

## THE SYNTHESIS AND CHARACTERIZATION OF NEW THERMOPLASTIC FIRE RESISTANT MATERIALS

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### ABSTRACT

Thermally stable high performance poly(arylene sulfide sulfone) homopolymers and aryl phosphine oxide containing comonomers in optionally controlled concentrations have been prepared and characterized. In general, tough thermoplastic materials have been produced that show significant char yield in air, which increase with the concentration of aryl phosphine oxide. Thus, they are considered candidates for fire safe thermoplastic materials. Preliminary cone calorimetry measurements have been conducted, which indicate that, indeed, the heat of combustion is reduced. Additional characterization studies are in progress.

### 1. INTRODUCTION

Organic materials are widely utilized in aircraft interiors for various important functions, such as carpets, seats, bins, appliance housings, communication devices, etc. The relevance of the fire safety of these materials to airline transportation is well acknowledged, but poorly understood. There is an important need to further identify fundamental relationships between the molecular structure of the materials and their behavior in fires. This should assist in the rational design of fire resistant cabins for commercial aircraft. It is considered that basic research on synthesis, characterization, and processing of new materials will be necessary to improve the fire performance of material systems. A summary of these features has recently been provided (1).

Thermoplastic materials offer attractive advantages including rapid processability by methodologies such as injection molding, film extrusion and fiber spinning. In addition, the likelihood of generating recyclable materials is recognized to be more straightforward than for the other option, e.g. thermosetting network systems. The author and his colleagues have been involved in novel phosphorus containing polymers now for over five years (6). Emphasis has been placed upon 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 an alternate possibility, and such systems would be favored where transparency and exceptionally high impact strength are sought. Both morphologies are possible in the systems investigated thus far. The triphenyl phosphine oxide unit is inherently non-coplanar and leads, in general, to amorphous homopolymers which display high transition temperatures, good optical transparency, very high char yields when exposed to either nitrogen or air (TGA experiments), ductile mechanical behavior, and good adhesion characteristics (especially to metals). Many of these same characteristics can be applied to semicrystalline copolymers where the composition of the triaryl phosphine oxide structure is limited to about 50 mole percent or less. Examples of systems already demonstrated include the poly(arylene ether ketone)s, polyimides, polybenzoxazoles, as well as polycarbonates, polyesters, and polyamides. In addition, poly(thioarylene phosphine oxides), which are analogous to polyphenylene sulfides, have also been synthesized.

Initial characterization of the homo- and copolymers was limited to thermogravimetric analysis (TGA) and rather crude laboratory Bunsen burner testing. However, these preliminary evaluations repeatedly demonstrated significant qualitative, but apparently fundamental, differences between the high performance aromatic polymers that contained hydrolytically stable phosphorus and their controls.

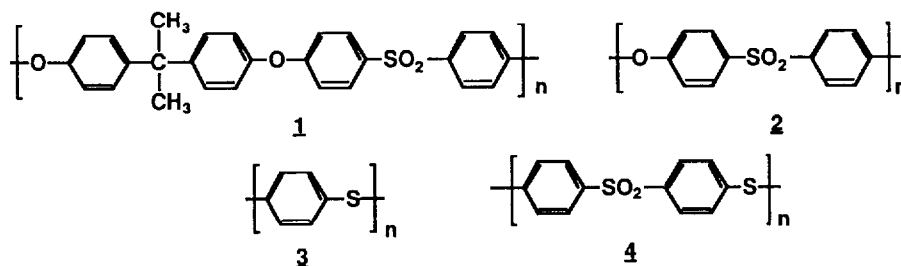
Some of the homo- and copolymers, as mentioned earlier, showed remarkably high weight retention in both inert atmospheres, such as nitrogen, as well as more aggressive air or oxygen systems.

All of the materials described in this section appear to be melt processable, if properly designed to the appropriate molecular weights. These extensive laboratory experiments have recently been expanded to assess the fire resistance of the new material systems via cone calorimetry. This has been possible through the joint collaboration with the NIST Fire Research Laboratory, under the guidance of Dr. T. Kashiwagi.

