1d** have also been investigated and are shown in Figure 4.2.5.3. These materials showed a high modulus up to temperatures approaching the glass transition temperatures, and exhibited a

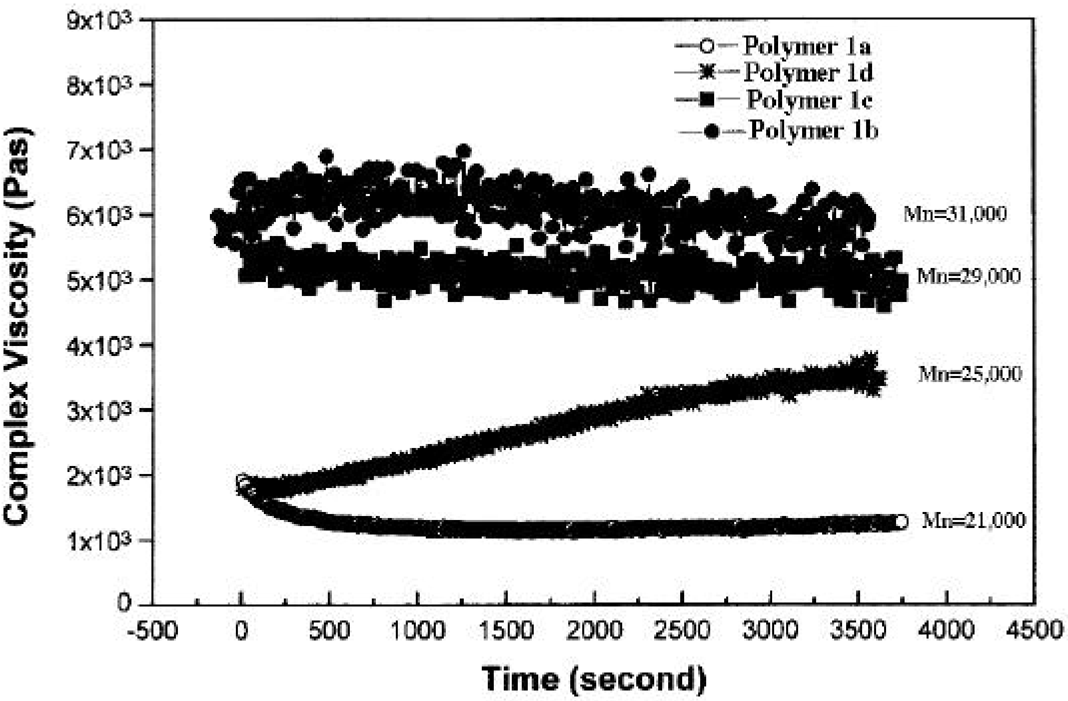


Figure 4.2.5.2 The effect of endgroups on melt viscosities of PPSS at 300°C

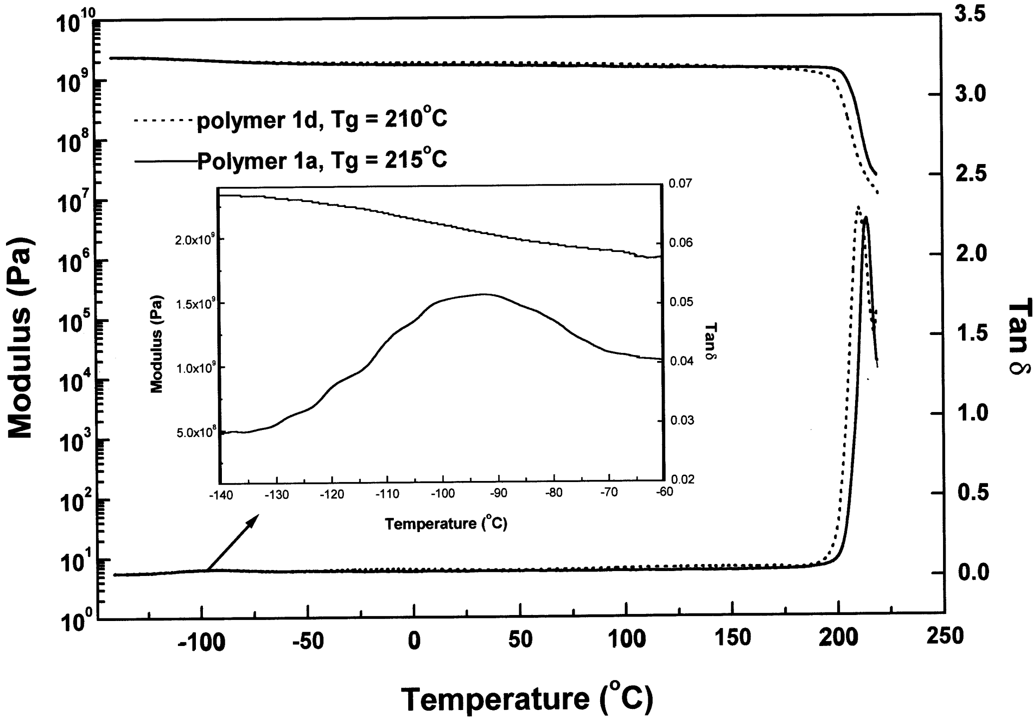


Figure 4.2.5.3 DMA analyses of polymer **1a** and **1d** (1Hz, 2°C/min.)

secondary relaxation at -93$^{o}$C.  It should be pointed out that these low temperature beta transitions are often considered to be important to molecular motion, which may result in desirable impact resistant properties.  The relaxation motions may play a role in absorbing the energy of the impact without failure. Therefore, the fact that beta transitions are observed for the PPSS polymers at low temperature is an indicator of molecular motion well below $T_g$, which is often tied to enhanced ductility.

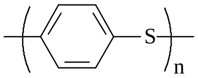
### 4.2.6  Conclusions

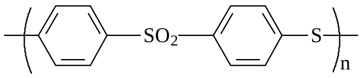
Poly(phenylene sulfide sulfone)s with well designed endgroups were successfully synthesized.  The molecular structures of the end groups were confirmed by $^{13}$C and $^{1}$H NMR analyses.  In comparison with the mercaptide endcapped PPSS, the PPSS with diphenyl sulfone, 4-chlorophenylphenyl sulfone, and t-butylphenoxide endgroups showed much higher initial degradation temperatures, as judged by 2% weight loss, higher char yields at 650$^{o}$C in air, and significantly improved melt stability.

## *4.3 A New Simplified Approach for the Synthesis of Poly(Phenylene Sulfide Sulfone) Homo- and Phosphine Oxide Containing Co-Polymers Using an A-A Type Dithiol Monomer*

### 4.3.1 Introduction

Poly(phenylene sulfide) (PPS) is an important commercially available engineering thermoplastic, which has been the focus of continued intensive research for the past two decades. It is a semicrystalline polymer with a $T_g$ of approximately 85°C, and a $T_m$ of about 285°C (15, 62). PPS is considered to be inherently fire resistant, and displays excellent chemical resistance. PPS is an important molding resin, which has been used in many applications such as a matrix material for thermoplastic composites. The related sulfide sulfone polymer, however, has has not been well studied, and references to it are predominately found only in the the patent or commercial trade literature. poly(phenylene sulfide sulfone) (PPSS) has been described as an amorphous polymer with a $T_g$ around 217°C (119). It is prepared by the nucleophilic polycondensation reaction of sodium sulfide and 4,4′-dichlorodiphenyl sulfone as the activated aromatic halide in N-methyl-2-pyrrolidinone (NMP), at elevated temperature and pressure (120, 123). Unfortunately, this procedure is quite complicated and the reaction mechanism is unclear. For example, in order to obtain high molecular weight polymers, high pressure (150-180 Psi) and high temperature (185-200°C) must be utilized, along with inorganic salts such as sodium acetate and strong base (NaOH or $Na_2CO_3$) (122-124). Furthermore, in order to obtain high molecular weight PPSS, water must be present in the reaction medium, and the proper molar ratios of NMP-to-water (0.85/1) and NMP-to-NaSH (8/1) are critical (122-124).

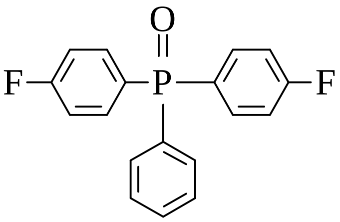




The synthesis of novel phosphorus containing polymers, which are well known to be fire resistant, has been extensively studied (139, 141, 135-137). Particular emphasis has been placed on hydrolytically stable, melt processable, high performance polymeric materials that are capable of demonstrating either high glass transition temperatures and/or high semicrystalline melting points. The latter are of interest for applications requiring excellent chemical resistance, such as for textile fibers and many engineering thermoplastic applications. Amorphous, high glass transition temperature materials are also desirable for applications requiring transparency and exceptionally high impact strength. As an example, the triphenylphosphine oxide unit is inherently non-coplanar and leads, in general, to amorphous homopolymers displaying high transition temperatures, good optical transparency, very high char yields when exposed to either nitrogen or air, ductile mechanical behavior, and good adhesive characteristics (especially to metals). A number of aryl phosphine oxide containing monomers have been developed, and the properties of the resulting polymers, including poly(arylene ether)s, polyimides, polyesters, polyamides, and polycarbonates, derived from them with a variety of aryl phosphine oxide contents have been evaluated (139, 141, 175, 177, 178). It is interesting to incorporate a triphenylphosphine oxide moiety into the PPSS backbone because of its high temperature stability, flame resistance, and improved interaction between the polar phosphine oxide groups of the polymer matrix and the functionalized carbon or glass fibers. Our early study (194) showed that it was difficult to prepare high molecular weight phosphine oxide containing PPSS polymers via the traditional high pressure method, possibly due to the varying reactivities of the aromatic halides, as well as the poorly understood unusual condensation reaction mechanism. A new simplified approach has been developed based on a new A-A type dithiol monomer, which allows novel high molecular weight aryl phosphine oxide containing poly(phenylene sulfide sulfone)s to be prepared. This section describes the synthesis and characterization of poly(phenylene sulfide sulfone) homopolymers and a series of related copolymers with a variety of triphenyl phosphine oxide contents, via direct polycondensation in DMAc, in the presence of anhydrous potassium carbonate.

## 4.3.2 Monomer Synthesis and Characterization

### 4.3.2.1 Bis-(4-fluorophenyl)phenylphosphine Oxide (BFPPO)



This activated halide monomer was synthesized utilizing Grignard chemistry via the reaction of *p*-bromofluorobenzene and phenylphosphonic dichloride, as described in Section 3.1.3.2. These reactions were conducted at room temperature and afforded yields of 80-85% after recrystallization in a THF/cyclohexane (1/5 v/v) solution. The melting point was 130-131°C and the molecular structure was confirmed using $^1$H and $^{31}$P NMR in $CDCl_3$. These spectra are shown below in Figure 4.3.2.1.1 and 4.3.2.1.2. There are five different aromatic protons shown as $H_{a,b}$ (7.65 ppm), $H_c$ (7.56 ppm), $H_d$ (7.48 ppm), and $H_e$ (7.16 ppm). These protons appear as higher multiplets, due to coupling with phosphorus, which has a spin of 1/2. The phosphorus shows a singlet at 28.1 ppm and the small side peaks equidistant on either side of the major phosphorus peak are side bands.

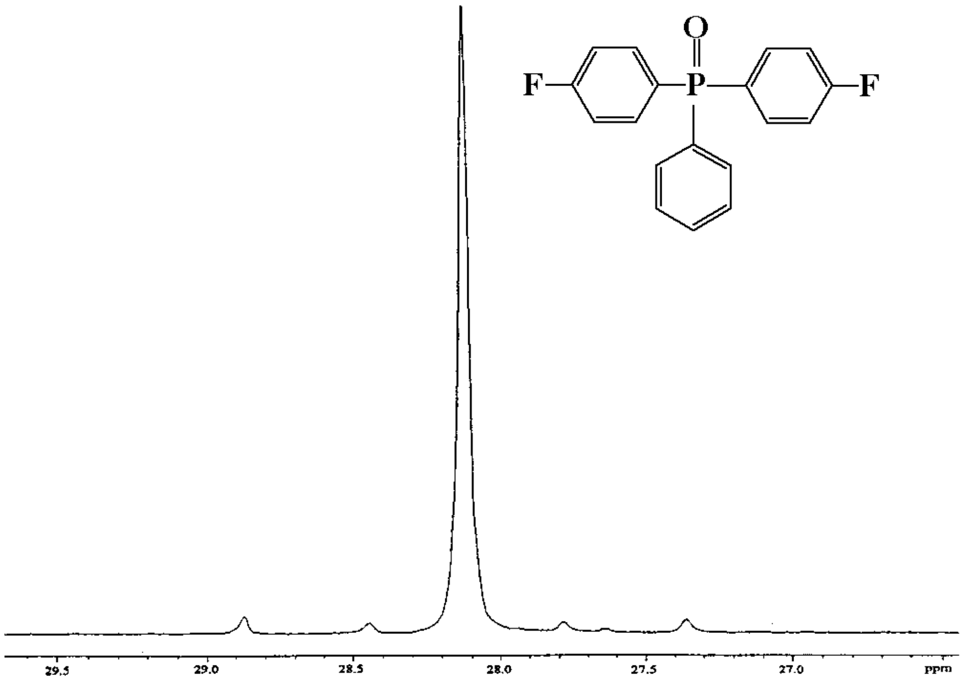


Figure 4.3.2.1.1 $^{31}$P NMR spectrum of BFPPO in CDCl$_3$

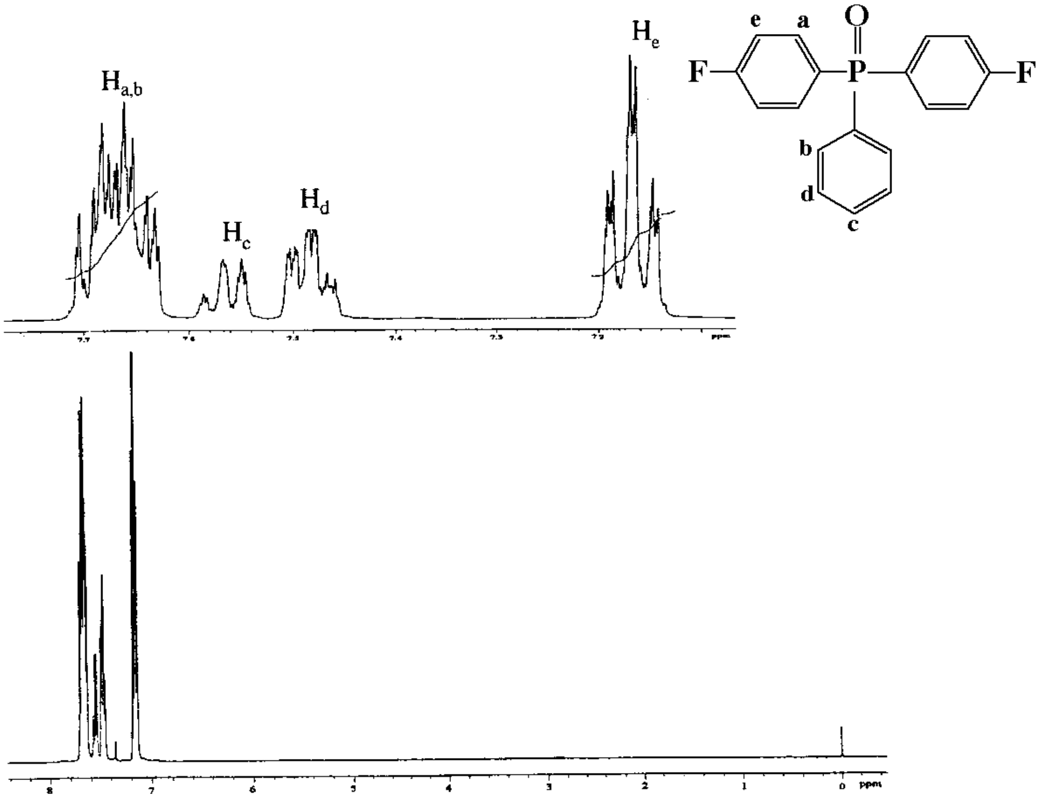
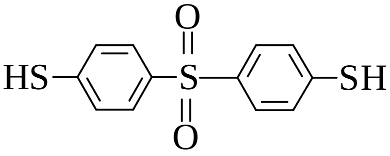


Figure 4.3.2.1.2 $^1$H NMR spectrum of BFPPO in CDCl$_3$

### 4.3.2.2 Bis-(4-mercaptophenyl) Sulfone (BMPS)



The synthesis of the dithiol monomer, bis-(4-mercaptophenyl) sulfone (BMPS), is described in Section 3.1.3.4. The synthetic approach used for preparing the BMPS is based on a sulfone activated chloro-displacement by the hydrosulfide via an aromatic nucleophilic substitution reaction. By reacting 4,4′-dichlorodiphenyl sulfone with a large excess of sodium hydrosulfide in DMSO in the presence of potassium carbonate, the dithiol monomer, BMPS, was obtained in 66% yield. The reaction temperature was controlled at around 120$^{o}$C for 20 hours. Higher temperature resulted in lower yield, due to the formation of low molecular weight oligomers, which were insoluble in basic aqueous solution. The BMPS monomer was purified by precipitation twice from basic aqueous solution, to afford white powder crystal with a sharp melting point at 144-145$^{o}$C. The molecular structure of this material was confirmed using $^{1}$H and $^{13}$C NMR in $CDCl_3$. These spectra are shown below in Figure 4.3.2.2.1 and 4.3.2.2.2. The two different aromatic protons appear at $H_a$ (7.25 ppm) and $H_b$ (7.33 ppm) and the thiol group appears up field at 3.64 ppm. The protons have an integration ratio of 4 aromatic protons/1 thiol proton. The $^{13}$C NMR spectrum shows 4 different peaks corresponding to the 4 different carbons present in the BMPS. The elemental analysis results were also in excellent agreement with the designed chemical structure of the BMPS (Calc.: C, 51.03%, H, 3.56%, S, 34.06%: Found: C, 50.96%, H, 3.49, S, 34.56%).

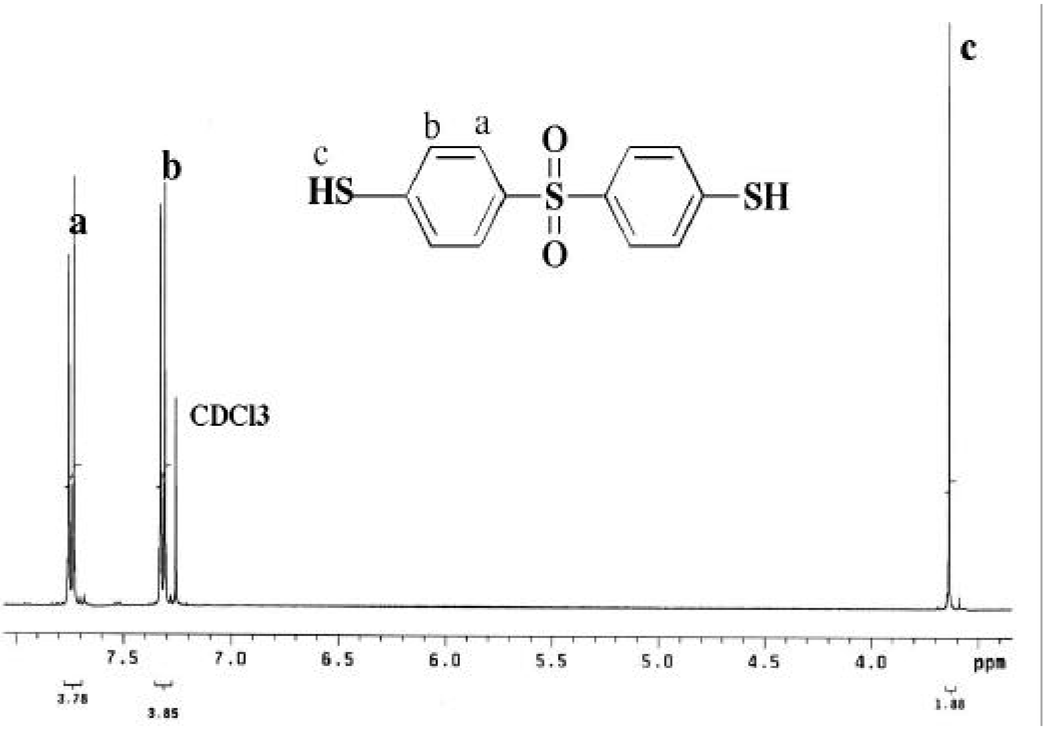


Figure 4.3.2.2.1 $^{1}H$ NMR spectrum of bis-(4-mercaptophenyl) sulfone in $CDCl_3$

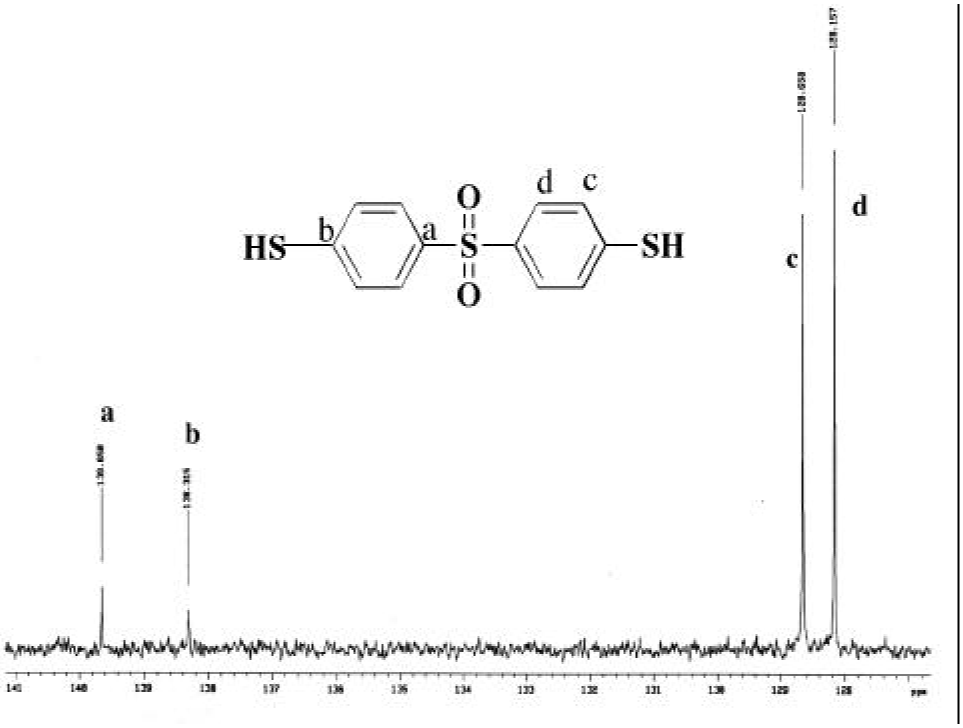
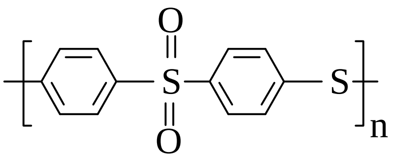
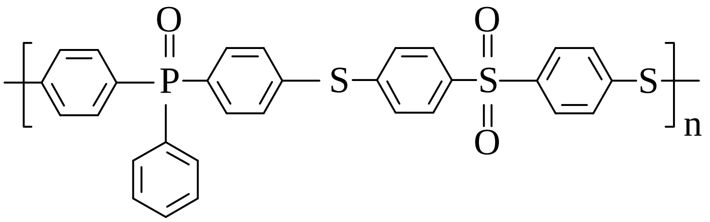
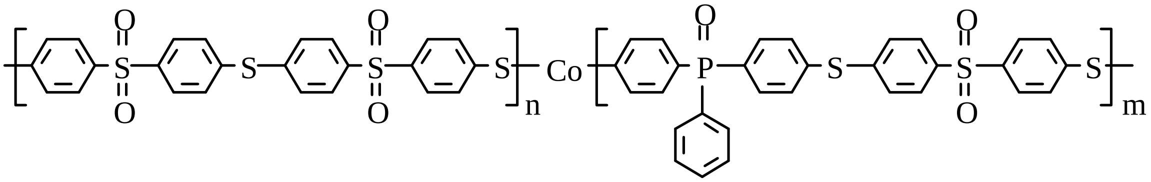


Figure 4.3.2.2.2 $^{13}C$ NMR spectrum of bis-(4-mercaptophenyl) sulfone in $CDCl_3$

### 4.3.3 Polymer Synthesis and Molecular Structure Characterization


**PPSS**


**2a**



Molar Ratio of n/m: **2b**, 75/25; **2c**, 50/50; **2d**, 25/75

It was earlier reported that 4,4′-sulfonyldiphenol could be used as a diol monomer for poly(ether sulfone) (195). Since thiophenoxide is a better nucleophile than phenoxide, the new A-A type dithiol monomer, bis-(4-mercaptophenyl) sulfone (BMPS), was expected to be sufficiently reactive toward activated dihalides in base catalyzed aprotic dipolar solvents. By using BMPS as the dithiol monomer and 4,4′-dichlorodiphenyl sulfone (DCDPS) and/or bis-(4-fluorophenyl) phenylphosphine oxide (BFPPO) as the activated dihalides, poly(phenylene sulfide sulfone) (PPSS) and related phosphine oxide containing copolymers have been successfully synthesized in DMAc in the presence of potassium carbonate. This method provides a novel simplified approach of preparing not only the traditional PPSS, but also a series of new phosphine oxide containing poly(phenylene sulfide sulfone) derivatives. The method eliminates the necessity of high pressure and temperature, as well as the use of water and sodium acetate as additives in the traditional high pressure procedure (122-124).

