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The Synthesis, Characterization, and Systematic Fire Safety Evaluation of High Volume and Specialty Hydrolytically Stable Phosphine Oxide Containing Polymeric Materials

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United States Department of Commerce
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Final Report

January, 1997

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I. Executive Summary

This project has investigated the incorporation of either triphenyl phosphine oxide or diphenyl methyl phosphine oxide moieties into the chain. The basis for these studies was the anticipation that the phosphorus would enhance the fire resistance of thermoplastic and thermosetting materials, without the potential hazard of extraction or vaporization that are common for many fire retardant additives. An additional driving force was the expectation that the mechanical properties of such aryl phosphine oxide modified polymers would be interesting and maintained, independent of their concentration. The latter is not true for the physical additives that are normally observed to embrittle ductile engineering thermoplastics if employed beyond a certain concentration level. The new concept has been successfully explored synthetically for a wide variety of macromolecular materials including polyesters, polyamides, polyarylene ethers, polyimides, and epoxy resin networks cured with aromatic phosphorus containing diamines. In all cases, it has been possible to prepare materials that display attractive chemical structure, physical property relationships. Fire resistance testing in our laboratories using simplified Bunsen burner-type approaches always show the materials to be self-extinguishing. In addition, thermal degradation studies utilizing thermogravimetric analysis (TGA) methodologies always generate significant char yields in air at elevated temperatures, which contrasts with most high performance non-phosphorus containing materials. The yields in inert atmospheres, such as nitrogen, are not as significantly changed, but are still uniformly high. This preliminary positive behavior led to the study of selected systems by cone calorimetry in conjunction with Dr. T. Kashiwagi of the NIST Fire Laboratories. The quantity of these research polymers required for these studies was a somewhat limiting feature and restricted the more detailed studies to the polyamides, such as Nylon 6,6, polycarbonate, such as bisphenol-A based polycarbonates, and a fairly extensive study of poly(arylene ether)s, including detailed structure/property comparisons of poly(arylene ether phosphine oxide)s with commercially important poly(arylene ether sulfone)s. Limited studies were also initiated with aromatic polyimides, epoxy resins, and poly(thio arylene ether) materials, such as PPS and the analogous poly(arylene sulfide sulfone). The most extensive results have been obtained with the modified polyamides, modified polycarbonates, and modified poly(arylene ether)s, and these form the basis of this final report. The other results, while quite interesting, need further verification before firm conclusions can be drawn.

For the polyamide (Nylon 6,6) triaryl phosphine oxide copolymers, it was demonstrated that either amorphous or semicrystalline materials could be made containing 10, 20 and 30% of the triaryl phosphine oxide, by functionalizing to a dicarboxylic acid prior to copolymer synthesis. The heat release rate at 40 kw/m^2 was systematically reduced with increasing phosphorus comonomer concentration over the range studied (10, 20, 30%). Similarly, the derived heat of combustion data also showed a favorable trend. In contrast, the specific extinction coefficient measurements demonstrated that the increased smoke, which was interpreted as being related to the slow burning aryl phosphine oxide residues. In addition, increased carbon monoxide yields were also observed. Analogous results were obtained with the

polycarbonate copolymers. Again, high char yields, heat release rate reduction was observed, but again, higher smoke density and carbon monoxide was undesirably noted.

The most extensive study was conducted with poly(arylene ether) triphenyl phosphineoxide containing copolymers, and the results were compared with the commercial polysulfones. In this case, isothermal TGA measurements in air of the control and phosphine oxide copolymers were studied and it could be easily demonstrated that whereas the polyether sulfone was completely volatilized at 550 or 600°C in no more than 60 minutes, the phosphine oxide copolymers could be demonstrated to maintain 20-30% char yield in air at temperatures up to 600°C for at least 3 hours. The nature of the char has been investigated to some extent and is observed to contain a relatively high concentration of phosphorus. The char consists of several different chemical entities as judged by the presence of 3 or more phosphorus 31 NMR peaks. In one controlled dynamic TGA experiment, the char yield at 700°C was demonstrated to be a function of the theoretical weight percent phosphorus, within the range of about 5-14%. The heat release rates were investigated by cone calorimetry at 40 kw/m². The phosphorus containing polymers average peak heat release rate was moderately lower than the polyether sulfone, although the data may have been within experimental error. The materials' heat release rate behavior as a function of time was interesting. The wholly aromatic poly(arylene ether sulfone) ignited after a longer delay time and had a similar or slightly higher heat release rate than the phosphine oxide containing polymers. However, the phosphine oxide containing polymers did not generate a steady flame during combustion and extinguished shortly after ignition -- even in the cone calorimetry at 40 kw/m². The influence of chemically incorporated phosphorus on the heat release rate of the polymers described, including Nylon 6,6, bisphenol-A polycarbonate and the poly(arylene ether)s are described in this report. As anticipated, ductile mechanical behavior could be maintained for the poly(arylene ether phosphine oxide)s and this is documented within this report. In general it was observed that the phosphine oxides produced higher moduli and higher tensile strengths at room temperature than the control poly(ether sulfone)s. It was hypothesized that dipolar intermolecular interactions involving the polar phosphine oxide group might be responsible for this desirable behavior.