The data indicate that the heat release rate by these cone calorimetry measurements has been significantly reduced. There are certainly many additional unanswered questions concerning

both the proper molecular design and the most appropriate fire test methodologies. For example, it is possible to replace one of the three phenyl groups with an alternate structure, such as a methyl group. This would increase the fraction of phosphorus in the repeat unit and might also reduce undesirable residual soot formation.

Considerable interest has developed in the synthesis, characterization and properties, including fire resistance, of poly(arylene ether)s. The sulfur containing analogs to the poly(arylene ether)s, although important, are much less well studied (2,3). By far and away the most important sulfur containing material in this classification is poly(phenylene sulfide). A related sulfide sulfone has been investigated relatively briefly in the literature and in commercial practice and references to its investigation are mostly limited to either the patent literature or the commercial trade literature. The sulfide sulfone has been described as an amorphous polymer in its relatively brief literature. The general reaction involves utilizing sodium sulfide as the nucleophile and 4,4'-dichlorodiphenyl sulfone as the active aromatic halide. It is of interest to prepare not only homopolymers, but also copolymers, which could produce semicrystalline materials, and also copolymer of 4 with an appropriate triaryl phosphine oxide monomers. In particular, we have synthesized 4,4'-dichlorodiphenyl phenylphosphine oxide as an appropriate comonomer in these syntheses. We expect that there will be some further enhancement by conducting those types of chemistries. In this paper we report the synthesis of homopolymers utilizing a modified patent literature procedure (4,5). Complementary studies are proceeding at the present time.



## 2. EXPERIMENTAL

**2.1 Materials** Monomer grade 4,4'-dichlorodiphenyl sulfone was also kindly supplied by the Amoco Chemical Company. N-Methyl pyrrolidone, sodium sulfide nonahydrate, sodium hydrosulfide, sodium acetate (anhydrous) were obtained from Aldrich and were used as received.

### 2.2 Preparation of 4,4'-dichlorodiphenyl phenylphosphine oxide

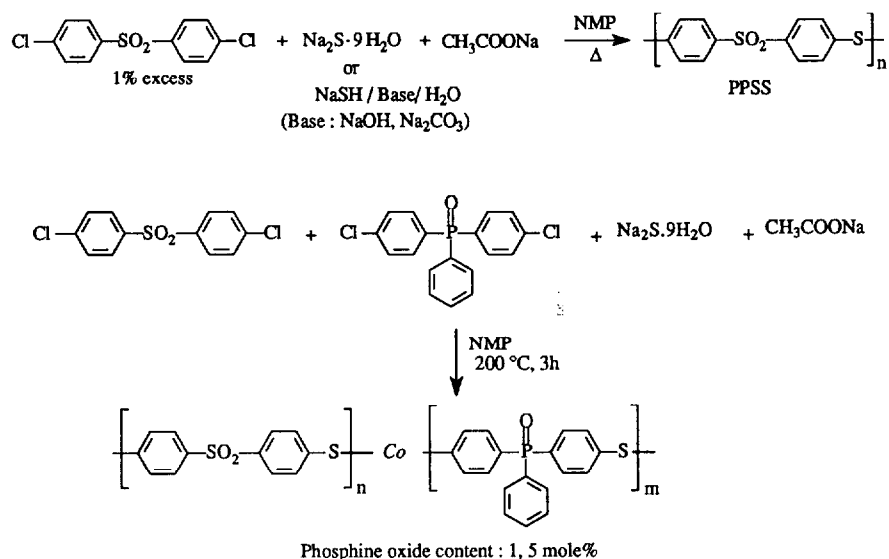
The phosphine oxide monomer was prepared and purified by a variation of a known Grignard technique (6).