Poly(phenylene sulfide sulfone)s (PPSS) were prepared using a two-stage aromatic nucleophilic substitution reaction of BMPS and DCDPS in DMAc/$K_2CO_3$ (Scheme 3.2.2). In the first stage, potassium carbonate was used to convert the thiol groups of BMPS to thiophenoxide, the resulting water was removed via the toluene azotrope at 135$^{o}$C. In the second stage, high molecular weight polymers were formed at 160$^{o}$C by polycondensation. The molecular weight of the resulting PPSS was strongly dependent upon the initial monomer concentration in DMAc. For example, a high monomer concentration (>15 wt.%) resulted in low molecular weight PPSS, which was due to the precipitation of the growing polymer chains from solution. This phenomenon has been also explained in Section 4.1.4. Poly(thioarylene sulfone phosphine oxide) (**2a**) was synthesized from BMPS and BFPPO using similar reaction conditions (Scheme 3.2.8). Similarly, the poly(thioarylene sulfone/phosphine oxide) copolymers (**2b**-**2d**) with varying concentrations of the triphenyl phosphine oxide unit were synthesized by reacting BMPS with a mixture of DCDPS and BFPPO via the DMAc/$K_2CO_3$ route (Scheme 3.2.9). As expected, incorporating the kinked structure of triphenyl phosphine oxide into the polymer backbone destroyed the potential solvent induced crystallization of the polymer, and high molecular weight polymers (**2a**-**2d**) were easily obtained, even at monomer concentrations of 25 wt.%.

The molecular structure of polymer **2a** was confirmed by $^{1}$H and $^{31}$P NMR in $CDCl_3$, and was compared with the BFPPO starting material. These spectra are shown in Figures 4.3.3.1-4.3.3.2. The $H_a$ signal shifted to 7.44 ppm from 7.16 ppm in the $^{1}$H NMR spectra following polymerization, due to the replacement of fluoro atoms by sulfur, and the phosphorus signal shifted from 28.41 ppm (singlet) to 28.62 ppm (multipeaks) in $^{31}$P NMR spectra. Furthermore, all of the peaks in the polymer spectrum are broader (multipeaks) than those of the monomer, indicating that there are different sequences in the polymer backbone, as well as a higher viscosity.

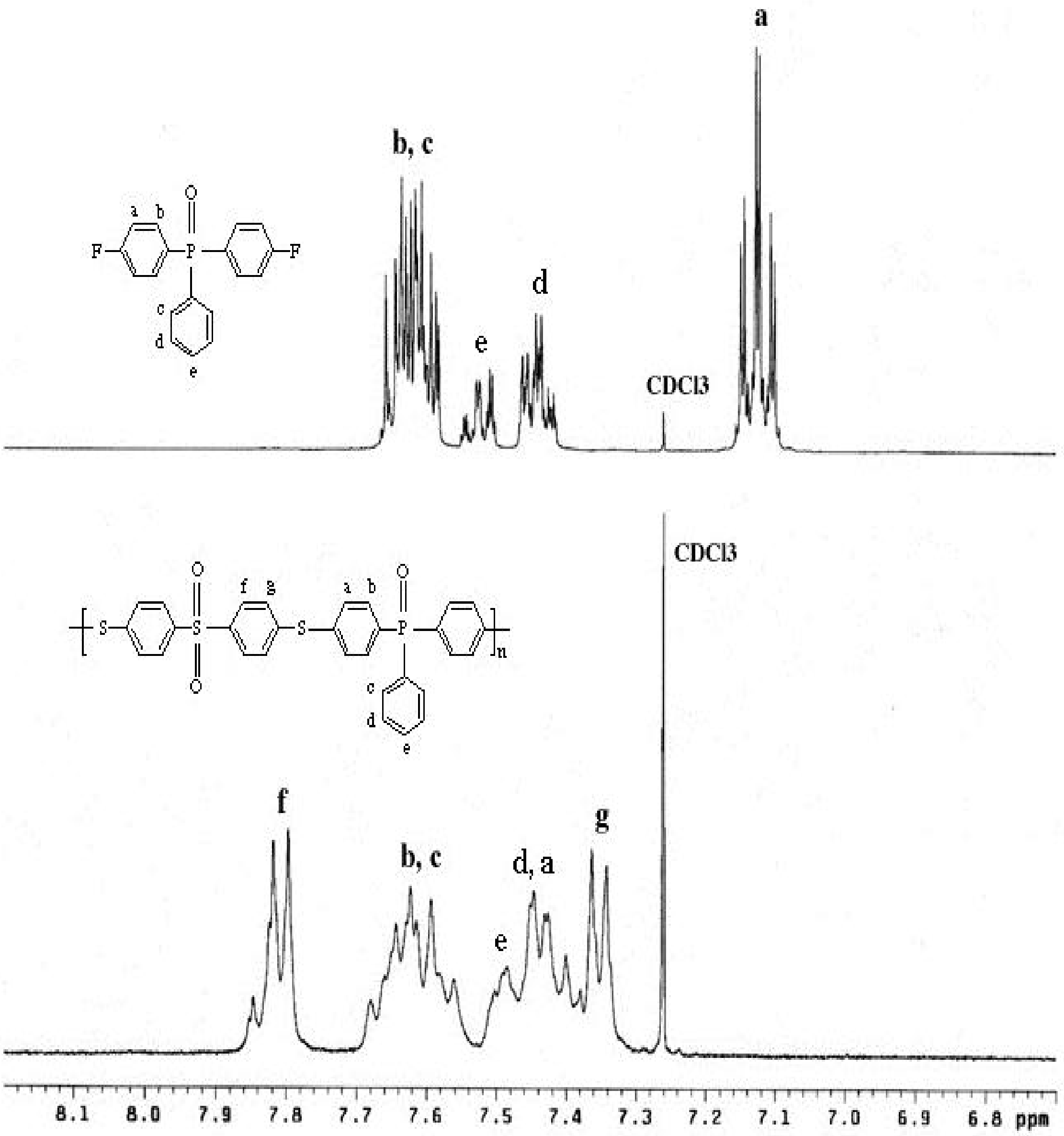


Figure 4.3.3.1 Comparison of $^1$H NMR spectra of polymer **2a** and monomer BFPPO

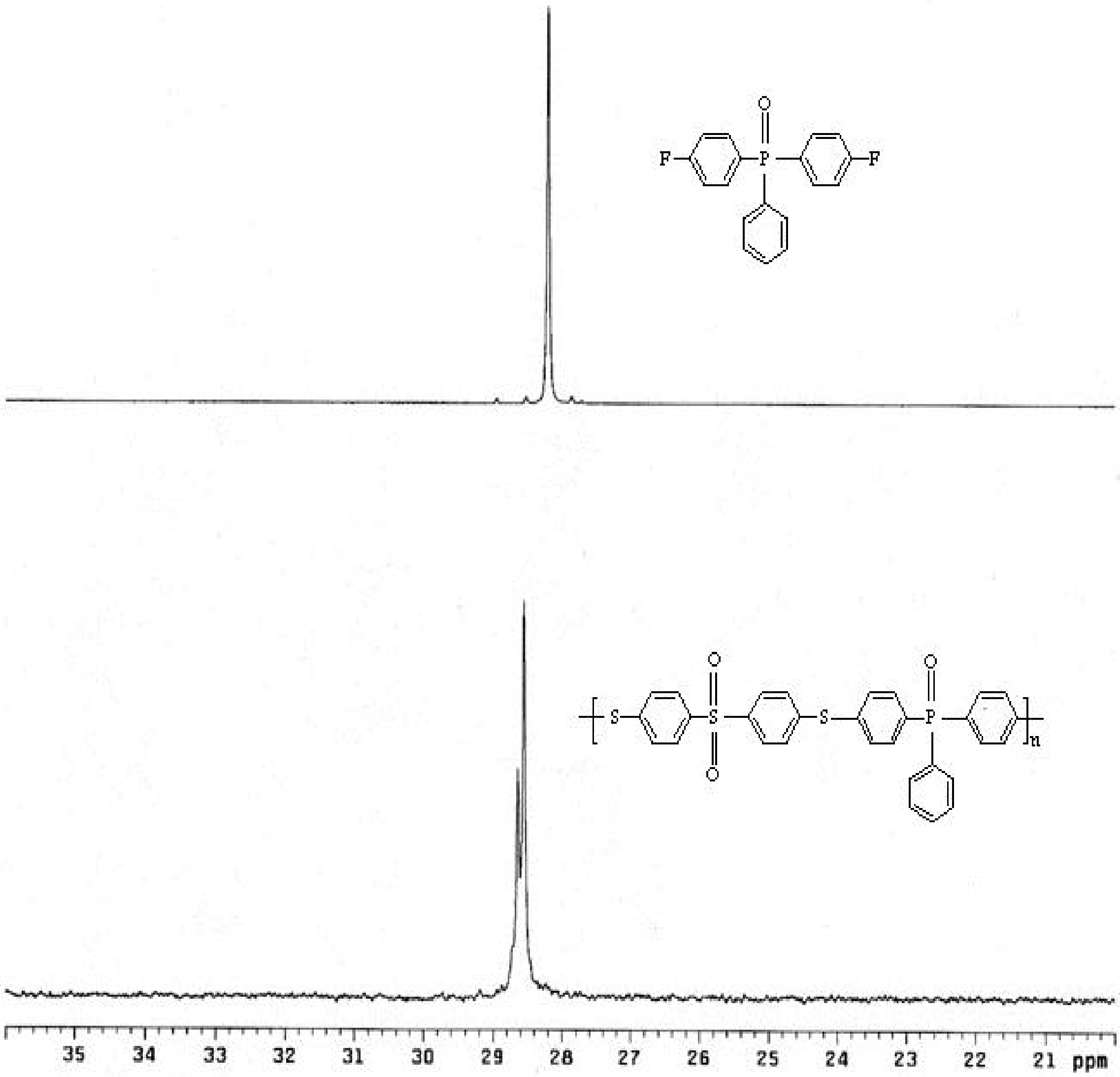


Figure 4.3.3.2 Comparison of $^{31}$P NMR spectra of polymer **2a** and monomer BFPPO

## 4.3.4 Intrinsic Viscosity and GPC Analyses

Table 4.3.4.1 lists the number average molecular weights and molecular weight distributions of the polymer samples, as measured by universal calibration GPC. As shown in Table 4.3.4.1, the molecular weights of these materials are sufficient high to be considered to be well above their entanglement molecular weight. It should be noted that the molecular weight of the PPSS is, in general, lower than those of phosphine oxide containing polymer samples, which is probably related to the solvent induced crystallization of PPSS during polymerization in DMAc. These polymers all have monomodal GPC traces, as shown in Figure 4.3.4.1, and the $M_w/M_n$ ratio, which is a measure of the molecular weight distribution, appears to be in the expected range of about 2.0. Intrinsic viscosity measurements were conducted in NMP solution at 30°C and the results are listed in Table 4.3.4.1. The intrinsic viscosity of these polymers increased with molecular weight and varied from 0.36 to 0.52.

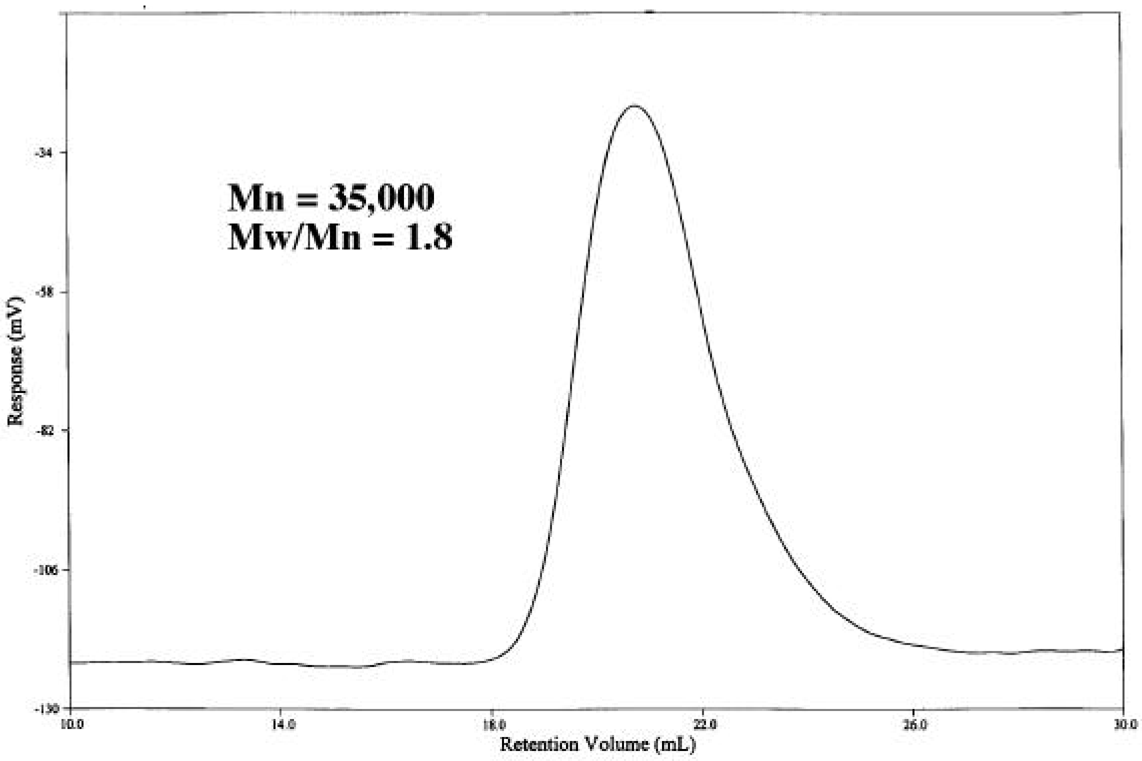


Figure 4.3.4.1 GPC chromatography of PPSS in NMP (60°C, 0.02M $P_2O_5$)

Table 4.3.4.1 Molecular Weight and Intrinsic Viscosity Analysis of PPSS and Phosphine Oxide Containing Polymers **2a-2d**

| Polymer | $M_n$ (g/mole) | $M_w$ (g/mole) | $M_w/M_n$ | $[\eta]^a$ (dL/g) |
|---|---|---|---|---|
| PPSS | 35,000 | 64,000 | 1.8 | 0.36 |
| 2b | 44,000 | 87,000 | 2.0 | 0.52 |
| 2c | 41,000 | 81,000 | 2.0 | 0.44 |
| 2d | 38,000 | 65,000 | 1.7 | 0.39 |
| 2a | 38,000 | 65,000 | 1.7 | 0.38 |

[a] measured in NMP at 30$^o$C.

## 4.3.5 Thermal Stability and Fire Resistance Behavior of Phosphine Oxide Containing Poly(Arylene Sulfide Sulfone) Copolymers

The glass transition temperatures ($T_g$s) of the polymers were measured by differential scanning calorimetry (DSC) at a heating rate of 10$^o$C/minute under nitrogen atmosphere. It can be seen from Table 4.3.5.1 that while the $T_g$s of these polymers ranged from 216$^o$C to 222$^o$C, the phosphine oxide containing PPSS derivatives had a slightly increased $T_g$ when compared to the parent PPSS. This is probably due to the increased bulkiness and dipole moment of the phosphine oxide monomer, compared to the sulfone derivative.

Thermogravimetric analysis (TGA) was utilized to determine weight loss and, by implication, thermal stability of these polymers in both air and nitrogen atmospheres. The char yield, in air and nitrogen, was also used as a measure of a polymer’s anticipated fire resistance. Char yield is an easily obtained, but important, measurement that correlates with a material’s ability to sustain combustion (151). Figure 4.3.5.1 illustrates how char yield may affect polymer combustion. When a polymer is heated to a combustion temperature, the degradation reaction may form small molecular weight byproducts and/or highly crosslinked char. It has been proposed that this char may act as a barrier that restricts oxygen from reaching the flame front, thus quenching the combustion reaction (142). On the other hand, the low molecular weight byproducts generated during combustion may be flammable or non-flammable. Clearly, flammable byproducts are essentially fuel and can undergo further combustion, produce heat that further continues the burning process. One of the major objectives of this thesis research was to investigate whether one could minimize the combustion processes by synthesizing engineering thermoplastics that contain phosphorus and/or sulfur, which produce significant char during degradation, thereby disrupting the combustion cycle.

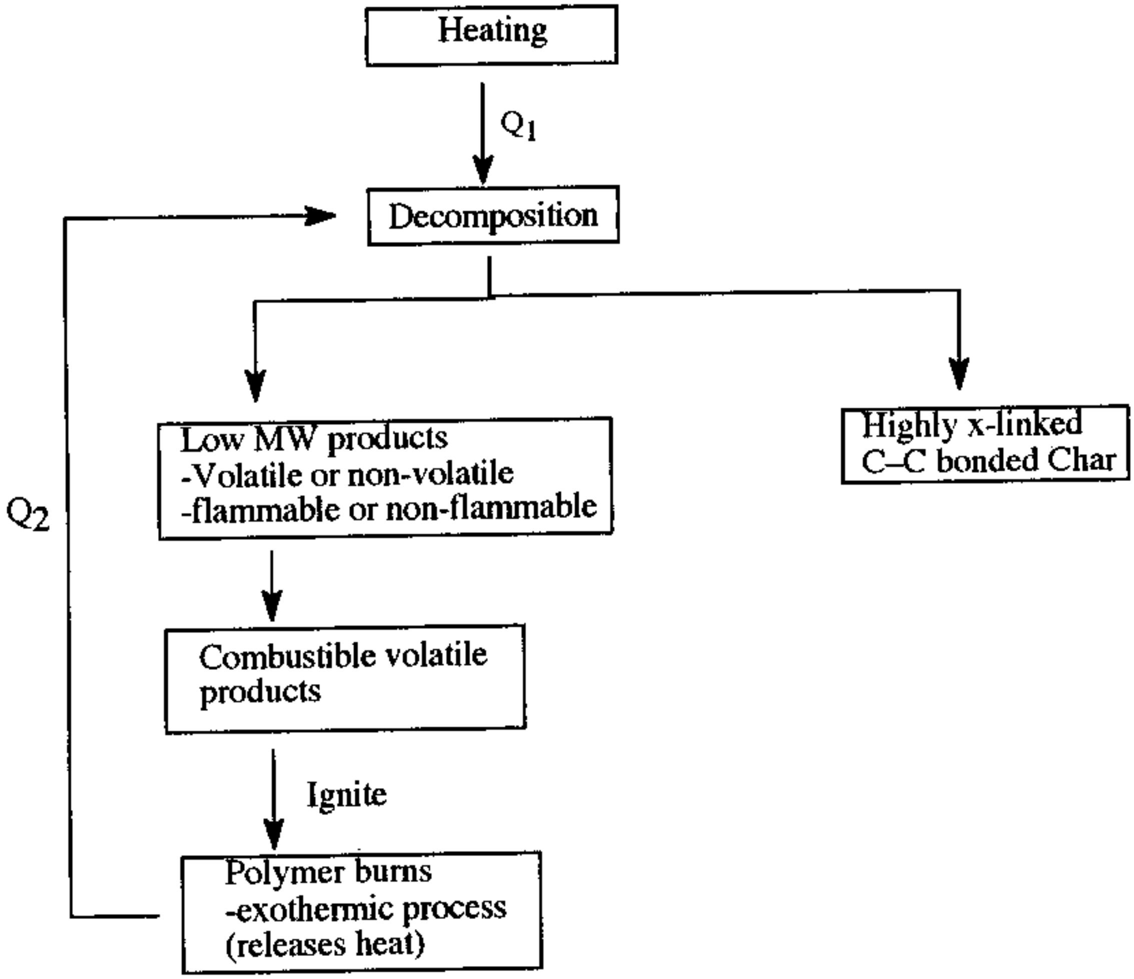


Figure 4.3.5.1 An illustration of a polymer combustion cycle (142)

The phosphine oxide containing polymers have been reported to show an increased char yield in air over similar ketone and sulfone derivatives (139, 141). Table 4.3.5.1 and

Figure 4.3.5.2 illustrate the effect of phosphine oxide incorporation upon the TGA char yield in air of various sulfide-sulfone polymers. Figure 4.3.5.2 compares the TGA thermograms of four phosphine oxide containing PPSS derivatives with the parent PPSS. It is evident from the thermograms that the phosphine oxide containing thermoplastics have much higher char yields than that of PPSS at 750°C in air. Table 4.3.5.1 also compares the theoretical mass percent phosphorus with the observed char yield. Clearly, the percent concentration of phosphorus has a direct influence on char yield. For example, the poly(phenylene sulfide sulfone) homopolymer (PPSS) was completely volatilized after exposure to 750°C in air. On the other hand, the phosphine oxide containing polymers studied showed 16 to 23 percent char yield at 750°C. These data clearly indicate that incorporating phosphorus into the polymer backbone plays a key role in promoting char formation.