In summary, phosphine oxide containing copolymers have been extensively investigated, which has resulted in 3 Ph.D. theses, and a number of refereed publications. The hypothesis that the structure/property relationships could be maintained by chemically incorporating aryl phosphine oxide have been verified. Reductions in heat release rate have been achieved. However, the materials promote additional smoke and carbon monoxide. Additional studies utilizing additional material systems such as polyimides and siloxane containing copolymers should be conducted.

II. Introduction¹⁻³

Organic polymers are one of the most versatile and widely utilized class of materials used today. They are utilized in many applications ranging from adhesives, aircraft interiors, and electronic components. However, except for a limited number of so called inherently flame

resistant polymers such as polytetrafluoroethylene (Teflon), polyvinyl chloride, etc. thermoplastics are not very flame resistant. The flame resistance of polymers has been improved using two different techniques. Firstly, by physically blending a flame retardant additive such as Sb_2O_3 in combination with brominated aromatics or various phosphates with the polymer. Secondly, by incorporating flame retardant structures into a polymeric backbone. Flame retardant additives used in synthetic polymers include organic halogen and organic phosphorus compounds. A flame retardant additive interferes with one or more of the steps of the combustion cycle, which can include; heating of the polymeric material, its subsequent degradation and the further combustion of volatiles that may be generated.

A flame retardant additive may perform its function during one or more of these three steps. It is preferred that the additive function during more than one of these steps. Thus, 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. 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. The flame retardant additive behaves in a similar manner as in the second stage by reacting with radicals during the combustion of volatiles to quench the propagating nature of the fire.

The effectiveness of the halogen depends on the many factors, including the halogen used, the polymeric structure and the concentration of halogen. The effectiveness of the halogen follows the order $\text{Br} > \text{Cl} > \text{F}$ and generally large amounts of halogen (between 15-30 wt. %) are required. Those halogens bonded to aliphatic carbons are better flame retardants than aromatic halogens. 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 with physically blended flame retardant additives including compatibility issues such as; 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.

In order to avoid this problem with aging one may add halogens bonded to the backbone of thermoplastics. This approach has been effective for polyolefins and epoxies. This incorporation has resulted in an increased char yield and higher limiting oxygen index which is one of the often used measurement methodologies. Commercially, tetrabromobisphenol-A or its diglycidylether is often used to cure epoxies for use in printed circuit boards and other applications where fire resistance is needed. The disadvantage with halogen based flame retardants is the fact that upon combustion toxic hydrogen halide gases are emitted. Phosphorus or nitrogen containing additives, and others are being investigated as a possible way to overcome this problem.

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 mechanism for the vapor phase inhibition of phosphine oxide flame retardant additives has been proposed.

Inagaki et. al.⁴ has 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 blue flame, therefore, the higher LOI indicates that a material may be more flame resistant. In general, these studies show that as the amount of phosphorus is increased the LOI increases linearly, within the range tested.

Phosphorus containing fire retardants may also behave as condensed phase inhibitors. Condensed phase inhibition involves changes in the polymer substrate to promote crosslinking and the formation of a char which serves two purposes. Firstly, it behaves as an insulating layer protecting the underlying polymer from the heat and flames. Secondly, it can act as a barrier preventing oxygen from reaching the uncombusted polymer, therefore inhibiting further combustion

The condensed mechanism is the one of choice 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 of loading as is essential for the vapor phase mechanism.

Another area of interest is the mechanism of char formation and how to induce high char yields in polymers in order to make them more flame resistant and a possible mechanism for char formation is shown in figure 1. In this mechanism, 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 byproducts that do not form char and, may in fact, 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. 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.

The combustion of polymeric materials is a complex process which includes environment, ignition, flame growth, fire retardants, and “burn out” to name a few. A single flammability test is thus 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 materials combustion behavior. The areas of combustion behavior researchers are interested in include; ease of ignition, flame spread, ease of extinction, smoke obscuration, smoke toxicity and heat release rate.