**2.3 Polymerization** Preparation of high molecular weight polyphenylene sulfide sulfone is described in the patent literature (4,5). The synthesis of poly(phenylene sulfide sulfone) is described briefly below based on procedures derived from Reference 4 and 5. Dichlorodiphenyl sulfone was reacted with either sodium sulfide nonahydrate and sodium acetate in NMP or it was prepared using sodium hydrosulfide, plus either sodium hydroxide or sodium carbonate, along with sodium acetate in NMP, to which distilled water had been intentionally added. The NMP-to-water ratio utilized, following the patent references 4 and 5, were about 0.85-to-1. The NMP-to-sulfur ratio utilized was about 8-to-1. There was 1 mole percent excess of the activated dichlorodiphenyl sulfone utilized in the stoichiometry to attempt to ensure that the endgroups in the polymer chain would be mostly the relatively stable chlorophenyl groups. The synthetic variables studied so far include the choice of the base, its purity, the reaction temperature, and the reaction time. In general, the best results have been obtained by reacting the reagents for about 3 hours at 200°C. Longer times and higher reaction temperatures have been less successful. High molecular weight polymers with number average molecular weights ( $M_n$ ) as high as 44,000 g/mol (Daltons) have been obtained.

**2.4 Characterization** Molecular weights were determined by quantitative gel permeation chromatography using a Waters 150C GPC equipped with an intrinsic viscosity and refractive index detector utilizing methodology developed in our laboratory (7,8). Glass transition temperatures were measured using a Perkin Elmer DSC 7 at a heating rate of 10°C per min. in nitrogen. TGA analysis was performed in air and nitrogen at a heating rate of 10°C/min. using a Perkin Elmer TGA 7. Dynamic Mechanical Analysis was also employed using a Perkin Elmer DMA 7 at a heating rate of 2°C/min. and at 1Hz. The materials were compression molded into tough ductile films at 280°C and basic stress-strain behavior was investigated utilizing an Instron Table Model 1123 equipped with a strain gauge extensometer. Samples in the shape of dog bones were cut (ASTM D-638-5) from compression molded films of thickness in the range of 0.66-0.85 mm. Refractive index measurements were performed on solution cast films, which were subsequently dried, using a Metricon Model 2010 refractometer at 632 nm.

### 3. RESULTS AND DISCUSSION

Scheme 1



PPSS and PPSS-*co*-PO (copolymers with phosphine oxide) were prepared (Scheme 1) in an analogous manner as reported in the patent literature (4,5). These reactions were conducted in a pressure reactor at 200°C and 100-150 psi. The endgroups were designed to be principally chlorophenyl, which enhances the melt stability, by using a 1 mole% excess of the chloro monomer. The other choice, mercaptide-type endgroups, are generally less desirable for stability concerns. Commercially useful molecular weights have been achieved that range from 14,000 to 44,000 number average molecular weight. The weight-to-number average ratio, which is a measure of the molecular weight distribution, appears to be in the expected range of about 2.0. The glass transition temperatures for PPSS and PPSS-*co*-PO range from 210-220°C.

PPSS exhibited interesting solubility characteristics. The solubility of PPSS and PPSS-*co*-PO has been examined in various solvents (Table 1). The sulfide-sulfone homo or copolymer is resistant to many solvents which will dissolve the analogous polyether sulfones such as Udel and Victrex. This is true both at room temperature and at elevated temperatures.

Table 1  
Solubility Behavior of PPSS and PPSS-co-PO

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, crystallized out of solution upon standing

These polymers were soluble in several polar solvents, but an interesting phenomena occurs. After the materials were dissolved and they were allowed to sit for a few hours the materials crystallized out of the solution. The 5% phosphine oxide containing copolymer took much longer to crystallize out as compared to the PPSS homopolymer and 1% phosphine oxide copolymer. This phenomena could be very important and was explored in Table 2, where the susceptibility of molded PPSS homopolymer films to environmental stress-cracking and crazing (ESC) was studied. An examination of Table 2 shows a remarkable degree of resistance to important organic liquids. This may be a result of crystallization on the surface and is being studied currently. In addition, PPSS films exhibited a very high refractive index value of 1.705 which are typical of aromatic sulfur containing polymers.