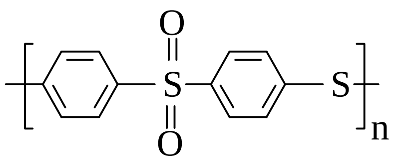
TGA analysis showed that all of the polymers were thermally stable to over 480°C in both air and nitrogen, based on their 5% weight loss (Table 4.3.5.1). It is interesting to note from Figure 4.3.5.3 and Table 4.3.5.1 that in a nitrogen atmosphere, all of the polymers studied showed very similar degrees of thermal stability based on 5% weight loss, with very high char yields ranging from 30.7% to 36.2%.

Table 4.3.5.1 Thermal Analysis of High Molecular Weight PPSS and Phosphine Oxide Containing PPSS Derivatives **2a-2d**

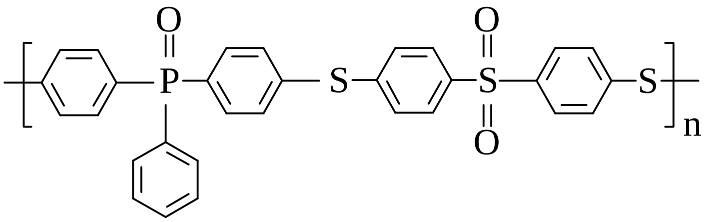
| Polymer | %P[a] | $T_g$[b] (°C) | TGA, °C[c] (5% weight loss) | | TGA, %[c] Char yield at 750°C | |
|---|---|---|---|---|---|---|
| | | | $N_2$ | air | $N_2$ | air |
| PPSS | 0 | 216 | 486 | 488 | 36.2 | 0 |
| 2b | 1.5 | 217 | 487 | 495 | 35.8 | 16.2 |
| 2c | 2.9 | 219 | 486 | 496 | 32.3 | 20.4 |
| 2d | 4.4 | 220 | 490 | 502 | 31.0 | 21.9 |
| 2a | 5.6 | 222 | 490 | 497 | 30.7 | 23.0 |

[a] calculated mass percent of phosphorus in the polymer backbone,

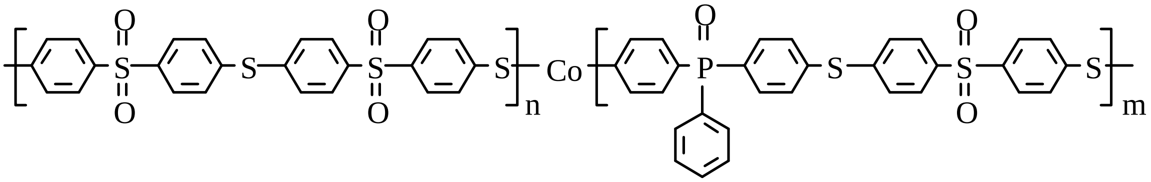
[b] second heat, heating rate of 10°C/minute under $N_2$; [c] heating rate of 10°C/min.



**PPSS**



**2a**



Molar Ratio of n/m: **2b**, 75/25; **2c**, 50/50; **2d**, 25/75

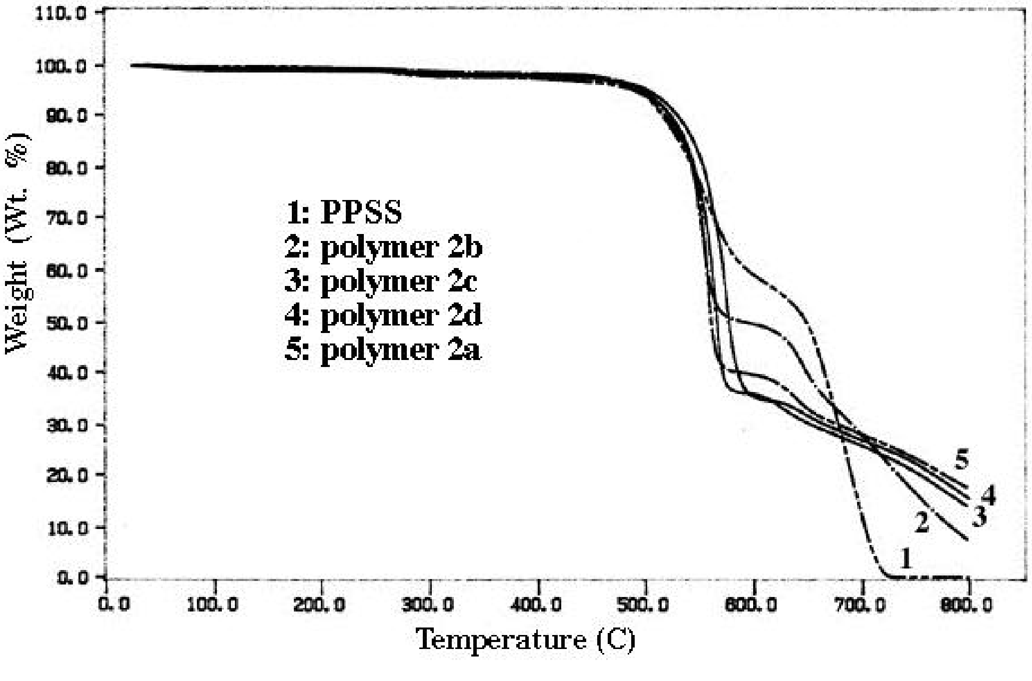
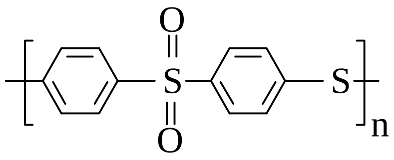
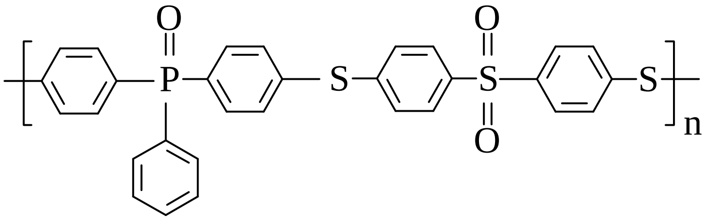


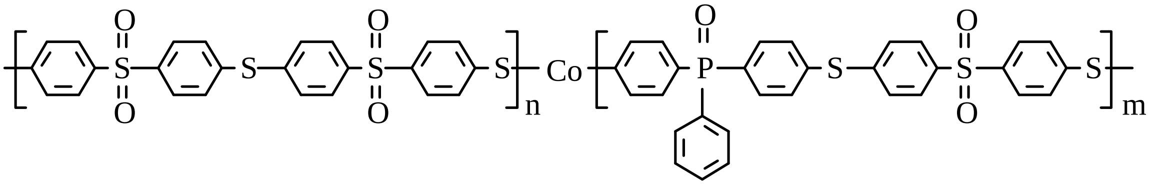
Figure 4.3.5.2 Effect of triphenylphosphine oxide content on the thermal stability and char yield of poly(thioarylene sulfone) copolymers in air (10°C/min.)



**PPSS**



**2a**



Molar Ratio of n/m: **2b**, 75/25; **2c**, 50/50; **2d**, 25/75

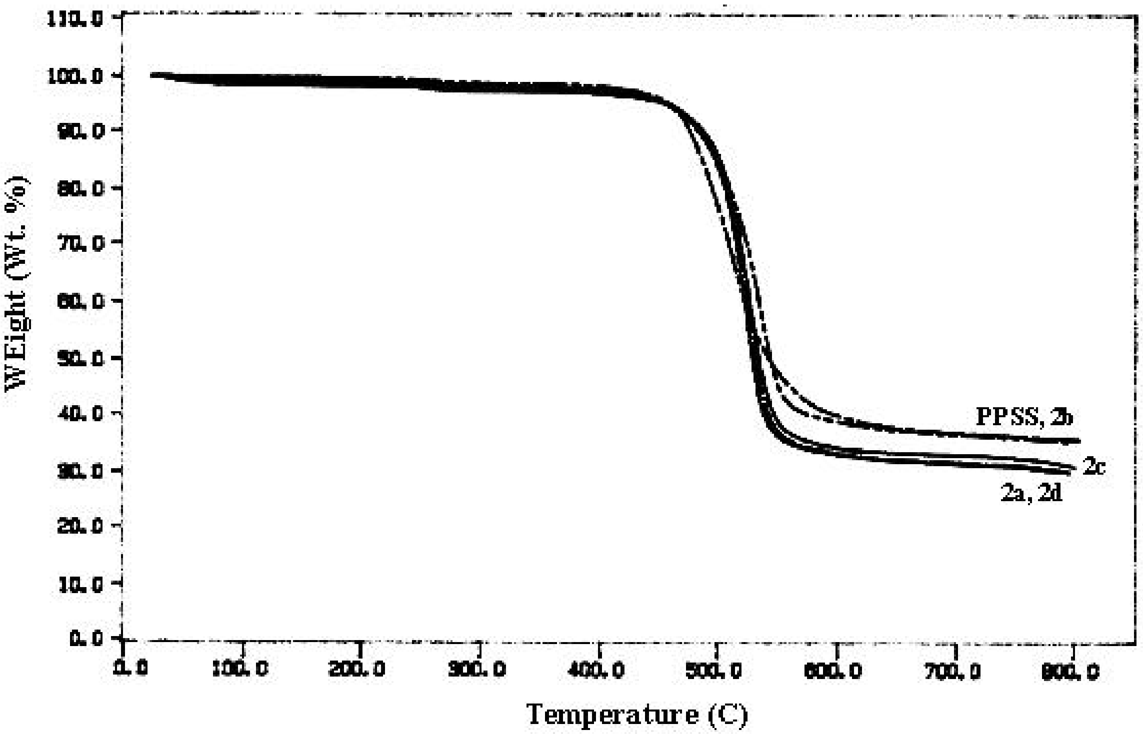


Figure 4.3.5.3 TGA thermograms of polymers **2a-2d** and PPSS in $N_2$ ($10^{o}$C/min.)

In order to better understand why the phosphine oxide containing PPSS derivatives retained significant char even at 750°C in air, compared to PPSS homopolymer, X-ray photoelectron spectroscopy (XPS) was utilized to analyze the polymer surface. Figure 4.3.5.4 illustrates the phosphorus and sulfur spectra of poly(thioarylene sulfone phosphine oxide) (**2a**) before and after TGA degradation at 750°C in air. One sees from Figure 4.3.5.4 that the phosphorus peak shifted from a binding energy of 132.5 eV, due to the original triphenylphosphine oxide moiety within the polymer backbone, to a higher binding energy position at 134.8 eV, due to a highly oxidized form of phosphorus. This phosphorus peak position compares well with a binding energy of 134.8 eV found for the phosphorus 2p photopeak in a triphenyl phosphate standard, indicating the possible formation of a surface phosphate layer. There are two sulfur peaks in Figure 4.3.5.4, which correspond to the sulfone and sulfide moieties within the polymer backbone. After TGA degradation at 750°C in air, the sulfone peak at 168.0 eV had disappeared, which may be due to the extrusion of $SO_2$. However, the sulfide peak at 163.9 eV remained, possibly due to the formation of crosslinked sulfide chars (75). Table 4.3.5.2 also compares the theoretical surface atomic percent of polymer **2a** with the measured values by XPS before and after TGA degradation at 750°C in air. As seen from Table 4.3.5.2, the atomic concentrations of polymer **2a** before degradation, measured by XPS, were in good agreement with the designed polymer structure. On the other hand, the degraded product displayed an increase in both phosphorus and oxygen content, but a decrease in sulfur content at the polymer surface. These XPS results suggest that the phosphorus and sulfide moieties in the polymer backbone can form surface layers at high temperature, which likely protect the material from further degradation

Table 4.3.5.2  XPS Analysis of Surface Atomic Concentrations of Polymer **2a**

| | Carbon | Oxygen | Sulfur | Phosphorus |
|---|---|---|---|---|
| Theoretical value (%) | 81.1 | 8.1 | 8.1 | 2.7 |
| Measured value (%) (before degradation) | 81.4 | 8.6 | 7.4 | 2.2 |
| Measured value (%) (after degradation)[a] | 71.1 | 21.0 | 3.9 | 3.2 |

[a] at 750°C, in air.

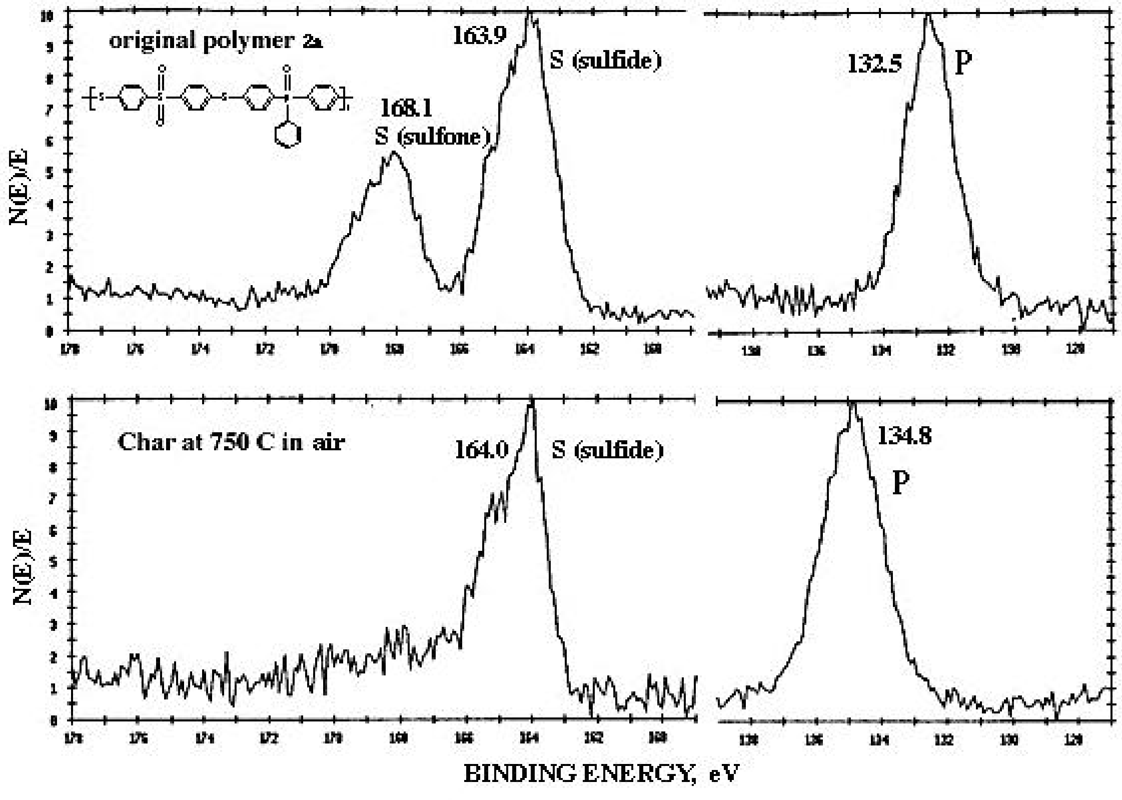


Figure 4.3.5.4  Comparison of XPS phosphorus and sulfur spectra of polymer **2a** before and after TGA degradation at 750°C in air

### 4.3.6 Influence of Molecular Structures and Polymer Compositions on Solubility and Refractive Index Values

Table 4.3.6.1 shows the solubility of various polymers exposed to several common organic solvents at a concentration of 10 wt.% at room temperature. Some of these polymers exhibited rather unique time-dependent solubility characteristics. For example, even though the sulfide-sulfone homopolymer (PPSS) was soluble in several polar solvents, such as NMP, DMAc, and DMSO, an interesting phenomenon occurred. After the polymer was dissolved and allowed to sit for a period of a few minutes to several days, the material precipitated from the solution. This instability is due to solvent-induced crystallization, which was discussed in Section 4.1.4. On the other hand, the aryl phosphine oxide modified PPSS derivatives showed a significant increase in solubility compared to the poly(phenylene sulfide sulfone). As shown in Table 4.3.6.1, the triphenyl phosphine oxide containing polymers remained soluble in most of the solvents examined by desrupting the tendency toward solvent induced crystallization. With high concentrations of triphenyl phosphine oxide comonomer incorporation, the solubility of the polymers was increased, possibly due to enhanced intermolecular dipolar interactions between the polymer chains and the solvent molecules, as well as the non-coplanar structure of the triphenylphosphine oxide.

Table 4.3.6.1 The Effect of Triphenyl Phosphine Oxide Based Comonomer on the Solubility[a] of PPSS and Copolymers

| Polymer | %P[b] | NMP | DMAc | DMSO | $CHCl_3$ |
|---|---|---|---|---|---|
| PPSS | 0 | 2 days[c] | 15 min[c] | 20 min[c] | no |
| 2b | 1.5 | yes | 1 day[c] | 5 days[c] | no |
| 2c | 2.9 | yes | yes | yes | yes |
| 2d | 4.4 | yes | yes | yes | yes |
| 2a | 5.6 | yes | yes | yes | yes |

[a] 10 wt.% polymer solution at room temperature for 10 days,
[b] mass percent of phosphorus in the polymer backbone,
[c] polymer precipitated out of solution after the time indicated.

The effect of incorporating phosphine oxide comonomer on refractive index and other optical properties was also an area of interest. The refractive indices of solution cast films of the polymers **2a**-**2d** and PPSS were measured on a Metricon 2010 Prism Coupler at a wavelength of 632.8 nm. Thin films prepared from the polymers were cast from NMP solution onto a glass plate. They were allowed to dry overnight at 80°C and placed in a vacuum oven, where the temperature was slowly increased to 170°C over a period of 12 hours. Table 4.3.6.2 illustrates the effect of phosphine oxide incorporation upon the index values of the amorphous thermoplastics. The presence of a phosphine oxide moiety in the polymeric backbone did not have a significant effect on refractive index when compared to the sulfide-sulfone homopolymer. However, when polar and kinked triphenyl phosphine oxide units were incorporated into the polymer backbone, solubility was significantly improved as shown in Table 4.3.6.1, which is an important feature for processing solution cast films. As evidenced in Table 4.3.6.2, all of the polymers studied exhibited very high refractive indices, possibly due to the high content of polarizable high electron density groups, such as sulfur, phosphorus, and aromatic rings in the polymer structure.

Table 4.3.6.2 The Effect of the Backbone Structure on the Refractive Index of the Polymers **2a**-**2d** and PPSS

| Polymer | %P[a] | Refractive Index[b] |
|---|---|---|
| PPSS | 0 | 1.6914 |
| 2b | 1.5 | 1.6917 |
| 2c | 2.9 | 1.6899 |
| 2d | 4.4 | 1.6906 |
| 2a | 5.6 | 1.6902 |

[a] mass percent of phosphorus in the polymer backbone,

[b] measured on Metricon 2010 Prism Coupler at a wavelength of 632.8 nm.

The UV-Visible spectra of these polymers were also studied to determine if the triphenyl phosphine oxide groups within the polymer backbone had an effect on its UV-

Vis absorption. The UV-Vis spectra for poly(thioarylene sulfone phosphine oxide) (**2a**), poly(thioarylene sulfone/phosphine oxide) (**2c**) and poly(phenylene sulfide sulfone) (PPSS) are shown below in Figure 4.3.6.1. The data indicate that the PPSS showed absorption with $\lambda_{max}$ ranged from 270 nm to 310 nm in DMSO solution, which correspond to a $\pi$-$\pi$ transition in biphenyl groups. After the triphenyl phosphine oxide was incorporated into the polymer backbone, a red-shift was observed at around 280-320 nm, which suggests that a higher degree of conjugated systems was obtained in polymer **2a** compared to PPSS. The maximum absorption in polymer **2c** was observed between that of the PPSS and polymer **2a**. It can also be noted from Figure 4.3.6.1 that there was very low absorption at all in the visible light regions (400-600 nm), confirming that these polymers are colorless and transparent.