The heat release rate is another factor in characterizing the flammability of polymeric materials. It is currently regarded by many as the most important variable in fire resistance. Although most deaths in a fire occur due to inhalation of toxic gases, the heat release rate is considered for many to be the best predictor of a fire hazard. Heat release rate is usually analyzed utilizing cone calorimetry. The cone calorimeter applies a specific heat flux to a sample and measures the ignitability, heat release rate, and toxic gases emitted. 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. From the heat release rate, it is also possible to monitor the heat release behavior through the combustion cycle from ignition to burn out.

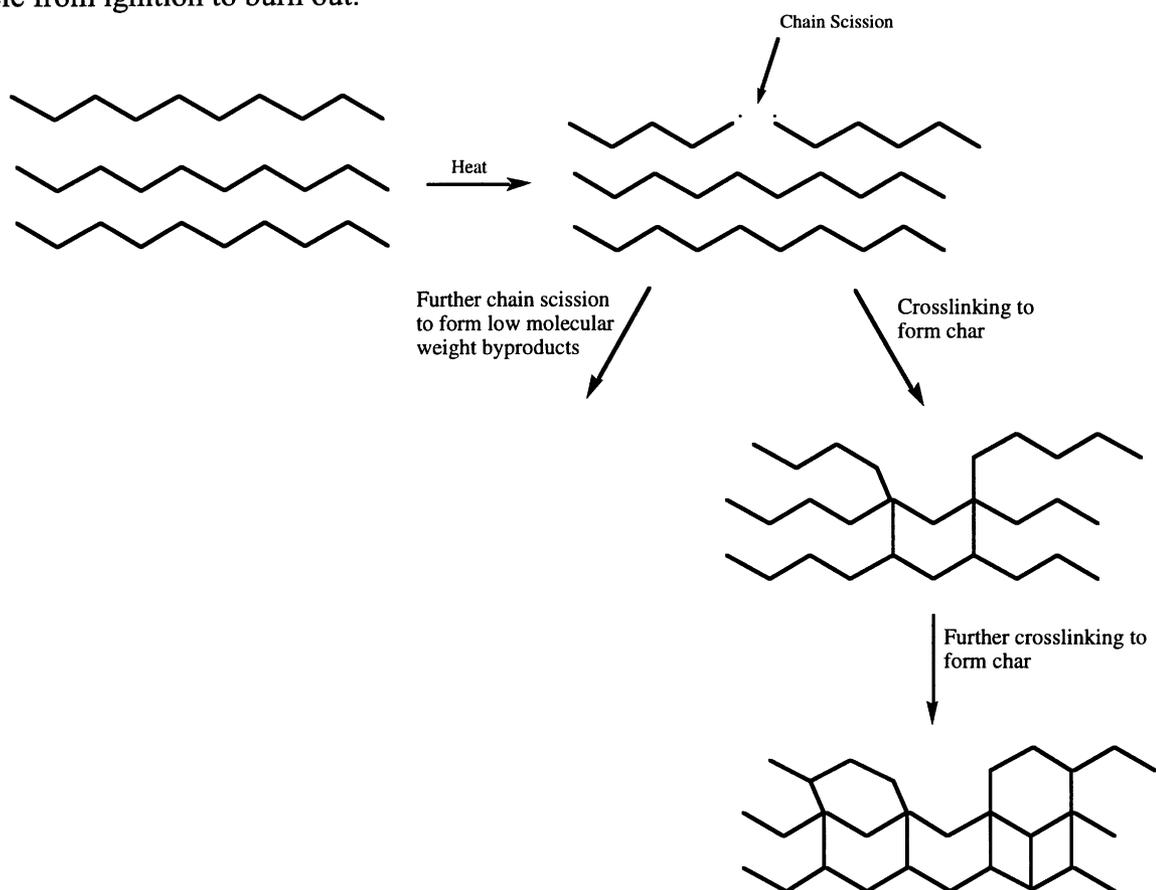


Figure 1 Possible mechanism for char formation ⁵

II-i. Polyamide(Nylon 6,6) Triarylphosphine Oxide Copolymers^{6,7}

It has been reported that phosphorus containing aliphatic diamines and dicarboxylic acids have been successfully incorporated into polyamides to improve flame resistance. The utilization