Table 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

The dynamic mechanical behavior of molded PPSS films has been investigated and is shown in Figure 1. The material show a high modulus up to temperatures approaching the glass transition temperature of 215°C, and show a secondary relaxation at -100°C, which is indicative of molecular motion well below  $T_g$  and is often tied to enhanced ductility. Mechanical properties of PPSS are shown in Table 3. The properties such as modulus and elongation are in the range of the polyarylene ether sulfones and would be considered to represent ductile behavior.

Table 3

Mechanical Properties of PPSS (ASTM D638-5, 1.0 mm/min.)

$M_n$	Tensile Strength (MPa)	Elongation at Break (%)
20K	74.5 ± 7.1	12.5 ± 3.1
25K	88.5 ± 0.5	17.4 ± 0.8
39K	92.9 ± 0.6	22.0 ± 3.7
43K	93.9 ± 0.7	22.3 ± 4.1

TGA thermograms of these polymers are shown in Figure 2. These materials display high thermal stability with decomposition temperatures around 500°C in either air or nitrogen. Polythioarylene phosphine oxide homopolymer (PTAPO) ( $M_n=5000$ ) shows significant amount of char at 700°C. The materials also show what appears to be a two-step degradation behavior in air, and by crude preliminary Bunsen burner tests certainly display self-extinguishing characteristics. Flammability behavior is currently being studied using cone calorimetry and this is provided in Figure 3.

#### 4. CONCLUSIONS

Moderate to high molecular weight polyphenylene sulfide sulfone homopolymers and copolymers containing triaryl phosphine oxide have been successfully prepared. These materials can be compression molded to produce tough, solvent resistant materials that show good thermal stability in air and that degrade via a two-step mechanism. These materials produce sizable amounts of char upon degradation, suggesting improved fire resistance. PPSS also exhibits a very high refractive index.

#### 5. CURRENT AND FUTURE STUDIES

Currently, a systematic series of copolymers based upon poly(arylene ether)s, poly(arylene sulfide)s, and poly(aryl ether imide)s, which vary in the concentration of aryl phosphine oxide comonomer are being prepared. These materials will be subjected to degradation studies, both by thermal analysis and cone calorimetry in selected cases.

#### 6. ACKNOWLEDGMENTS

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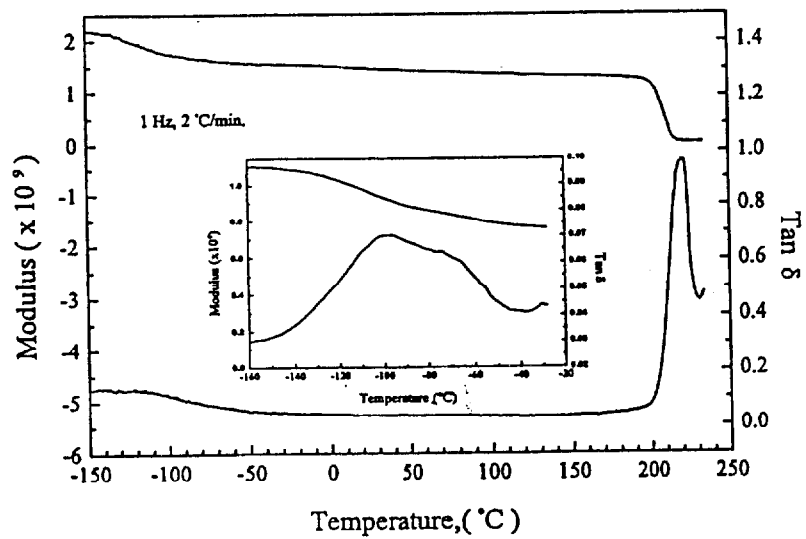