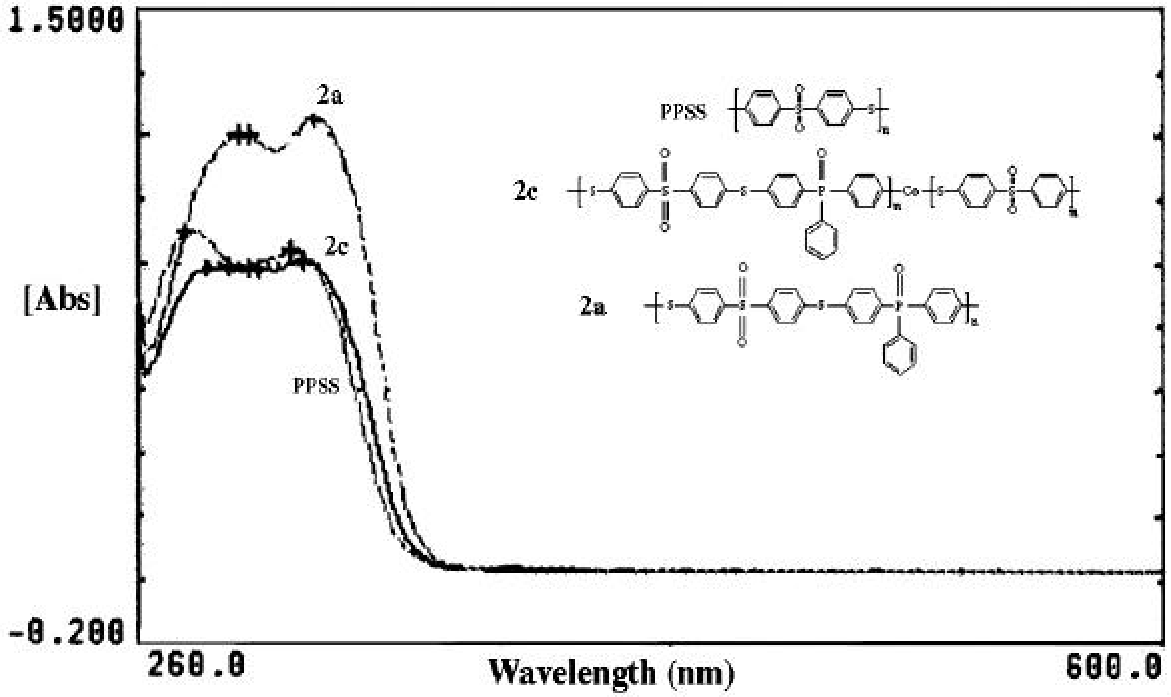


Figure 4.3.6.1 UV-Vis spectra of polymers **2a**, **2c**, and PPSS in DMSO (Conc. $1x10^{-4}$ - $1x10^{-5}$ M)

### 4.3.7 Conclusions

A new dithiol monomer, bis-(4-mercaptophenyl) sulfone (BMPS), was prepared and successfully used to prepare poly(phenylene sulfide sulfone)s (PPSS), as well as a series of new PPSS-related phosphine oxide containing polymers, via a simple DMAc/$K_2CO_3$ route. This new approach simplified the traditional high pressure procedure for PPSS by eliminating the necessity of high pressure and temperature, as well as the use of water and sodium acetate as additives. This modified approach also provided a rational pathway for preparing high molecular weight phosphine oxide containing PPSS copolymers. Compared with sulfide-sulfone homopolymer (PPSS), the new phosphine oxide containing materials exhibited enhanced solubility in common organic solvents, a slight increase in glass transition temperature, and very high char yields at 750$^{o}$C in air. XPS analysis results suggest that the sulfide and phosphorous moieties within the polymer backbone can form surface layers to protect the material from further degradation. All of these polymers showed very high refractive index (>1.69) values, and the number average molecular weight of these polymers ranged from
35,000 to 44,000 g/mole.

## *4.4 Synthesis and Characterization of Novel Fire Resistant Engineering Thermoplastics Containing Sulfone, Ketone and/or Phosphine Oxide Groups*

### 4.4.1 Introduction

Engineering thermoplastics are widely used in aircraft interiors for various important functions, such as carpets, seats, bins, appliance housings, communication devices, etc. Although it is universally acknowledged that these materials should be fire resistant, the mechanisms by which this occurs is not yet well understood. Thus, there is an important need to further identify the fundamental relationships between the molecular structure of these materials and their behavior in fire. As a consequence, much research has been carried out in recent years toward the development of new or improved thermoplastic resins. In this area, aromatic poly(ether ketone)s have been given special attention because of their chemical resistance and excellent mechanical and thermal properties.

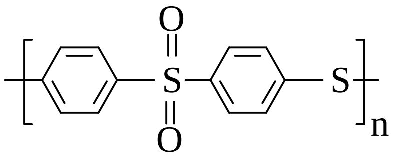
High molecular weight aromatic poly(ether ketone)s were first synthesized by a Friedel-Crafts condensation of isophthaloyl and terephthaloyl chlorides with diphenyl ether in methylene chloride solution, in the presence of aluminum chloride (107), and subsequently by reaction in liquid hydrogen fluoride solvent (108). The resulting materials are highly crystalline and very insoluble in all common solvents at ambient temperatures. The alternative method of synthesizing aromatic poly(ether ketone)s by nucleophilic substitution was known to be unsuccessful because the polymers precipitated from solution during polymerization. Rose, however, found that the nucleophilic substitution method could be used to produce high molecular weight poly(ether ether ketone) (PEEK) (110). He accomplished this via the condensation of 4,4′-difluorobenzophenone with hydroquinone in the presence of potassium carbonate, providing that the reaction was carried out in diphenyl sulfone solvent above 300$^{o}$C, to avoid precipitation of low molecular weight polymers from solution. Commercial interest in this material has been directed toward their use as an insulation material and as a high temperature matrix resin for composites. Several amorphous aromatic poly(ether ketone)s have been synthesized using bisphenols, such as 4,4′-(1-methylethyl idene) bisphenol, and since these polymers are much more soluble, the reaction can be carried out at lower temperatures in an aprotic dipolar solvent (111).

The sulfur containing analogs to the poly(ether ketone)s, although important, have not been well researched. In fact, only a few reports have been published on poly(thioether ketone)s, although conceptually their synthesis is similar to that of poly(ether ketone)s. In 1989, researchers at Dow Chemical reported the preparation of poly(thioether ketone)s from ketone-activated aromatic fluoro compounds by reaction with anhydrous sodium sulfide in N-cyclohexyl-2-pyrrolidinone (CHP) (113). Senn at Phillips Petroleum Company studied the synthesis and characterization of random-copoly(*p*-phenylene sulfide sulfone/ketone)s (PPSS/K) by a similar method used to prepare PPSS, in which sodium hydrosulfide reacts with the mixture of 4,4′-dichlorodiphenyl sulfone and 4,4′-dichlorobenzophenone at elevated reaction temperature and pressure (125). Hay et. al. recently synthesized a series of amorphous poly(thioether ketone)s by the direct polycondensation of ketone-containing aromatic fluoro compounds with 4,4′-dimercaptodiphenyl ether or 4,4′-dimercaptodiphenyl thioether in DMAc/$K_2CO_3$ (112). Poly(thioether ketone)s have also been prepared from masked bisthiophenols in the presence of potassium bicarbonate (117).

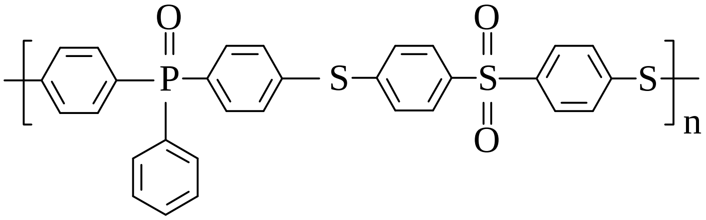
Our interest in the polyketone family of engineering thermoplastics has been directed toward the synthesis of amorphous, high molecular weight, thermooxidative stable materials with high glass transition temperatures and flame resistance. It was expected that introducing aryl phosphine oxide and/or sulfone moieties into poly(thioarylene ketone)s would result in significant changes in polymer properties. In general, aromatic poly(ether sulfone)s and poly(ether sulfone phosphine oxide)s are amorphous and have high glass transition temperatures. In addition, it has been found that aryl phosphine oxide containing polymers have demonstrated increased flame resistance and char yields compared to the nonphosphorus parent polymers (196-198). The insertion of triphenyl phosphine oxide moieties was also expected to enhance solubility and improve interphase interaction between the polar phosphine oxide groups of the polymer matrix and the functionalized carbon or glass fiber.

In this thesis, we report the synthesis and characterization of series of new amorphous, high molecular weight poly(thioether ketone)s containing sulfone and/or phosphine oxide groups, based on the newly prepared 4,4′-dimercaptodiphenyl sulfone and ketone or phosphine oxide activated dihalides, via a direct polycondensation in DMAc and potassium carbonate used as the base.

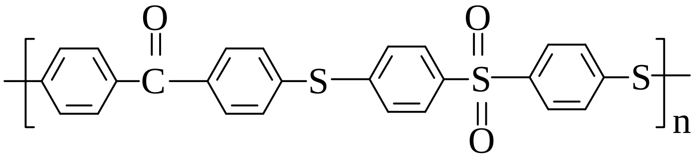
## 4.4.2 Polymer Synthesis and Molecular Structure Characterization



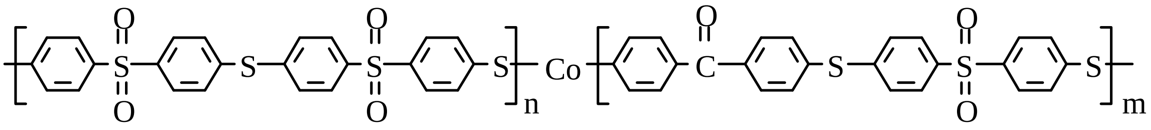
**PPSS**



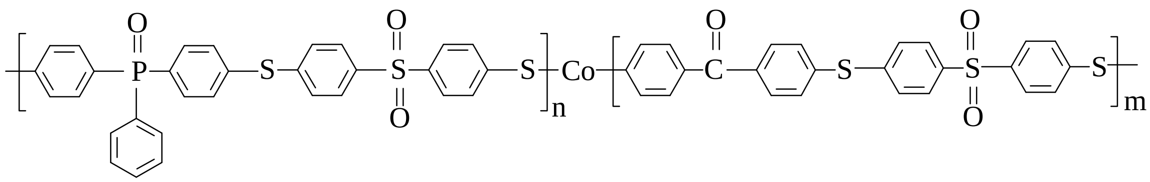
**2a**



**3a**



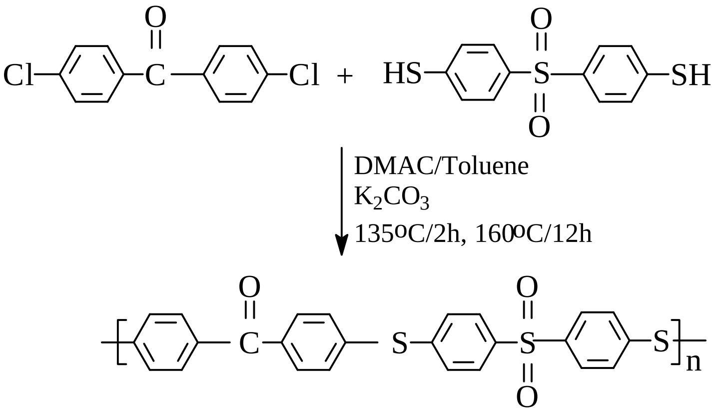
Molar Ratio of n/m: **3b**, 75/25; **3c**, 50/50; **3d**, 25/75



Molar Ratio of n/m: **4a**, 75/25; **4b**, 50/50; **4c**, 25/75

Two series of copolymers, poly(thioarylene sulfone/ketone)s **3b-3d** and poly(thioarylene sulfone ketone/phosphine oxide)s **4a-4c**, were prepared by aromatic nucleophilic substitution of the bis-(4-mercaptophenyl) sulfone (BMPS) with a mixture of 4,4′-dichlorodiphenyl sulfone (DCDPS) and 4,4′-difluorobenzophenone (DFBP) or bis-(4-fluorophenyl)phenyl phosphine oxide (BFPPO) and DFBP, in the presence of potassium carbonate as the base in N,N-dimethylacetamide (DMAc). As shown in Scheme 3.2.11 and 3.2.12, the monomer concentration was maintained at 20 wt.%, and any water present or generated during the bisthiophenoxide formation was removed as an azetrope with toluene. The reaction was maintained at the reflux temperature of 132$^{o}$C-135$^{o}$C for 2h, and upon completion of bisthiophenoxide formation and dehydration, the polymerization was heated to 160$^{o}$C to effect the displacement reaction. After a period of 6-10h, a dramatic increase in viscosity indicated the formation of high molecular weight copolymers **3b-3d** or **4a-4c**. Two homopolymers, poly(thioarylene sulfone ketone) **3a** and poly(thioarylene sulfone phosphine oxide) **2a**, were synthesized by polymerizing BMPS with DFBP or BFPPO, respectively, under similar reaction conditions.

For comparison purposes, poly(phenylene sulfide sulfone) (PPSS) was also synthesized via a direct polycondensation of BMPS and DCDPS in DMAc/$K_2CO_3$ at 15 wt.% monomer concentration. The higher monomer concentration yielded lower molecular weight PPSS obtained due to the crystallization of the polymer in DMAc, as mentioned in Section 4.3.2. Since the thiophenoxide anions are stronger nucleophiles than phenoxides, the poly(thioarylene sulfone ketone) homopolymer **3a** and poly(thioarylene sulfone ketone/sulfone) copolymers **3b-3d** can also be prepared from chloro compounds such as 4,4′-dichlorobenzophenone (DCBP), instead of fluoro monomer DFBP. For example, bis-(4-mercaptophenyl) sulfone (BMPS) reacted with DCBP in DMAc with 15 mol% excess potassium carbonate as the base, and after 12h at 160$^{o}$C, the poly(thioarylene sulfone ketone) **3a** with $M_n$ = 36,000 and $M_w/M_n$ = 1.9 was obtained (Scheme 4.4.2.1). As a consequence, the enhanced reactivity of BMPS makes it possible to use more economical chloro monomers, thus promoting a more cost-effective synthetic route for producing these types of polymers.



Scheme 4.4.2.1 Synthesis of poly(thioarylene sulfone ketone) **3a** from 4,4′-dichlorobenzophenone (DCBP)

The molecular structures of the polymers **3a** and **4b** were compared to the starting materials of BMPS, DFBP, and BFPPO and were characterized by $^1$H NMR in $CDCl_3$. These spectra are shown below in Figures 4.4.2.1 and 4.4.2.2. From Figure 4.4.2.1, the $H_a$ signal shifted to 7.78 ppm from 7.80 ppm following polymerization due to the replacement of fluoro atoms by sulfur atoms, while the $H_b$ signal shifted down field from 7.19 ppm to 7.40 ppm. Both the $H_c$ and $H_d$ signals shifted down field after the dithiol groups became sulfide groups. Furthermore, all of the peaks in the high viscosity polymer spectrum are broader than those in monomer cases, which indicated that there are different sequences in the polymer backbone. A similar phenomenon was observed for the polymer **4b** in Figure 4.4.2.2.

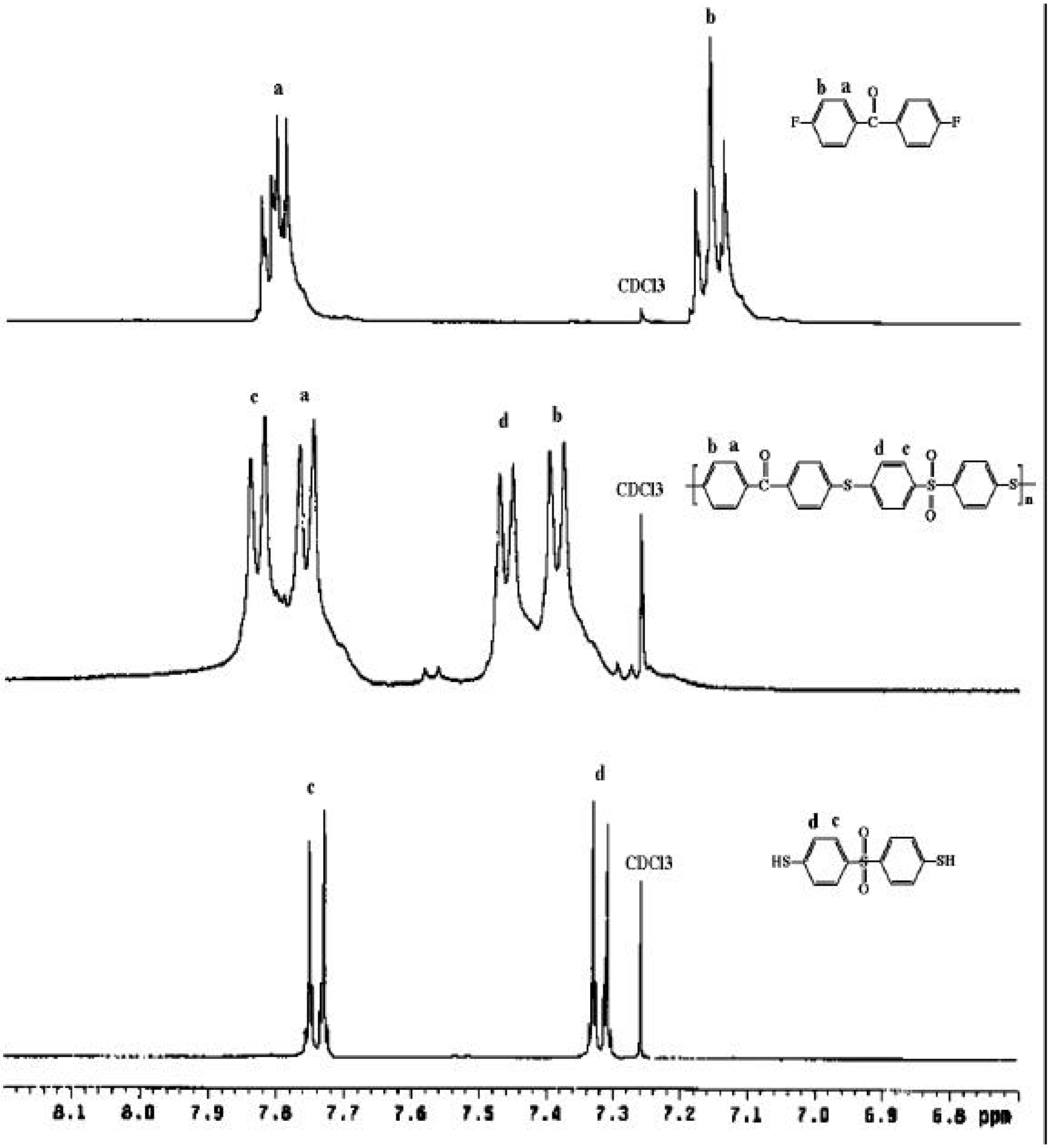


Figure 4.4.2.1 $^{1}$H NMR spectrum of the polymer **3a** compared with those of the starting materials BMPS and DFBP in $CDCl_3$

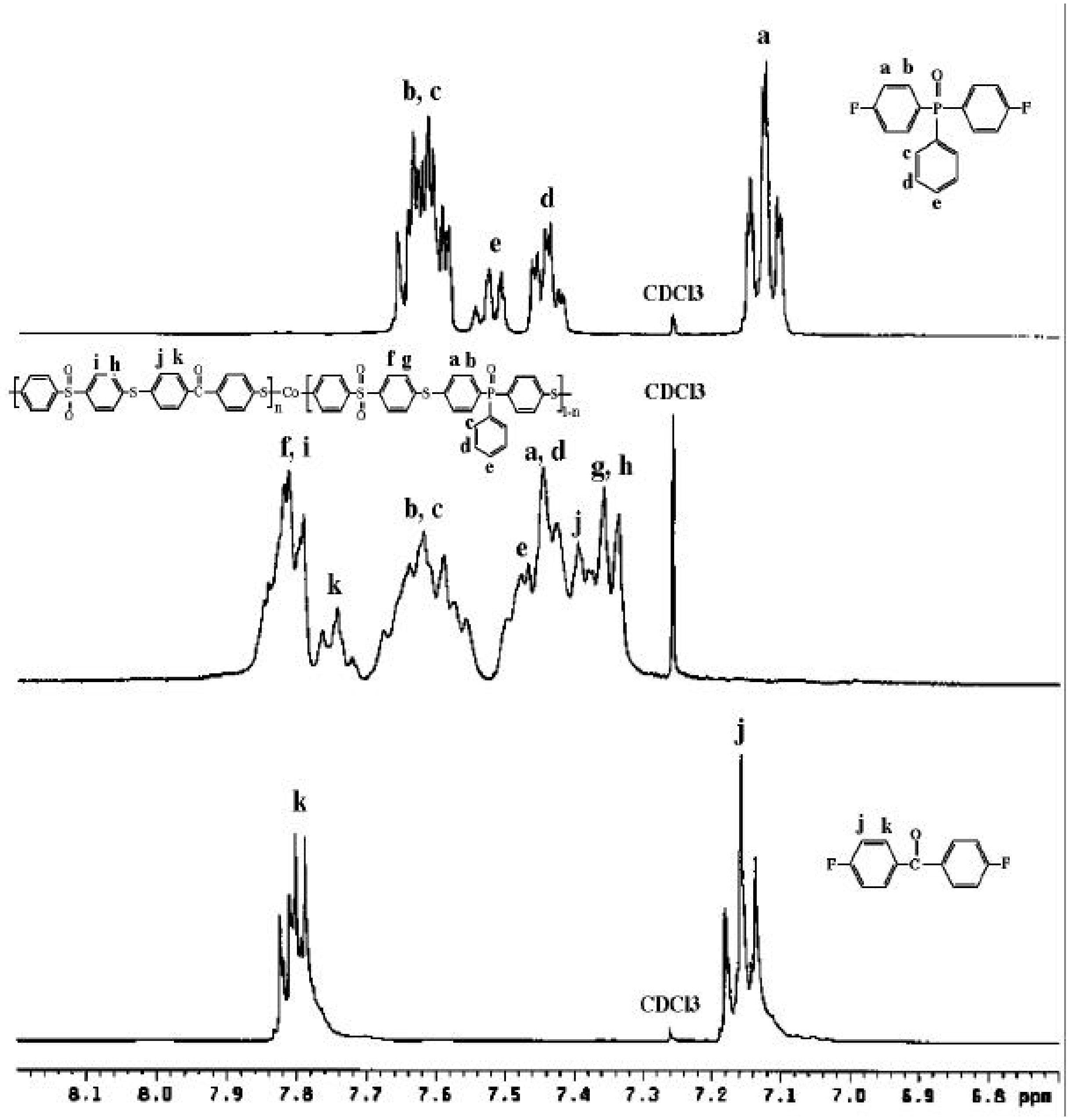


Figure 4.4.2.2 $^1$H NMR spectrum of the polymer **4b** compared with those of the starting materials of BMPS and BFPPO in $CDCl_3$

## 4.4.3 Intrinsic Viscosity, GPC and Solubility Characterization

The number average molecular weights and $M_w/M_n$ ratios of the polymer samples were measured by universal calibration GPC and the results are listed in Table 4.4.3.1. All of the polymers are high molecular weights and could be cast into transparent flexible films. The number average molecular weights ($M_n$) ranged from 33,000-59,000 for polymers **3a-3d**, and 30,000-35,000 for polymers **4a-4c**. These polymers all had monomodal GPC traces and polydispersities of 1.7-2.2, indicating they are typical linear polycondensation reactions. Intrinsic viscosities, which were taken at 30°C in N-methyl-2-pyrrolidinone (NMP) solution, varied from 0.36-0.61 and increased with molecular weights (Table 4.4.3.1).