of triaryl phosphine oxide monomer in demonstrably high molecular weight homo- or copolymeric systems has been a relatively recent development and extensive research in the area is currently underway. For the past few years, our research group has been interested in synthesizing new monomers by practical methods which allow for the incorporation of tri- or diaryl phosphine oxide structures into both specialty and high volume polymeric materials. Some of the polymeric systems studied include polyimides, poly(arylene ether)s, epoxies, polycarbonates and polyamides. In general, the triaryl phosphine oxide moiety affords thermal and oxidative stability coupled with high glass transition temperatures. Amorphous morphological structures are normally produced from triaryl phosphine oxide containing homopolymers due to the non-coplanar nature of the phenyl phosphine oxide bond. However, semicrystalline copolymers can also be prepared by controlled incorporation of the triaryl phosphine oxide comonomer. This strategy has been extended to synthesize crystallizable high volume polyamide copolymers such as nylon 6,6. It appears to have some promise for affording new high performance flame-resistant materials for textile and engineering applications. The flammability of the polymers was tested by using cone calorimetry and, qualitatively, by simple Bunsen burner tests.

II-ii. Polycarbonate Triphenylphosphine Containing Copolymers^{8,9}

The polycarbonate derived from bisphenol A and phosgene is an important engineering thermoplastic and incorporation of various phosphorus compounds into the backbone have been examined. Some hydrolytically stable materials have been reported, but more often incorporation of phosphorus compounds has usually created hydrolytically unstable phosphate linkages. Our objective was to synthesize hydrolytically stable bis(4-hydroxyphenyl)phenylphosphine oxide and react this monomer with phosgene and bisphenol A to afford random or statistical copolymers. This monomer had previously been used to synthesize perfectly alternating copolycarbonates. Our goal was to investigate the effect of comonomer concentration on copolymer properties, including fire resistance.

II-iii. Poly(arylene ether) Triphenylphosphine Containing Copolymers^{2,3}

Hydrolytically stable phosphorus containing monomers, such as 4,4'-bis(fluorophenyl)methylphosphine oxide (BFPMPO), 4,4'-bis(hydroxyphenyl)methylphosphine oxide (BOHPMPO), and 4,4'-bis(hydroxyphenyl)phenylphosphine oxide (BOHPPO) were synthesized and used in nucleophilic aromatic substitution polycondensation to prepare poly(arylene ether phosphine oxide) engineering thermoplastics. The synthesis and characterization of these novel polymers are described herein. It was determined that by incorporating the phosphine oxide moiety into the polymer backbone certain properties of the resulting poly(arylene ether) were substantially improved, such as an increase in T_g , thermal stability in air, modulus, and char yield compared with control poly(arylene ether sulfone)s. The

high char yields obtained for these polymers in air along with observed intumescence indicates that these materials have improved fire resistance. Preliminary cone calorimetry measurements support this conclusion.

III. Experimental

III-i Phosphorous Containing Polyamides:

Monomer preparation:

Adipic acid and hexamethylene diamine (HMDA) were purchased from Aldrich. The acid was used without further purification and the HMDA was purified by vacuum distillation. Pure nylon 6,6 salts were prepared from these two monomers in ethanol followed by recrystallization from an ethanol/water mixture.

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

The second step was to oxidize the phosphine sulfide group to phosphine oxide, which was almost quantitative. For example, the phosphine sulfide monomer BMPPS (186g, 576 mmole) was dissolved in acetic acid (750 ml) and 50% hydrogen peroxide (80g) was added into the solution dropwise. The temperature was raised to 85-90°C then decreased to 70°C after the addition of hydrogen peroxide. The reaction was allowed to continue for another 2-4 hours. The solution was filtered through celite to remove precipitated particles. Chloroform was used to extract the product, followed by washing with water and drying with magnesium sulfate. The solvent was removed and a viscous fluid, bis(4-methylphenyl)phenyl phosphine oxide (BMPP0) resulted.

The next step was to oxidize the methyl groups to carboxylic acid groups by using potassium permanganate. Thus, BMPP0 (152g, 496.2 mmole) was added in a 4-neck 2 liter flask equipped with an overhead stirrer and a condenser. Pyridine (600 ml) and water (300 ml) were added into the flask and the temperature was raised to 70°C. The potassium permanganate

(KMnO₄) (580g, 3.7 mole) was added in 6-8 aliquots at 30 minute intervals and after the last addition, the temperature was raised to 80-90°C for 12 hours. At the end of the reaction, the pyridine was removed by steam distillation and the excess KMnO₄ was filtered off. The red solution was then acidified with concentrated hydrochloric acid to pH-5. The bis(4-carboxyphenyl)phenyl phosphine oxide (BCPPO), collected was a white product. A second oxidation was frequently needed and was conducted with a stoichiometric amount of aqueous sodium hydroxide solution. The sodium hydroxide was used to dissolve the diacid (BCPPO) as the dicarboxylate salt. A slight stoichiometric excess (by NMR spectra) of KMnO₄ was added into the solution and the reaction was allowed to proceed at 80°C for 6-8 hours. Then, the solution was filtered, acidified and the product was collected. Yields of the BCPPO were about 74% after the second oxidation.