Figure 1: Dynamic Mechanical Analysis of PPSS

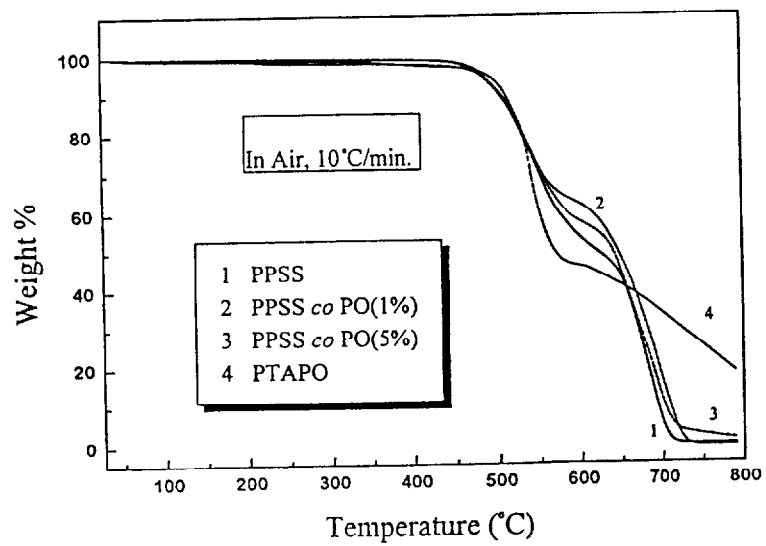


Figure 2. TGA Thermogram of PPSS and PPSS-co-PO

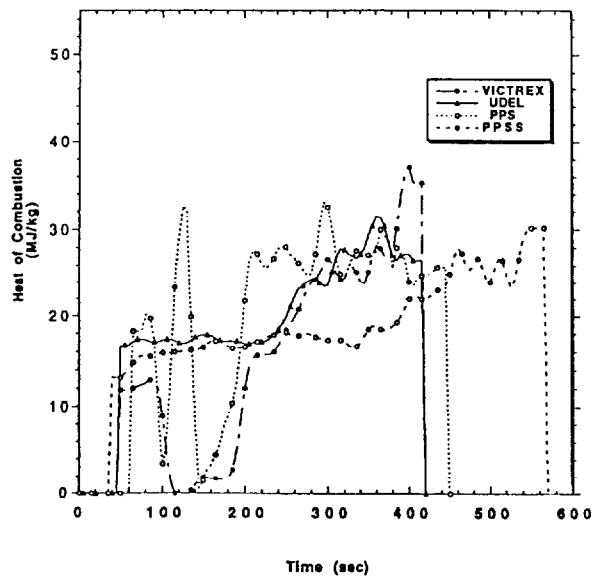
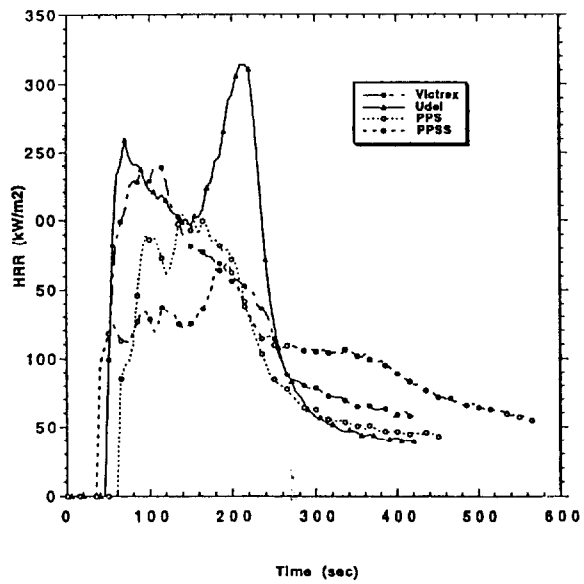


Figure 3. Cone Calorimetry Results at 70 KW/m<sup>2</sup>

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