Table 4.4.3.1 GPC Data and Intrinsic Viscosity for Polymers **3a**-**3d**, **4a**-**4c**, **2a**, and PPSS

| polymers | $M_n$ (g/mol) | $M_w$ (g/mol) | polydispersity ($M_w/M_n$) | $[\eta]^a$ (dL/g) |
|---|---|---|---|---|
| **3a** | 59K | 107K | 1.8 | 0.61 |
| **3d** | 48K | 89K | 1.9 | 0.56 |
| **3c** | 35K | 62K | 1.8 | 0.42 |
| **3b** | 33K | 70K | 2.1 | 0.44 |
| PPSS | 35K | 64K | 1.8 | 0.36 |
| **2a** | 38K | 65K | 1.7 | 0.38 |
| **4a** | 35K | 75K | 2.2 | 0.46 |
| **4b** | 30K | 61K | 2.0 | 0.40 |
| **4c** | 30K | 57K | 1.9 | 0.38 |

[a] measured in NMP at 30°C

It should be noted that the new polymers exhibited rather unique solubility characteristics. The solubility of copolymers **3b-3d** and **4a-4c**, homopolymers **2a**, **3a**, and PPSS were examined in various common organic solvents at room temperature (Table 4.4.3.2). In general, the triphenyl phosphine oxide containing homo- and co-polymers **4a-4c** and **2a** were amorphous and soluble in all of the solvents examined, except in DMSO for copolymers **4a-4c**. This enhanced solubility is believed result from the dipolar interaction between the highly polar phosphine oxide groups within the polymer backbone and the inherent dipole of the dipolar aprotic solvents. It is also believed that the kinked structure of the triphenylphosphine oxide groups impedes the formation of any crystalline structure. The solubility behavior of the poly(thioarylene sulfone ketone) homopolymer **3a** and poly(thioarylene sulfone ketone/sulfone) copolymers **3b-3d** was more complicated. While they are all soluble in NMP, the solubility of polymers **3a-3d** in DMAc, DMSO, and chloroform was highly dependent on their composition. Moreover, the poly(phenylene sulfide sulfone) homopolymer (PPSS) was initially soluble in several aprotic dipolar solvents such as NMP, DMAc, and DMSO, after which an interesting phenomenon occurred. After the polymer was dissolved and was allowed to sit for a period of a few minutes to a couple of days, the material precipitated out of solution due to the formation of crystal solvates, as discussed in Section 4.1.4.

Table 4.4.3.2. Solubility[a] of 10 wt.% Polymers **3a-3d**, **4a-4c**, **2a**, and PPSS

| polymers | NMP | DMAc | DMSO | $CHCl_3$ |
|---|---|---|---|---|
| **3a** | yes | 2 days[b] | no | 10 h[b] |
| **3d** | yes | yes | no | 5 h[b] |
| **3c** | yes | yes | no | no |
| **3b** | yes | 4 days[b] | 1 day[b] | no |
| PPSS | 2 days[b] | 15 min.[b] | 20 min.[b] | no |
| **2a** | yes | yes | yes | yes |
| **4a** | yes | yes | no | yes |
| **4b** | yes | yes | no | yes |
| **4c** | yes | yes | no | yes |

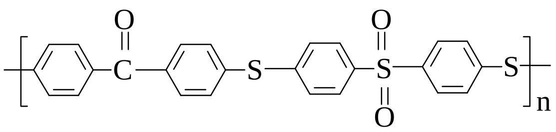
[a] room temperature for 10 days,

[b] polymer precipitated out of solution after the time indicated.

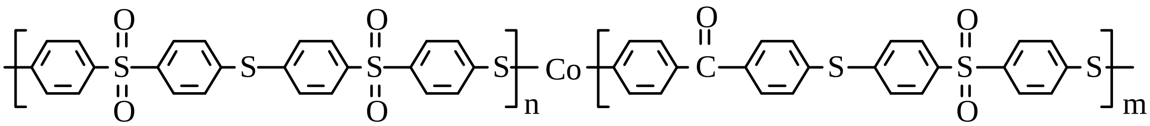
## 4.4.4 The Effect of Molecular Structure and Polymer Compositions on Thermal Stability and Fire Resistance Behavior

The glass transition temperatures ($T_g$s) of polymers **3a-3d**, **4a-4c, 2a**, and PPSS were analyzed by differential scanning calorimetry (DSC) at a heating rate of 10°C/min.

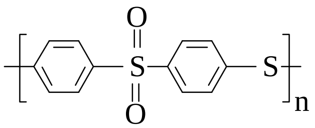
under an atmosphere of nitrogen, and these results are shown in Table 4.4.4.1. The $T_g$s of the ketone containing polymers **3a-3d** ranged from 176°C-206°C, while those of both the ketone and phosphine oxide containing PPSS derivatives **4a-4c** ranged from 183°C-210°C, compared to those of PPSS (212°C) and the poly(thioarylene sulfone phosphine oxide) (**2a**) (219°C) homopolymers. All of the polymers synthesized were amorphous and no melting endotherm was observed from the first DSC traces in the temperature range of 50°C-350°C. This is understandable, since the kinked groups of triphenyl phosphine oxide and diphenyl sulfone eliminated the possible crystallinity expected for the ketones. As shown in Table 4.4.4.1 and Figure 4.4.4.1, higher $T_g$s resulted with increasing sulfone and/or phosphine oxide content within the polymer backbone. In addition, the aryl phosphine oxide and sulfone are more bulky groups than that of the ketone, and thus segmental movement of the polymer chains was reduced. Furthermore, in polymer **3a**-**3d** and PPSS, the increase in $T_g$s was observed to be linear with increasing sulfone content. This was expected with the random copolymers in which the two monomers display relatively equal reactivity (Figure 4.4.4.2). It can also be noted from Figure 4.4.4.2 that the $T_g$s calculated from Fox equation are in good agreement with the values measured by DSC. This suggests that 4,4´- dichlorodiphenyl sulfone (DCDPS) and 4,4´-difluoro benzophenone (DFB) have relatively equal reactivities to the bis-(4-mercaptophenyl) sulfone (BMPS), and the feed molar ratio of the monomers could represent the composition of the resulting random copolymers.



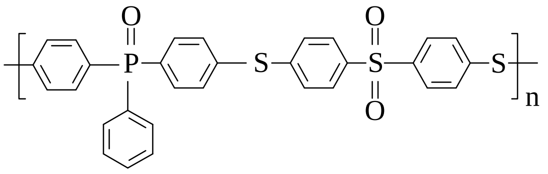
**3a**



**3c** (n/m=50/50)



**PPSS**



**2a**

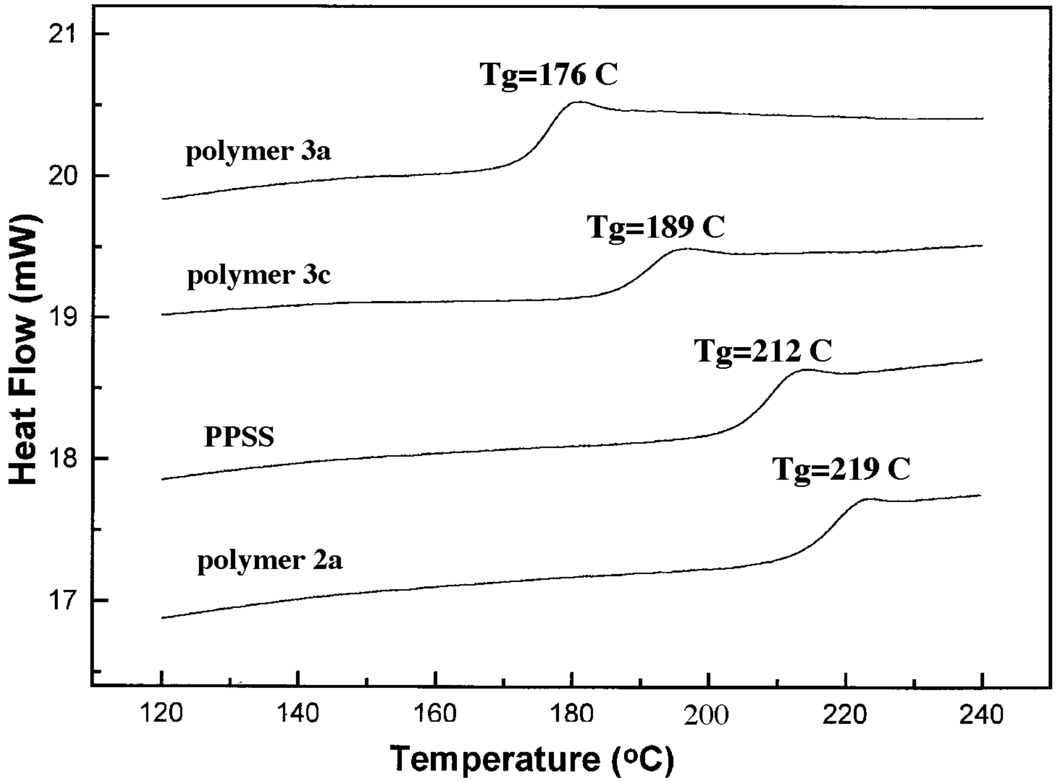


Figure 4.4.4.1 Influence of aryl phosphine oxide and ketone on $T_g$s for polymers **3a**, **3c**, **2a** compared to the PPSS

Table 4.4.4.1 Thermal Properties of polymers **3a-3d**, **4a-4c**, **2a**, and PPSS

| polymer | $T_g$, °C[a] | TGA, °C[b] (5% weight loss) | | TGA, %[b] char yield at 750°C | |
|---|---|---|---|---|---|
| | | $N_2$ | air | $N_2$ | air |
| **3a** | 176 | 536 | 534 | 52.6 | 3.5 |
| **3d** | 185 | 540 | 532 | 51.1 | 4.1 |
| **3c** | 189 | 504 | 513 | 43.1 | 0 |
| **3b** | 206 | 502 | 508 | 40.6 | 0 |
| PPSS | 212 | 505 | 503 | 38.5 | 0 |
| **2a** | 219 | 507 | 508 | 31.4 | 26.5 |
| **4a** | 210 | 505 | 514 | 35.8 | 26.7 |
| **4b** | 196 | 516 | 531 | 44.7 | 26.4 |
| **4c** | 183 | 506 | 512 | 50.1 | 13.2 |

[a] heating rate was 10°C/min. under nitrogen atmosphere

[b] heating rate was 10°C/min.

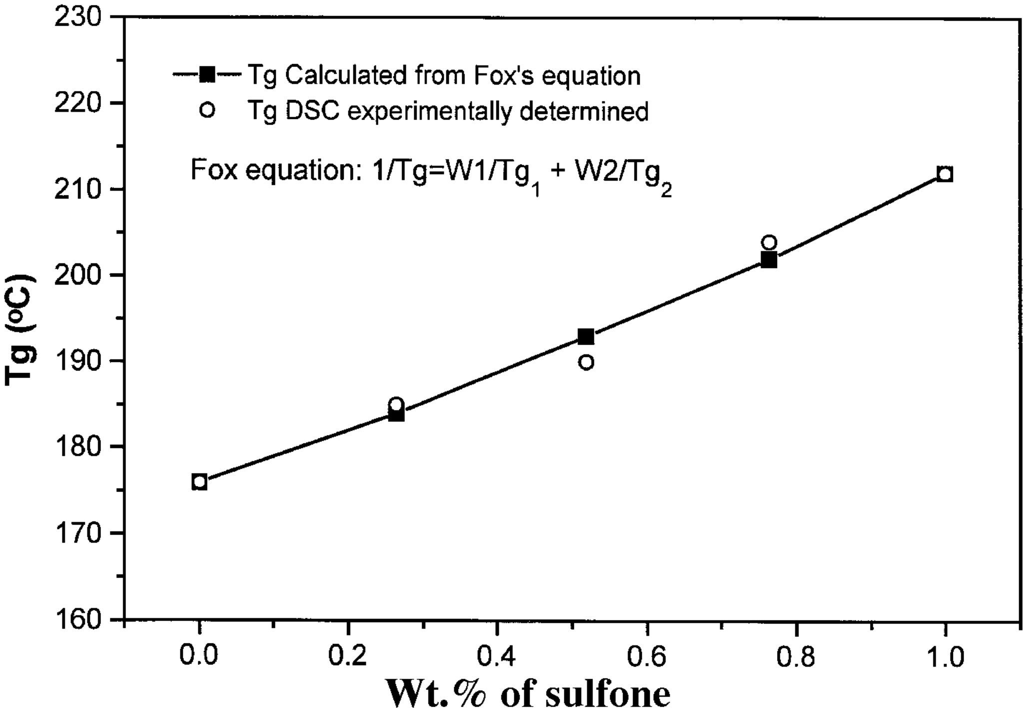


Figure 4.4.4.2 Plot of $T_g$s vs. wt. fraction of PPSS for polymers **3a-3d** and PPSS

The dynamic mechanical behavior of poly(thioarylene sulfone ketone) (**3a)** and poly(thioarylene sulfone phosphine oxide) **(2a)** were also investigated, and the dynamic mechanical spectra of the compression molded films of polymers **3a** and **2a** are presented in Figure 4.4.4.3. The $T_g$s of polymers **3a** and **2a**, as measured from tan δ, are in good agreement with the values measured by DSC.

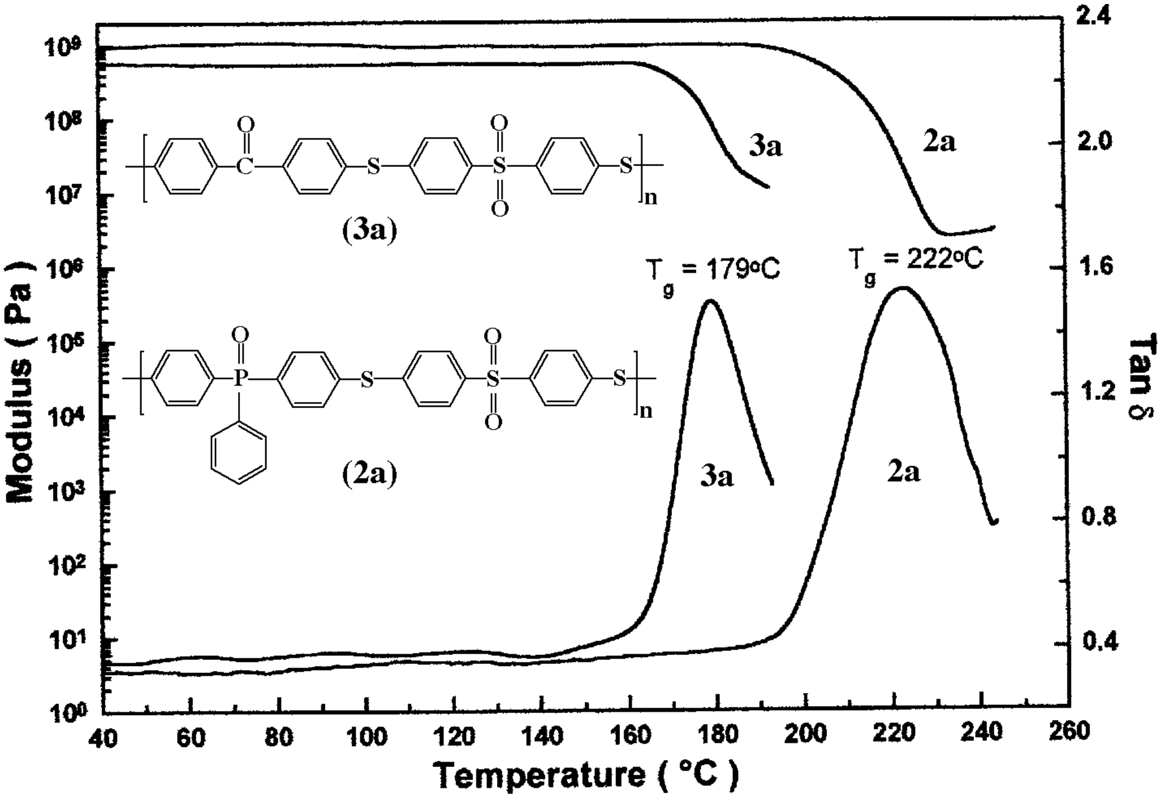


Figure 4.4.4.3 Dynamic mechanical analysis of polymers **2a** and **3a**

TGA thermograms of these polymers are shown in Figures 4.4.4.4 - 4.4.4.7. These materials displayed high thermal stability with initial decomposition temperatures above 500°C in either nitrogen or air atmosphere (Table 4.4.4.1). As shown in Figures 4.4.4.4 and 4.4.4.6 and Table 4.4.4.1, the polymers with higher ketone content exhibited enhanced 5% weight loss temperatures and very high char yield at 750°C in nitrogen. On the other hand, the aryl phosphine oxide containing homo- and co-polymers produced significant amounts of char at 750°C in air atmosphere (Figure 4.4.4.7 and Table 4.4.4.1). As observed in Section 4.3.5, the high char yield of aryl phosphine oxide containing polymers in air may result from the oxidation of phosphine oxide moiety within the polymer backbone at high temperature, whereby oxidized phosphorus formed some kinds of layers at the polymer surface to protect the material from further degradation. The converse results observed in nitrogen for polymers **4a**-**4c** appears to result from different degradation mechanisms.

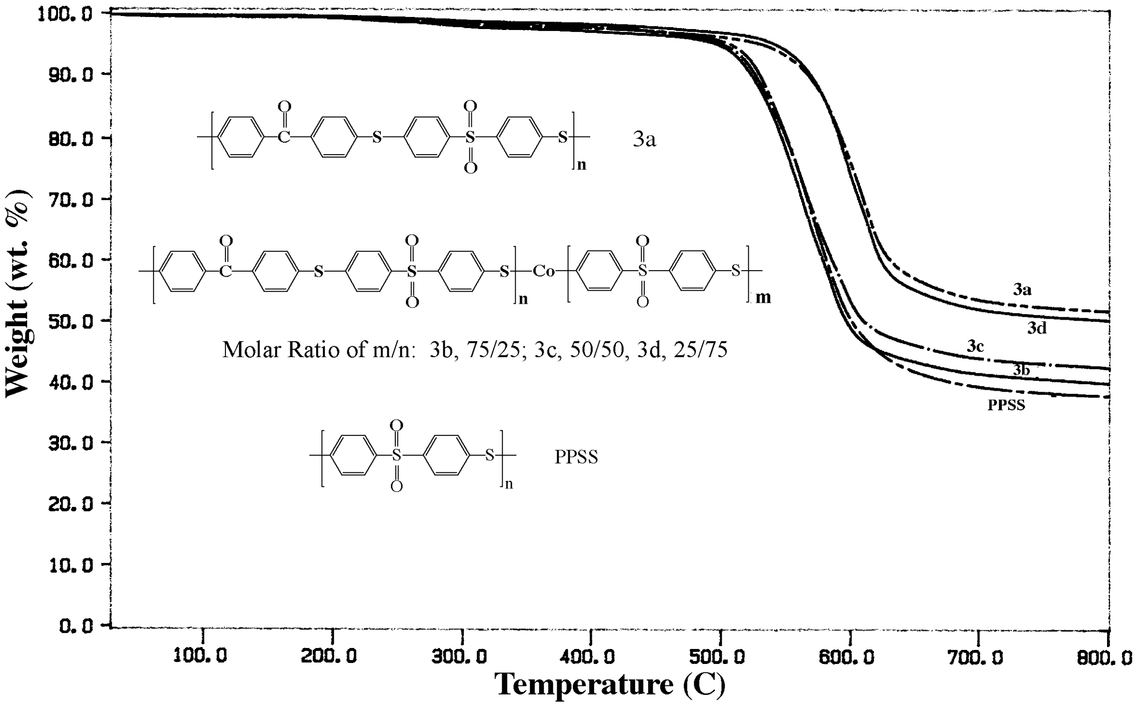


Figure 4.4.4.4 Effect of ketone groups upon the thermal stability and char yield of polymers **3a**-**3d** compared to PPSS in $N_2$ (10°C/min.)

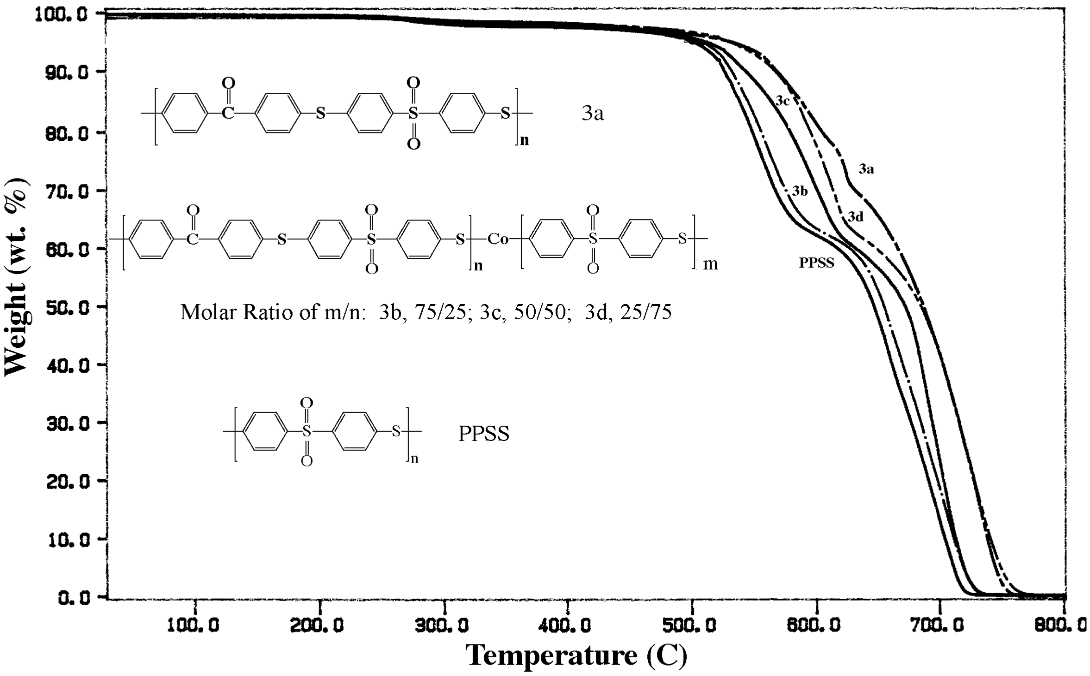


Figure 4.4.4.5 Effect of ketone groups upon the thermal stability and char yield of polymers **3a**-**3d** compared to PPSS in air (10°C/min.)

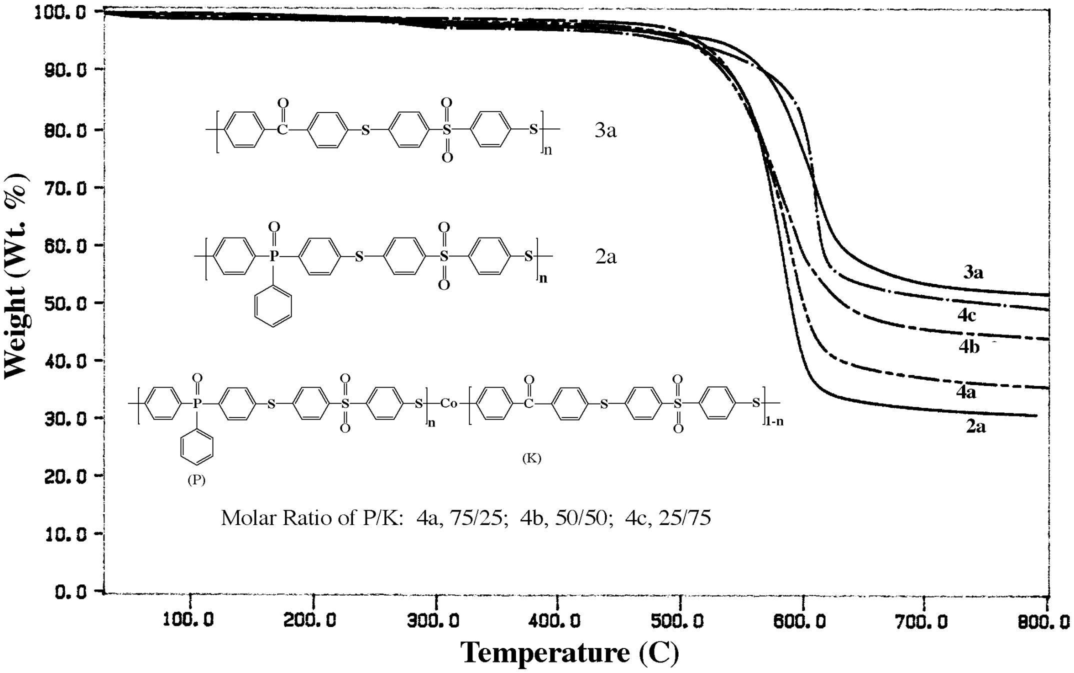


Figure 4.4.4.6 Effect of both ketone and phosphine oxide upon the thermal stability and char yield of polymers **4a**-**4c** compared to PPSS and **2a** in $N_2$ (10°C/min.)

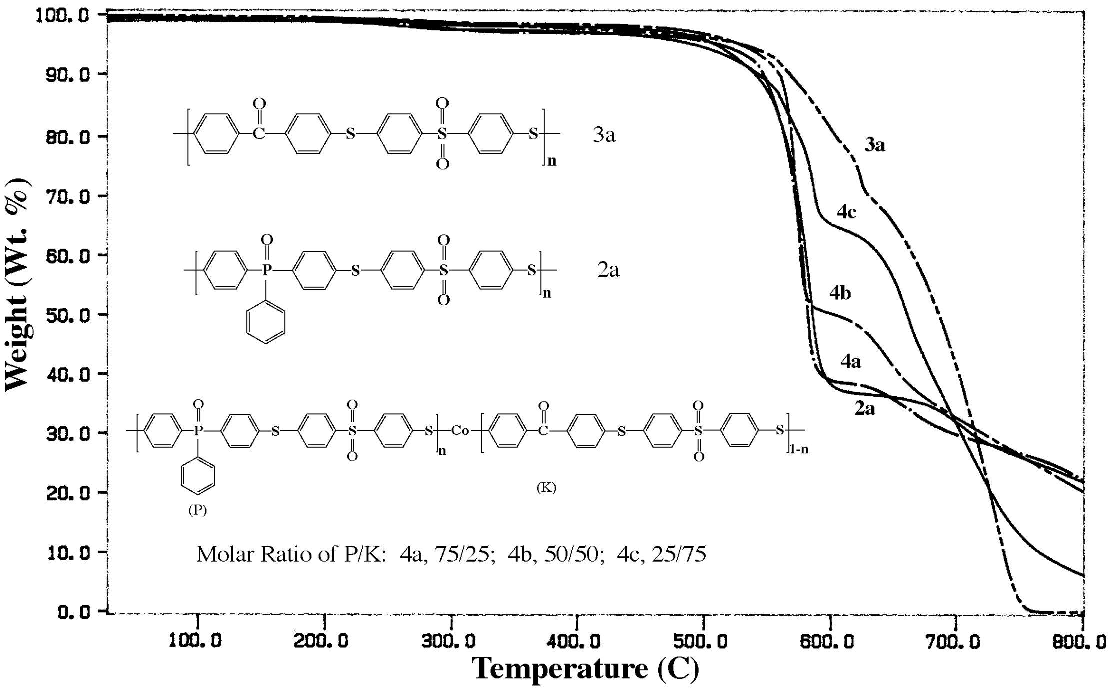


Figure 4.4.4.7 Effect of both ketone and phosphine oxide upon the thermal stability and char yield of polymers **4a**-**4c** compared to PPSS and **2a** in air (10°C/min.)

Micro calorimetry was used to further examine the fire resistance of the new ketone containing PPSS derivatives. Micro calorimetry determines the heat release rate and the amount of heat released by a polymer due to thermal degradation under a specific applied heat flux (50 kW/m$^2$) (142), The measurements were done in cooperation with Dr. Richard Lyon and Dr. Richard Walters of the FAA Fire Safety Section. The results are included in Figures 4.4.4.8-4.4.4.9 and Table 4.4.4.2. In comparison with commercially available poly(ether sulfone)s, such as Victrex and Udel, and poly(phenylene sulfide) (PPS), the new poly(thioarylene sulfone ketone) (**3a**) homopolymer, as well as related copolymers **3c** and **3d**, showed significantly reduced peak heat release rates and total heat release, suggesting that they are good candidates for use in fire resistant materials.

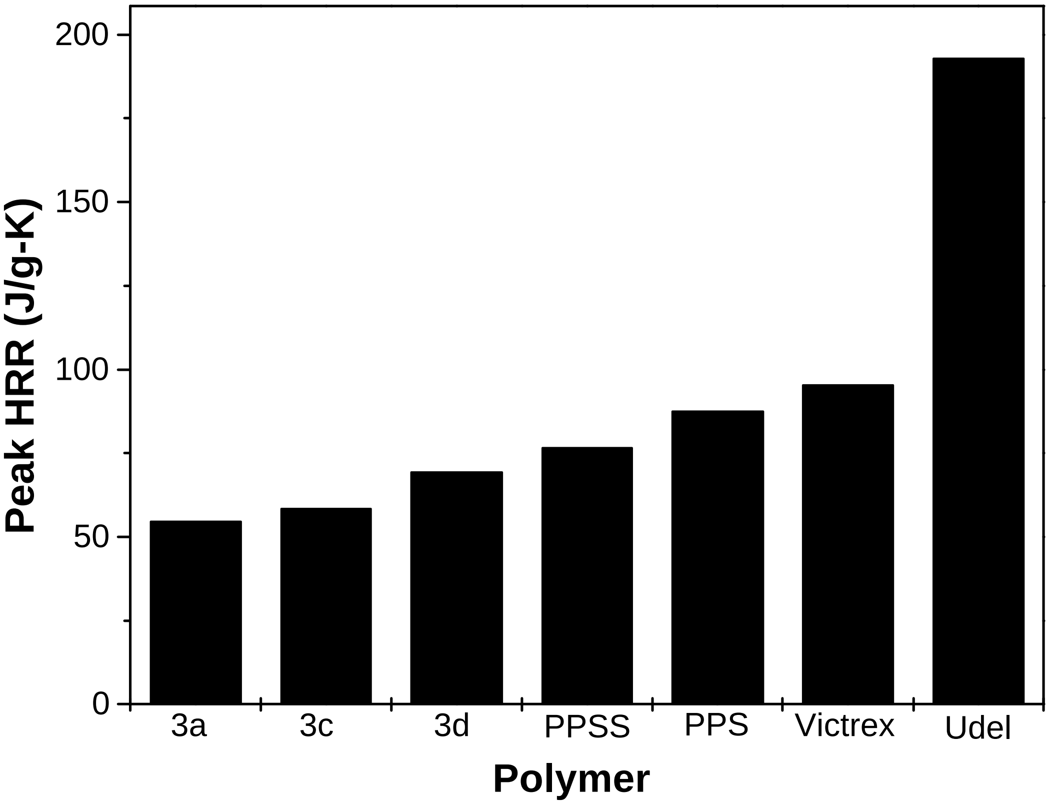


Figure 4.4.4.8  Comparison of peak heat release rate (HRR) of various polymers (micro calorimetry, hear flux: 50 kW/m$^2$)

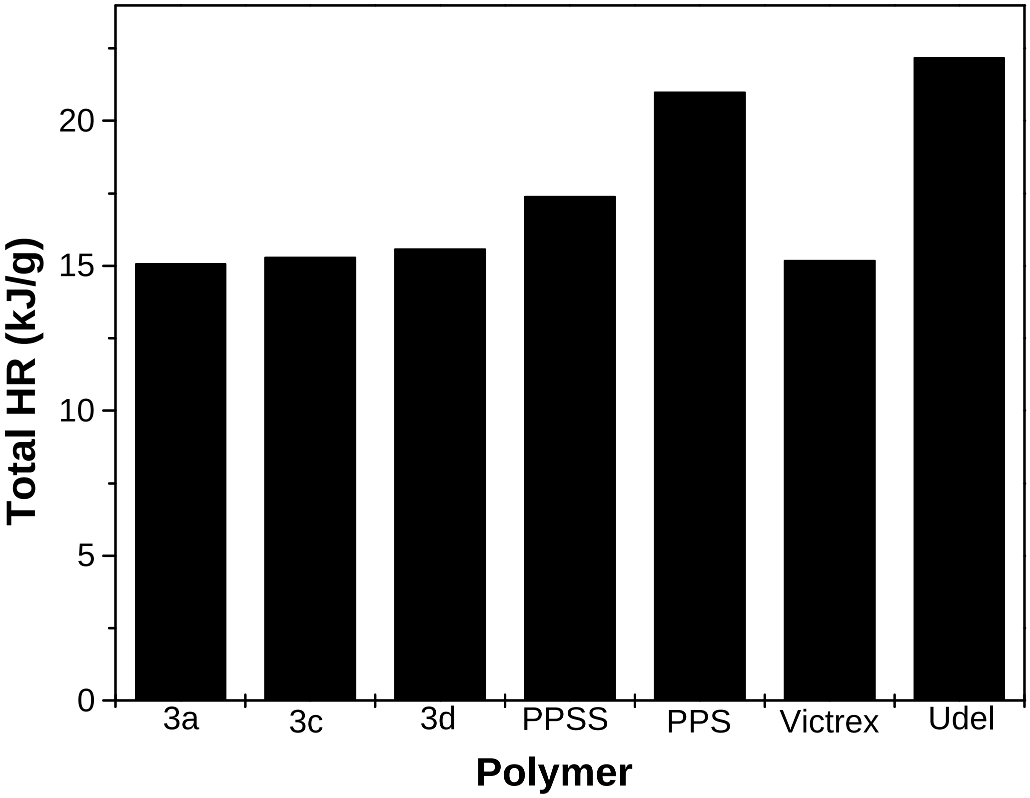
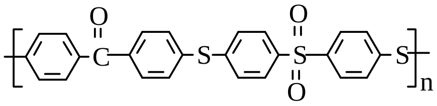
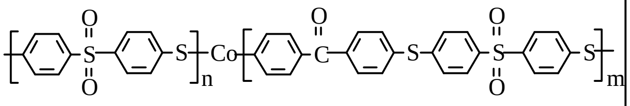
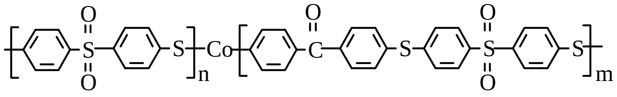
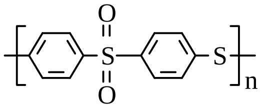
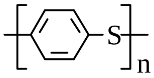
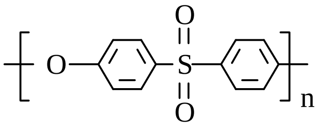
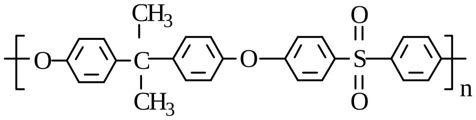


Figure 4.4.4.9 Comparison of total heat release (HR) of various polymers (micro calorimetry, heat flux: 50 $kW/m^2$)

Table 4.4.4.2 Comparison of Peak Heat Release Rate (µHRR) and Total Heat Release (µHR) of Various Polymers

| Polymer | Structure | Peak µHRR* (J/g-K) | Total µHR* (KJ/g) |
|---|---|---|---|
| **3a** |  | 54.8 | 15.1 |
| **3c** | <br>Molar ratio of n/m: 50/50 | 58.7 | 15.3 |
| **3d** | <br>Molar ratio of n/m: 25/75 | 69.5 | 15.6 |
| PPSS |  | 76.7 | 17.4 |
| PPS |  | 87.8 | 21.0 |
| Victrex |  | 95.6 | 15.2 |
| Udel |  | 193.1 | 22.2 |

*Samples tested using micro calorimetry at a heat flux of 50 kW/m$^2$.

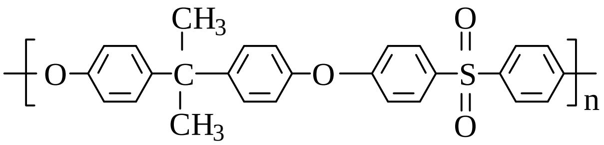
## 4.4.5 Conclusions

A series of new engineering thermoplastics, such as sulfone and/or phosphine oxide containing poly(thioarylene ketone) homo- and copolymers, were successfully synthesized by direct polycondensation in DMAc/$K_2CO_3$. All of the polymers formed were amorphous and had number average molecular weights ranging from 30,000 to 59,000. The two classes of copolymers, poly(thioarylene sulfone ketone/sulfone)s and poly(thioarylene sulfone ketone/phosphine oxide)s, displayed characteristics expected of random copolymers prepared from monomers with relatively equal reactivity, e.g., a linear relationship of $T_g$ with respect to composition. In addition, incorporating phosphine oxide groups into the polymer backbone resulted in enhanced solubility and very high char yields in an air atmosphere. Moreover, the presence of ketone moieties was found to dramatically increase polymer thermal stability in nitrogen, as judged by both 5% weight loss and char yields at 750°C, as well as significantly reduced heat release rates, as seen by micro calorimetry analysis.

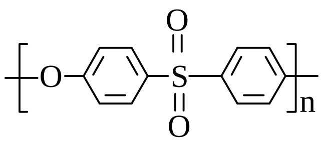
## 4.5 Novel Synthesis of Semi-Crystalline Poly(Arylene Sulfide Ketone) Homopolymer and Amorphous or Semi-Crystalline Sulfone Containing Copolymers via A-B Type Thiol-Functional Monomers

### 4.5.1 Introduction

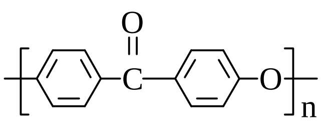
Engineering thermoplastics have found expanded use in the electronic, automotive, and aerospace industries due to their high retention of mechanical and physical properties under harsh operating conditions (105). As a consequence, significant research has recently been directed toward developing new or improved thermoplastic resins and, in particular, poly(arylene ether)s and poly(arylene sulfide)s containing either ketone or sulfone moieties. In general, aromatic polysulfones, such as Udel and Victrex, are amorphous and have a high glass transition temperature ($T_g$), but do not display the chemical resistant characteristics of crystalline materials. Even though the aromatic polyketones, such as poly(ether ether ketone) (PEEK) and poly(ether ketone) (PEK), are crystalline, they tend to have lower $T_g$s than the aromatic polysulfones and require very high processing temperatures due to their high crystalline melting points.



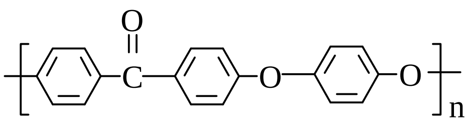
**Udel**



**Victrex**



**PEK**



**PEEK**

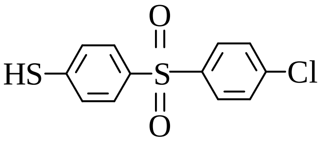
Several methods have been utilized to obtain materials with ketone and/or sulfone moieties, which possess both the thermal and the chemical properties desirable for practical high-temperature thermoplastics. First, several researchers have successfully synthesized amorphous precursors to aromatic polyketones from derivatized monomers

(199-202). These amorphous materials can then be readily transformed into crystalline aromatic polyketones. For example, the ketal formed from 4,4′-difluorobenzophenone and ethylene glycol is easily polymerized under mild conditions, resulting in an amorphous ketal-protected poly(ether ether ketone) (PEEK) (199). The product can then be easily hydrolyzed to crystalline PEEK. Second, polymer blends have been prepared that combine two materials, each possessing some of the desired properties for making a high temperature thermoplastic (203-204). Third, materials containing ketone and/or sulfone moities (125, 205-208) can be can be directly synthesized either via copolymerization of ketone and sulfone containing monomers, or polymerization of a single monomer containing both functional groups.

In the previous sections, the synthesis of amorphous poly(arylene sulfide)s that contain both sulfone and ketone moieties was described, such as poly(phenylene sulfide sulfone) (PPSS), poly(thioarylene sulfone ketone) (**3a**), and copoly(thioarylene sulfone/ketone) (**3b-3d**), via a new simplified method based on a new dithiol-functional monomer. As a extension to this work, semi-crystalline poly(phenylene sulfide ketone) homopolymers and amorphous or semi-crystalline random-copoly(phenylene sulfide sulfone/ketone)s have been prepared from self-polycondensation of the two new A-B type thiol-functional monomers, 4-chloro-4′-mercaptobenzophenone and 4-chloro-4′-mercaptodiphenyl sulfone, and are reported herein.

## 4.5.2 Monomer Synthesis and Characterization

### 4.5.2.1 4-Chloro-4′-Mercaptodiphenyl Sulfone (CMDPS)



CMDPS was synthesized by the aromatic nucleophilic substitution of 4,4′-dichloro- diphenyl sulfone (DCDPS) with sodium hydrosulfide in the presence of potassium carbonate as the base in DMSO, as described in Section 3.1.3.5. The 2 mol% excess of DCDPS relative to sodium hydrosulfide in the stiochoimetry was utilized to suppress the possible disubstituted products. The reaction was conducted for 4 hours at 80°C to afford a yield of 56% monomer grade material after precipitation twice from a basic aqueous solution. The melting point was 139-140°C and the molecular structure of this material was confirmed using $^{1}H$ and $^{13}C$ NMR in $CDCl_3$. The integration of the aromatic protons to the thiol proton yielded a ratio of 8/1. The $^{13}C$ NMR shows eight peaks corresponding to the eight different carbons present in this compound. These spectra are shown below in Figures 4.5.2.1.1 and 4.5.2.1.2. The elemental analysis results are also in good agreement with the designed chemical structure of the CMDPS (Calc.: C, 50.60%, H, 3.19%, S, 22.52%; Found: C, 50.56%, H, 3.19, S, 22.84).

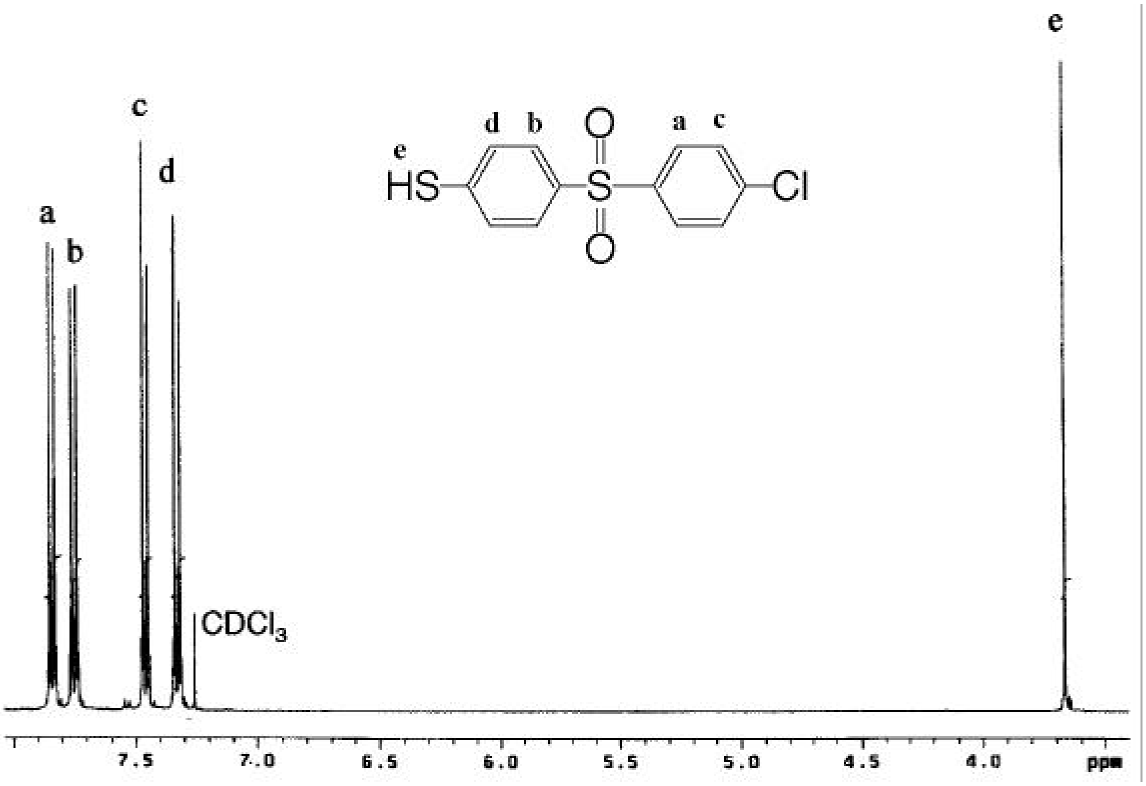


Figure 4.5.2.1.1 $^{1}H$ NMR spectrum of CMDPS in $CDCl_3$

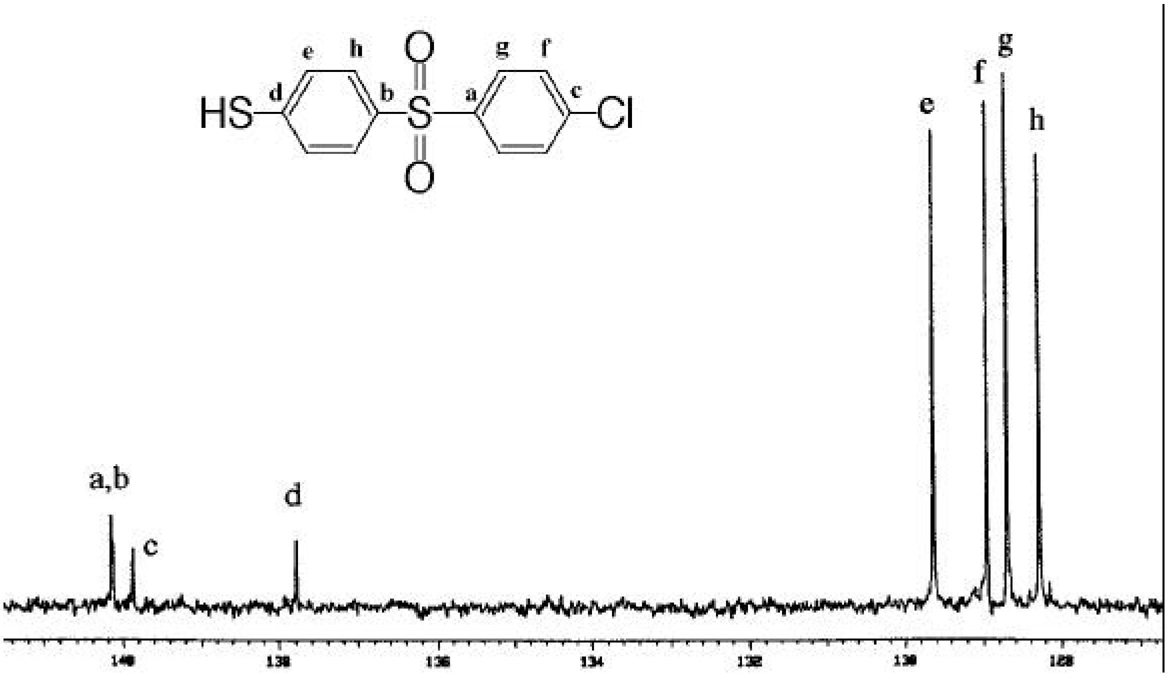
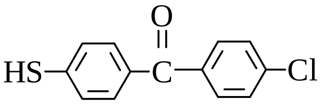


Figure 4.5.2.1.2 $^{13}$C NMR spectrum of CMDPS in $CDCl_3$

### 4.5.2.2 4-Chloro-4′-Mercapto Benzophenone (CMBP)



CMBP was synthesized by reacting 2 mol% excess of 4,4′-dichlorobenzophenone with sodium hydrosulfide in DMSO in the presence of potassium carbonate via an aromatic nucleophilic substitution as described in Section 3.1.3.6. The reaction was conducted at 60°C for one hour to afford a yield of 48% after precipitation twice from a basic aqueous solution. It was necessary to maintain the reaction at a relatively low temperature and short reaction time because if the reaction temperature was too high or the reaction time was too long, it was possible to obtain disubstituted products and oligomers. It is important to avoid these side reactions because separation from the desired product would likely be difficult. The melting point was 158-159°C and the molecular structure of this material was confirmed using $^1$H and $^{13}$C NMR in $CDCl_3$. These spectra are shown below in Figure 4.5.2.2.1 and 4.5.2.2.2. The four different aromatic protons appear at $H_a$ (7.72 ppm), $H_b$ (7.65 ppm), $H_c$ (7.45ppm), and $H_d$

(7.32ppm), and the thiol group shows an up field peak at 3.64 ppm. The protons have an integration ratio of 8 aromatic protons/1 thiol proton. The $^{13}C$ NMR shows nine different peaks corresponding to the nine different carbons in the CMBP. The elemental analysis results are also in excellent agreement with the designed chemical structure of the CMBP (Calc.: C, 62.77%, H, 3.62%, S, 12.89%; Found: C, 62.48%, H, 3.45%, S, 13.19%).

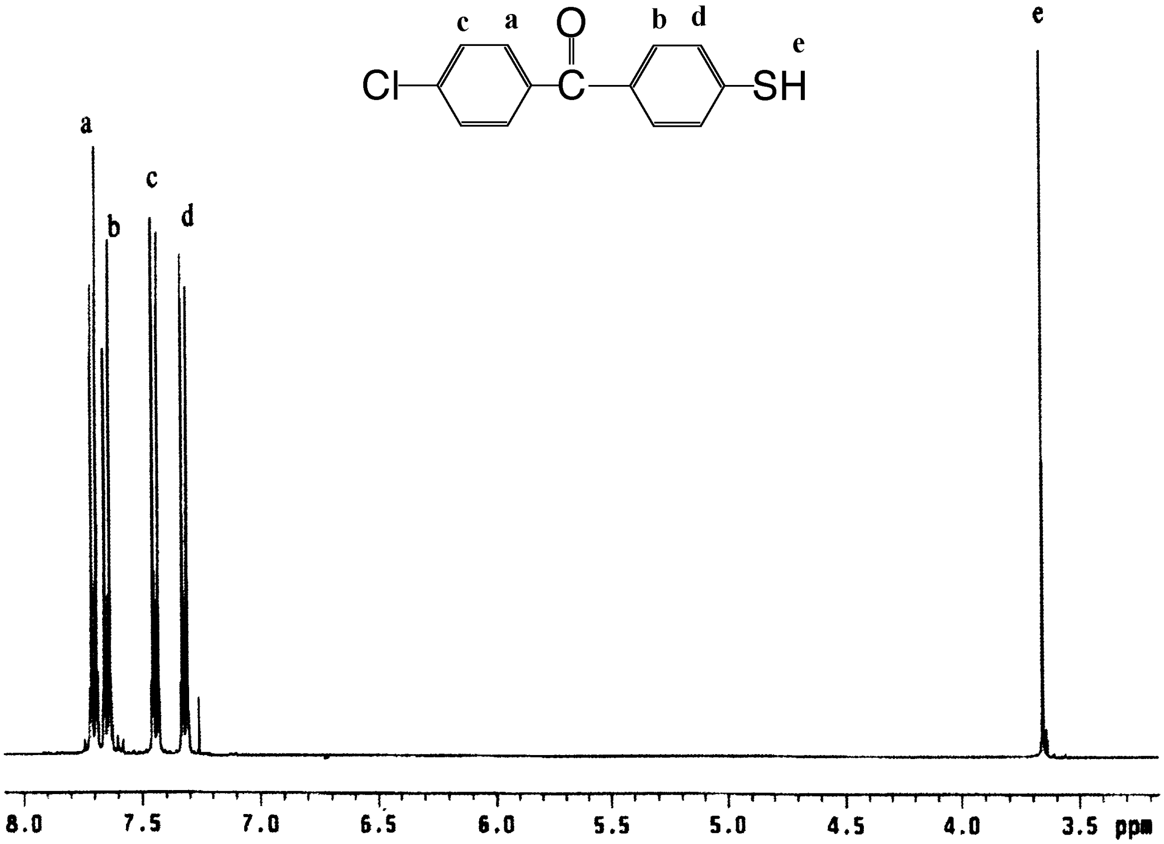


Figure 4.5.2.2.1 $^{1}H$ NMR spectrum of CMBP in $CDCl_3$

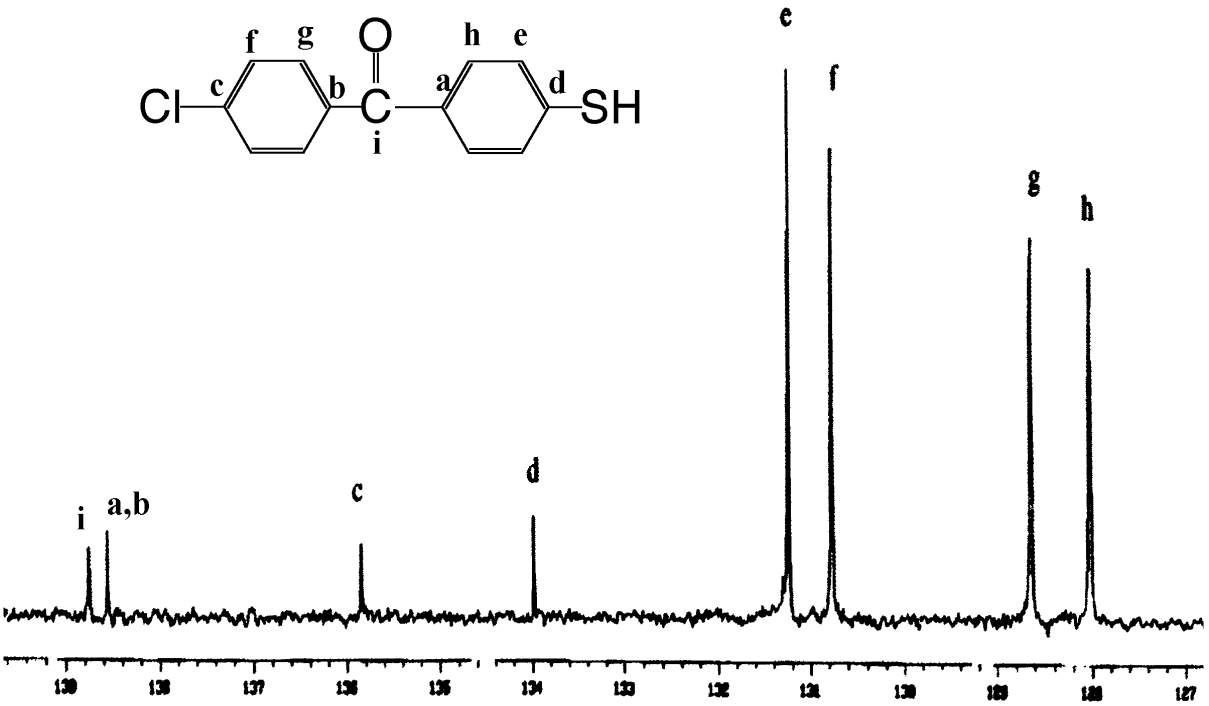
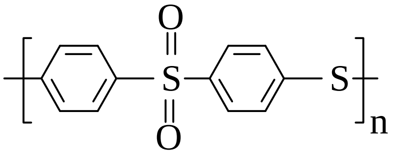
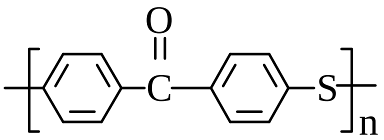


Figure 4.5.2.2.2 $^{13}$C NMR spectrum of CMBP in $CDCl_3$

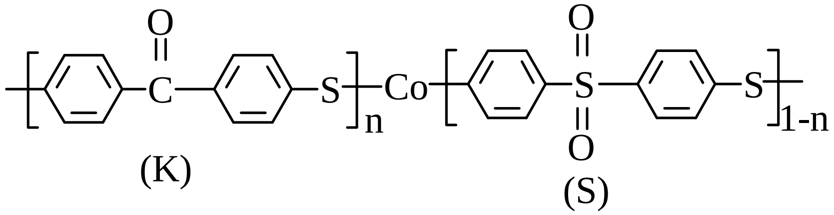
## 4.5.3 Polymer Synthesis



**PPSS**



**PPSK**



Molar Ratio of K/S: **5a**, 85/15; **5b**, 75/25; **5c**, 50/50;
**5d**, 25/75; **5e**, 15/85

It was reported that semi-crystalline poly(phenylene sulfide ketone) (PPSK) homopolymers and related sulfone containing copolymers could be synthesized via a high pressure reaction of sodium hydrosulfide with 4,4′-dichlorodiphenyl sulfone (DCDPS) and/or 4,4′-dichlorobenzophenone (DCBP) at elevated temperature in NMP (125). However, this method requires both high pressure and temperature, as well as the necessity of using water and sodium acetate as additives in the reaction system. The successful synthesis of the new A-B type thiol-functional monomers, 4-chloro-4′-mercaptobenzophenone (CMBP) and 4-chloro-4′-mercaptodiphenyl sulfone (CMDPS), makes it possible to prepare these materials using a simplified reaction scheme. In this new method, the PPSK was synthesized by a self-polycondensation of CMBP in N-cyclohexyl-2-pyrrolidinone (CHP) in the presence of potassium carbonate, as described in Section 3.2.13. CHP, which has a boiling point of 295°C, was used as the reaction solvent to prevent premature crystallization of low molecular weight polymers out of the reaction mixture, as earlier described by workers at Dow Chemical for the semi-crystalline polymers of PEEK and PEK (113). The reaction was initially run at 200°C for 20 minutes under nitrogen purge to dry the system. The temperature was then increased to 290°C for 1 hour to achieve high molecular weight. In a similar manner, the polymerization of a mixture of the two A-B type monomers, CMBP and CMDPS, at a molar ratio of 85/15 and 75/25 (CMBP/CMDPS) yielded semi-crystalline copoly(phenylene sulfide sulfone/ketone)s (**5a**-**5b**) (Scheme 3.2.14).

Amorphous copoly(phenylene sulfide sulfone/ketone)s (**5c**-**5e**) with S/K ratios of 50/50, 75/25, and 85/15 were synthesized by a self-polycondensation using a mixture of CMBP and CMDPS in DMAc in the presence of potassium carbonate, as described in Section 3.3.15. The polymerizations were conducted at 135°C for 4 hours to remove the water by-product via the toluene azeotrope. The temperature was then raised to 160°C to essentially complete the reaction of the functional groups, so that high molecular weight could be achieved.

Poly(phenylene sulfide sulfone) (PPSS) was also prepared by a self-polycondensation of CMDPS in DMAc/$K_2CO_3$ (Scheme 3.2.1.3). In comparison with the traditional high pressure procedure, and the new method based on an A-A type dithiol monomer, described in Section 3.2.1.1 and 3.2.1.2 respectively, this novel self-polycondensation reaction for PPSS is more straightforward and dramatically simplifies the polymerization conditions.

### 4.5.4 Intrinsic Viscosity and GPC Analyses

The number average molecular weights and $M_w/M_n$ ratios of the amorphous polymers **5c**-**5e** were measured by universal calibration GPC, and the results are listed in Table 4.5.4.1. From Table 4.5.4.1, it is shown that the materials are high molecular weight and were considered to be well above their entanglement molecular weight. It should be noted that the molecular weight of polymer **5c** is lower than those of other polymer samples. This is likely due to the partial crystallization of the material during polymerization in DMAc. In addition, these polymers all have monomodal GPC traces and the weight-to-number average ratio, which is a measure of the molecular weight distribution breadth, appears to be in the expected range of about 2.0, indicating they are typical polycondensation reaction without branching. The inherent viscosity of the amorphous materials **5c**-**5e** and PPSS was measured in NMP, while the measurements of the semi-crystalline PPSK and copolymers **5a**-**5b** were made in 98% sulfuric acid due to their lack of solubility in NMP at ambient temperatures. The inherent viscosity results are included in Table 4.5.4.1 and ranged from 0.30 to 0.39 for the semi-crystalline materials, which indicates that high molecular weights have been achieved.

Table 4.5.4.1 GPC and Inherent Viscosity Measurements of Homopolymers PPSK and PPSS and Copolymers **5a**-**5e**

| Polymer | Molar ratio K/S | $M_n$ (g/mole) | $M_w/M_n$ (GPC) | IV (dL/g) |
|---|---|---|---|---|
| PPSK | 100/0 | – | – | 0.37[b] |
| **5a** | 85/15 | – | – | 0.39[b] |
| **5b** | 75/25 | – | – | 0.30[b] |
| **5c** | 50/50 | 21,000 | 1.7 | 0.21[a] |
| **5d** | 25/75 | 32,000 | 1.8 | 0.37[a] |
| **5e** | 15/85 | 36,000 | 1.8 | 0.36[a] |
| PPSS | 0/100 | 35,000 | 1.9 | 0.38[a] |

[a] inherent viscosity (IV) measured in NMP at 25°C,

[b] inherent viscosity measured in 98% sulfuric acid with a concentration of 0.5g of polymer/100 mL of 98% sulfuric acid.

### 4.5.5 Thermal Transition and Fire Resistant Behavior

The thermal transitions of the polymers, including glass transition temperature ($T_g$s), melting point ($T_m$), and recrystallization temperature ($T_c$) were measured by differential scanning calorimetry (DSC) at a heating rate of 10°C/minute under a nitrogen atmosphere. It can be seen from Table 4.5.5.1 and Figure 4.5.5.1 that higher $T_g$s resulted from the increased sulfone content of the PPSS/K copolymers, which is likely due to increased bulkiness with higher sulfone content in the polymer backbone.

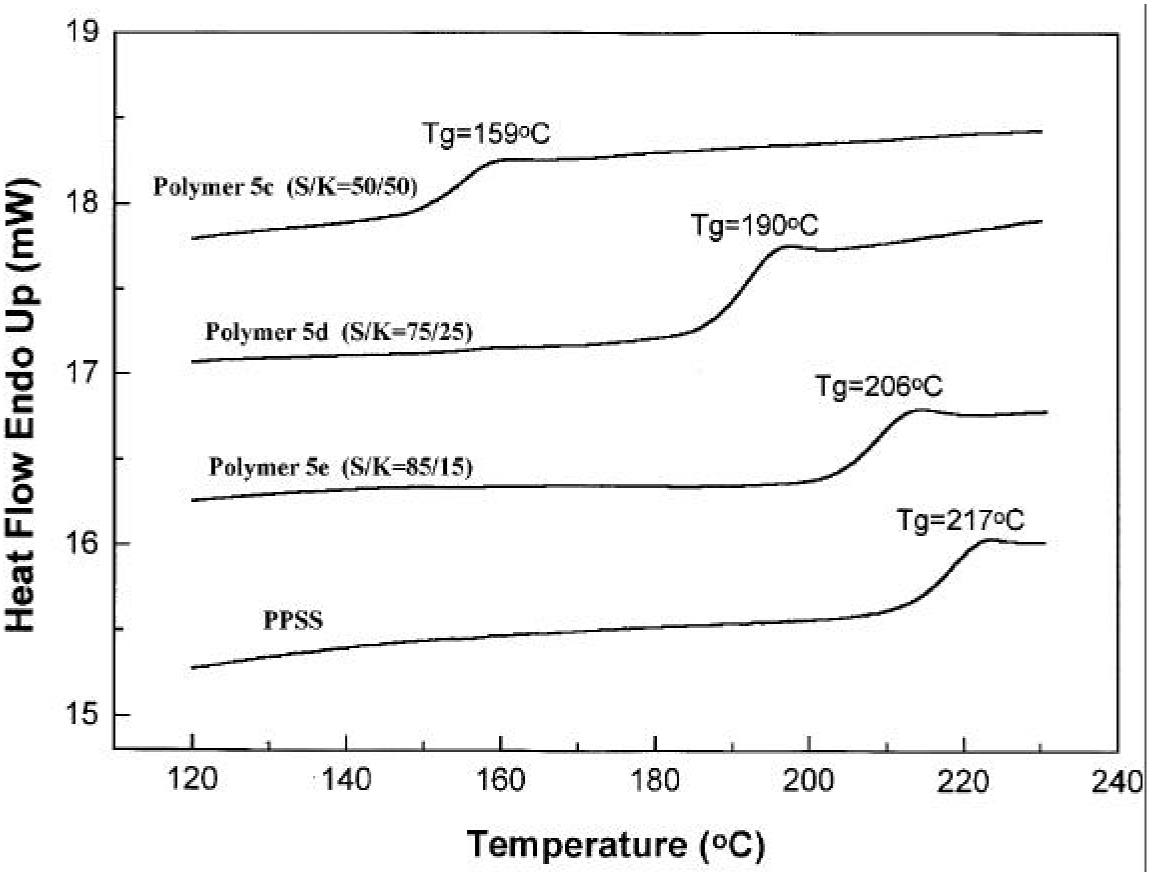


Figure 4.5.5.1 Influence of sulfone content on the glass transition temperatures

A melting endotherm for the semi-crystalline PPSK homopolymer was observed at 347°C, and a recrystallization temperature of 241°C was noted from the cooling (quench) (Figure 4.5.5.2). In addition, the melting point and recrystallization temperatures of semi-crystalline copolymers **5a** and **5b** decreased with increasing sulfone content (Table 5.5.5.1). No melting endotherm was observed for all other copolymers with S : K ratio greater than 25 : 75, which indicates they are amorphous materials.

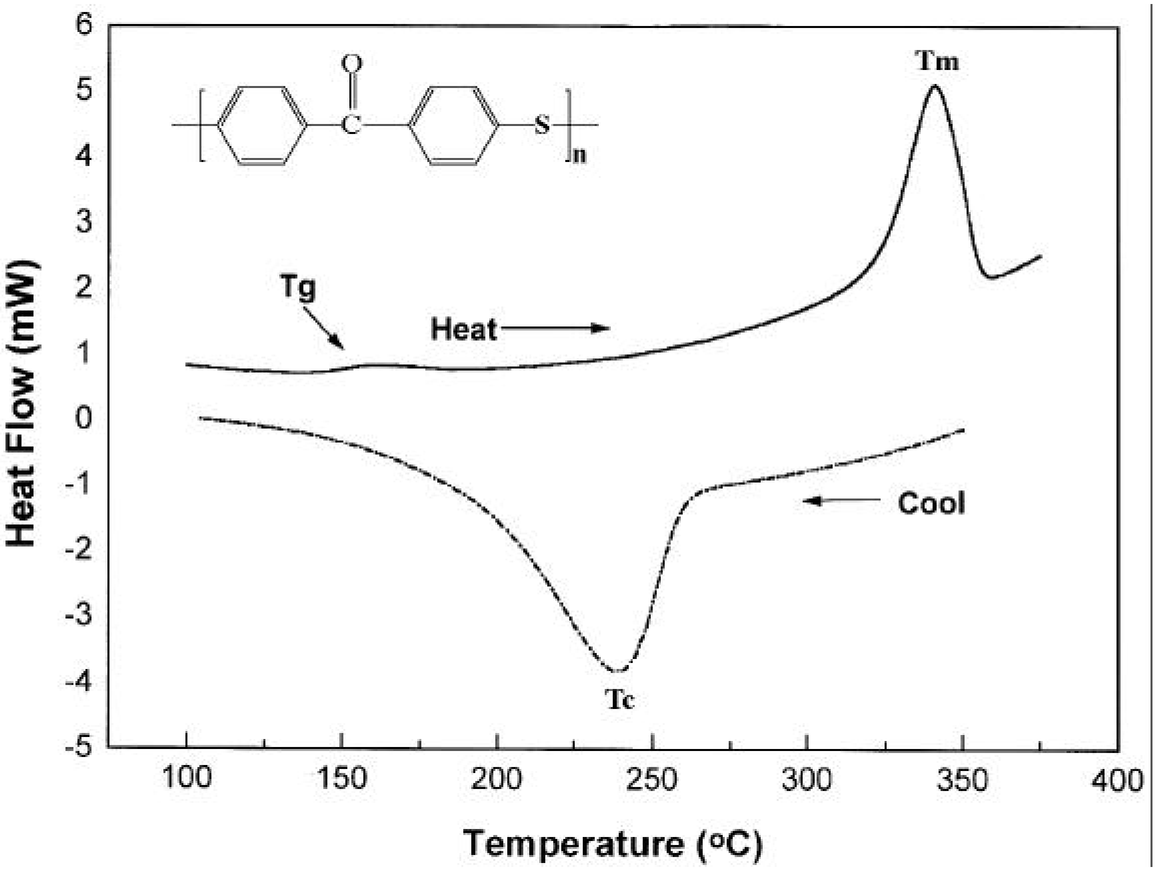


Figure 4.5.5.2 DSC heating and cooling curves for PPSK ($N_2$, 10°C/min. for heating)

Table 4.5.5.1 DSC Analysis of the Polymers

| Polymer | Molar Ratio K/S | $T_g$ (°C) | $T_m$ (°C) | $T_c$[a] (°C) |
|---|---|---|---|---|
| PPSK | 100/0 | 142 | 347 | 241 |
| **5a** | 85/15 | 149 | 317 | 222 |
| **5b** | 75/25 | 155 | 306 | 211 |
| **5c** | 50/50 | 159 | – | – |
| **5d** | 25/75 | 190 | – | – |
| **5e** | 15/85 | 206 | – | – |
| PPSS | 0/100 | 217 | – | – |

[a] obtained from fast cooling (quench).

Thermogravimetric analysis (TGA) was utilized to determine weight loss and, by implication, the thermal stability of these polymers in both air and nitrogen atmospheres. Char yield is an easily obtained, yet important, measurement that correlates the ability to sustain combustion (151), and is therefore used as a indicator of a polymer's anticipated fire resistance. Figure 4.5.5.3 below illustrates the effect of a ketone unit and microstructure upon the TGA char yield in air of various ketone containing homo- and copolymers. It is evident from the thermograms that the semi-crystalline PPSK homopolymer, which contains the highest ketone content, has a much higher char yield than those of the other materials at 700°C in air. Table 4.5.5.2 and Figure 5.5.5.4 show that semi-crystalline PPSK homopolymer and copolymers **5a** and **5b** have significant char yields at 700°C in nitrogen atmosphere, and that char yields increased with increasing ketone content.

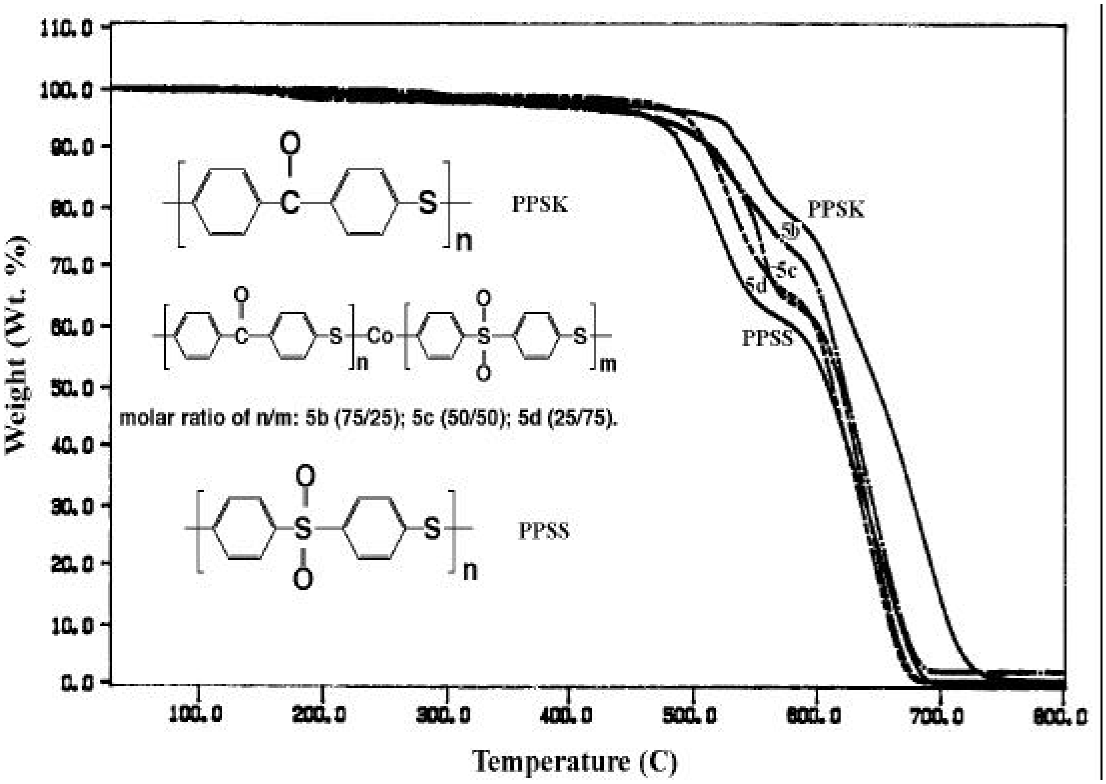


Figure 5.5.5.3 TGA thermal analysis of polymers in air (10°C/min.)

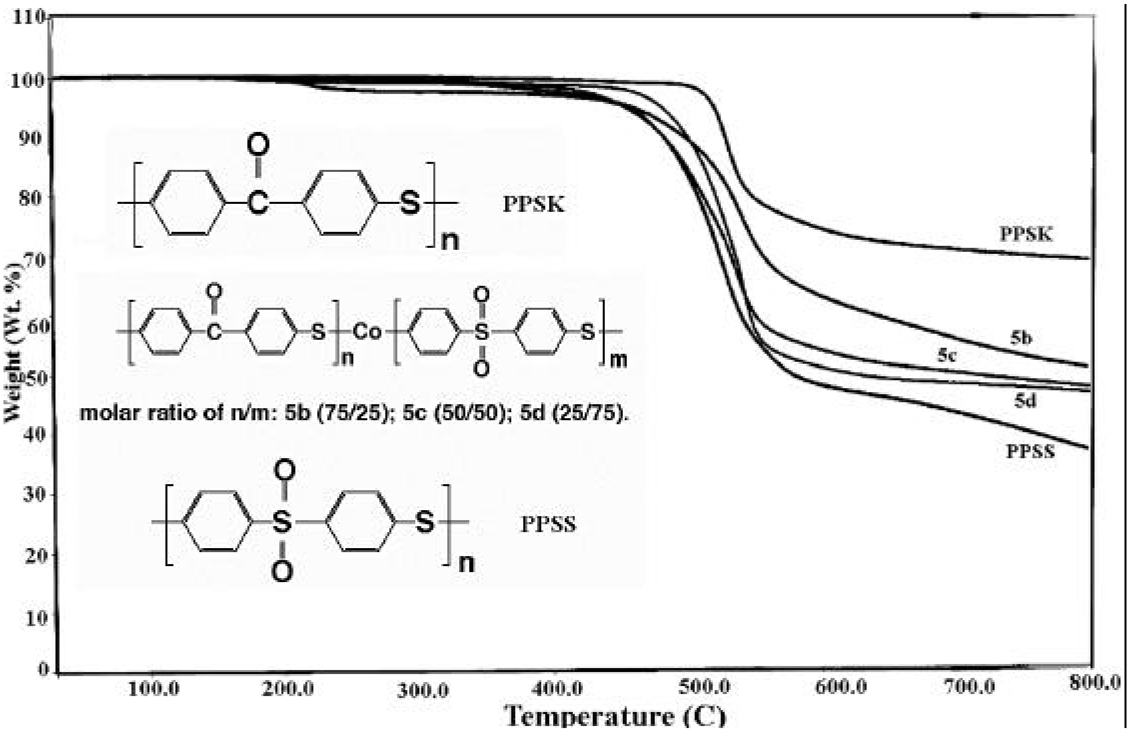


Figure 5.5.5.4 TGA thermal analysis of polymers in $N_2$ (10°C/min.)

Table 4.5.5.2 TGA Thermal Analysis of the Polymers

| Polymer | Molar Ratio K/S | TGA, °C[a] (5% weight loss) | | TGA, %[a] Char yield at 700°C | |
|---|---|---|---|---|---|
| | | $N_2$ | air | $N_2$ | air |
| PPSK | 100/0 | 524 | 518 | 69.5 | 14.2 |
| **5a** | 85/15 | 460 | 506 | 58.6 | 7.8 |
| **5b** | 75/25 | 454 | 470 | 54.9 | 3.0 |
| **5c** | 50/50 | 440 | 469 | 49.2 | 3.2 |
| **5d** | 25/75 | 472 | 494 | 47.6 | 0 |
| **5e** | 15/85 | 443 | 490 | 45.2 | 4.3 |
| PPSS | 0/100 | 441 | 464 | 43.1 | 0 |

[c]heating rate of 10°C/minute.

The flammability of the ketone containing polymers was further examined by micro calorimetry in cooperation with Dr. Richard Lyon and Dr. Richard Walters of the FAA

Fire Safety Section. Micro calorimetry determines the heat release rate and the total amount of heat released by a polymer due to thermal degradation under a specific applied heat flux (50 Kw/m$^2$) (142). These results are summarized in Figures 5.5.5.5 – 5.5.5.6 and Table 5.5.5.3. The poly(phenylene sulfide) (PPS) control had the highest peak heat release rate and total heat release of the samples analyzed, while the semi-crystalline polymers with high ketone content showed significantly reduced peak values and total heat release, which indicates that they have excellent potential fire resistance.

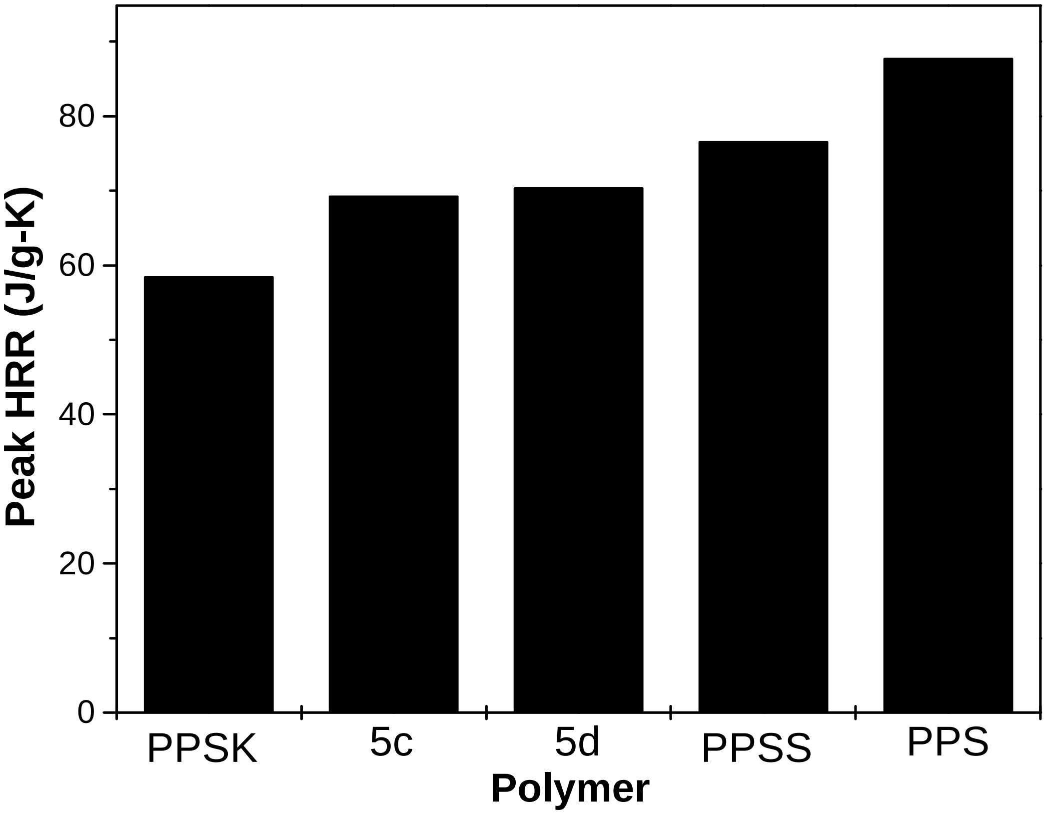


Figure 5.5.5.5 Comparison of peak heat release rate (HRR) of various polymers (micro calorimetry, heat flux: 50 kW/m$^2$)

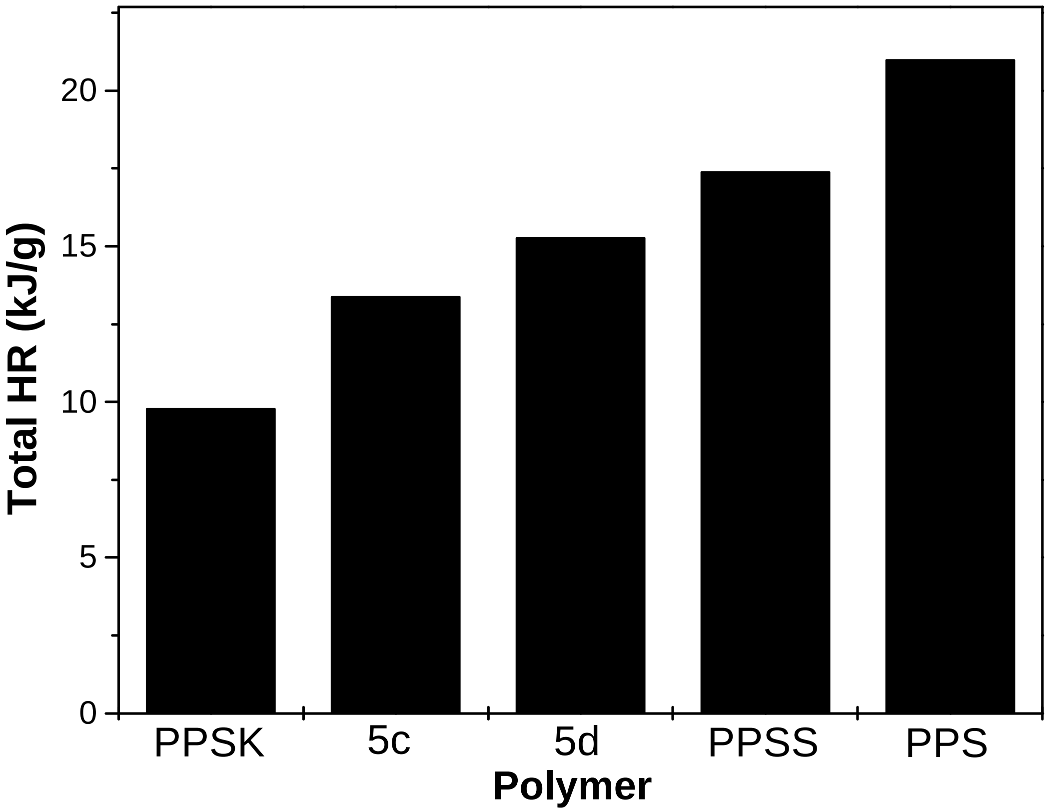
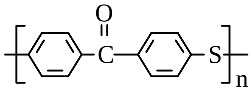
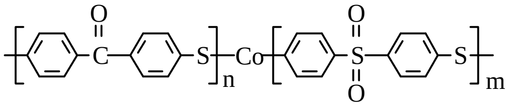
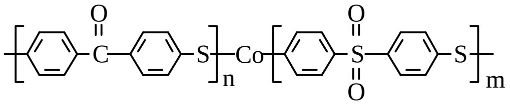
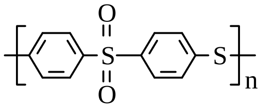
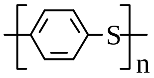


Figure 5.5.5.6 Comparison of total heat release (HR) of various polymers (micro calorimetry, heat flux: 50 kW/m$^2$)

Table 4.5.5.3 Comparison of Peak Heat Release Rate (μHRR) and Total Heat Release (μHR) of Various Polymers

| Polymer | Structure | Peak μHRR* (J/g-K) | Total μHR* (KJ/g) |
|---|---|---|---|
| PPSK |  | 58.5 | 9.8 |
| **5c** | <br>(n/m = 50/50) | 70.5 | 13.4 |
| **5d** | <br>(n/m = 25/75) | 69.3 | 15.3 |
| PPSS |  | 76.7 | 17.4 |
| PPS |  | 87.8 | 21.0 |

*Samples tested using micro calorimetry at a heat flux of 50 kW/$m^2$.

## 4.5.6 Conclusions

Poly(phenylene sulfide ketone) (PPSK) and poly(phenylene sulfide sulfone) (PPSS) homopolymers, as well as random copoly(phenylene sulfide sulfone/ketone)s have been successfully synthesized in high yields by the novel self-polycondensation of the new A-B type thiol-functional monomers. The PPSK and copolymers with sulfone / ketone mole ratios (S : K) ≤ 25 : 75 were semi-crystalline, while the copolymers with S : K ratios > 25 : 75 were amorphous. These materials exhibited an increase in glass transition temperature with increasing sulfone content. The TGA and micro calorimetry analyses show that the semi-crystalline materials with high ketone content had much higher char yields and dramatically lower heat release rates, in comparison with the amorphous copolymers and the PPSS control, indicating good potential fire resistance.

# Chapter 5.0 THESIS CONCLUSIONS

High molecular weight poly(phenylene sulfide sulfone)s (PPSS) have been successfully synthesized via a pressure procedure under the following optimum reaction conditions: reaction temperature 175°C - 200°C, reaction time 3 - 5 hours, and water-to-NaSH molar ratio of 9.4:1 to 15:1. These materials could be compression molded to produce tough, solvent resistant films that showed good thermal stability in air and degraded via a two-step mechanism, which first involved loss of the sulfone link. TGA and cone calorimetry results showed that the PPSS displayed good fire resistance, and was also found to have a very high refractive index value (1.69).

PPSS with well designed thermally stable endgroups were successfully synthesized, and the molecular structures of the end groups were confirmed by $^{13}C$ and $^{1}H$ NMR analyses. In comparison with mercaptide containing PPSS, the new systems with endgroups derived from diphenyl sulfone, 4-chlorophenylphenyl sulfone, and t-butylphenoxide showed much higher initial degradation temperatures, as judged by 2% weight loss, higher char yields at 650°C in air, and significantly improved melt stability.

New A-A and A-B type thiol-functional monomers, bis-(4-mercaptophenyl) sulfone, 4-chloro-4′-mercaptodiphenyl sulfone and 4-chloro-4′-mercaptobenzophenone, were prepared with high purity, and were successfully used to prepare poly(phenylene sulfide sulfone) (PPSS) and new PPSS aryl phosphine oxide and/or ketone containing copolymers via a DMAc/$K_2CO_3$ route. This simplified method has several advantages over the traditional high pressure route for preparing PPSS. It eliminates the necessity of high pressure and temperature, the use of water and sodium acetate as additives, and provides a rational methodology for preparing novel high molecular weight phosphine oxide and/or ketone containing PPSS copolymers. Compared to the sulfide-sulfone homopolymer (PPSS), the new phosphine oxide containing materials exhibited enhanced solubility in common organic solvents, and significant char yields at 750°C in air were achieved. XPS analysis suggests that the phosphorus moieties within the polymer backbone formed phosphate-like layers on the polymer surface, which protects the bulk materials from further degradation. In addition, the presence of ketone moieties within the polymer backbone dramatically increased polymer thermal stability in nitrogen as judged by both 5% weight loss temperatures and char yields at 750°C, and they exhibit unique solubility behavior. The two classes of copolymers, poly(thioarylene sulfone ketone/sulfone)s and poly(thioarylene sulfone ketone/phosphine oxide)s, display characteristics expected of random copolymers prepared from monomers with relatively equal reactivities, e.g., a linear relationship of $T_g$ with respect to composition.

Poly(phenylene sulfide ketone) (PPSK) homopolymer and random copoly(phenylene sulfide sulfone/ketone)s have been successfully synthesized in high yield by a novel self-polycondensation of the new A-B type thiol-functional monomers, 4-chloro-4′-mercaptodiphenyl sulfone and 4-chloro-4′-mercaptobenzophenone. The PPSK and copolymers with sulfone / ketone mole ratios (S : K) ≤ 25 : 75 were semi-crystalline, while the copolymers with S : K ratios > 25 : 75 were amorphous. These materials exhibited an increase in glass transition temperature with increasing sulfone content. TGA and micro calorimetry analyses show that the semi-crystalline materials with high ketone content had much higher char yields and dramatically lower heat release rates, in comparison with the amorphous copolymers and the PPSS control, indicating enhanced fire resistance.

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