Polymerization:

The triphenylphosphine oxide dicarboxylic acid was successfully incorporated into nylon 6,6 copolymers at 0, 10, 20 and 30 mole% concentrations via conventional melt processes. In a typical copolymerization reaction, pure nylon 6,6 salts were prepared from adipic acid and hexamethylene diamine in ethanol, followed by recrystallization from a methanol/water mixture. Then, the triphenyl phosphine oxide dicarboxylic acid monomer and an equimolar amount of hexamethylene diamine were dissolved into water in a glass vessel.

The pH value of this solution was adjusted to 7.5 and a controlled amount of the nylon 6,6 salt was added into the solution at a concentration of about 60-70%. Copolymerization was conducted in a two stage reaction. In the first stage, the materials were transferred into a Parr® reactor, purged with argon, pressurized to 75 psi and then slowly heated to 250-260°C. During the course of the copolymerization, the pressure increased to 250-350 psi and it was maintained at this pressure for 2-3 hours. For the second stage, the pressure was slowly reduced to atmospheric over 1 hour, and then vacuum (0.5 torr) was applied to the system at 270-280°C. After 1-2 hours, a light yellow viscous nylon 6.6/triphenyl phosphine oxide co-polyamide was formed, which was cooled and isolated.

Characterization:

The purity of the monomers were analyzed by ¹H and ³¹P-NMR. Intrinsic viscosity values of the copolymers were determined in m-cresol at 25°C. Differential scanning calorimetry (DSC) and dynamic thermal gravimetric analysis (TGA) were performed by using Perkin-Elmer 7 series at a heating rate of 10°C per minute. The dynamic mechanical analysis (DMA) measurements were also conducted by the same instrument at a heating rate 5°C per minute, a frequency of 1 Hz and a 3-point bending test mode. The samples for DMA and other measurements were compression molded from dry copolymers at 270°C, followed by annealing at 155°C for 5 minutes. ESCA (electron spectroscopy for chemical analysis) measurements were performed with a Perkin-Elmer 5400 instrument. The samples for the ESCA measurements were 20% copolymers which were heated in air at different testing temperatures for 2-5 minutes prior to analysis.

Cone calorimetry test:

The tests were performed at the National Institute of Standards and Technology by utilizing a cone calorimeter under a constant heat condition of 40 kW/m². The sample used was a compression molded film with a size of 10cm x 10cm x 0.3cm.

III-ii. Phosphorous Containing Polycarbonates

General:

4-bromophenol was obtained from Aldrich, recrystallized from carbon tetrachloride, and dried under reduced pressure. THF was vacuum distilled from a sodium / benzophenone complex. Dichlorophenylphosphine oxide, 3,4-dihydro-2H-pyran, and magnesium turnings were obtained from Aldrich and were used as received. High purity 2,2-Bis(4-hydroxyphenyl)propane (bisphenol A) was kindly provided by Dow Chemical and used as received. Methylene chloride was HPLC grade and was used as received from Baxter. Phosgene was obtained from Matheson.

Synthesis of p-bromophenyl tetrahydropyranyl ether:

p-Bromophenol (138.0 g; 0.79 moles) was added to a round bottom flask along with a magnetic stirbar and dihydropyran (130.0 ml; 1.42 moles) (containing 4 drops concentrated hydrochloric acid) was added dropwise from an addition funnel. After 1 hour reaction time, the product was dissolved in ether, washed three times with 10% sodium hydroxide, followed by three times with distilled water. The ether was stripped by rotary evaporation and the resulting yellow oil was recrystallized twice from 95% ethanol, to yield 151.65 g (0.59 moles; 74% yield) of white crystals with m.p. 55-56°C (lit.23 m.p. 57-57.5°C).

Synthesis of bis(4-hydroxyphenyl)phenylphosphine oxide:

Magnesium turnings (14.33 g; 0.59 moles) and a crystal of I₂ were placed in a flame dried, 3 neck, 2000 ml round bottom flask equipped with an addition funnel, condenser and overhead stirrer while purging with argon. Positive argon pressure was maintained throughout the reaction. 20 ml THF were added to the magnesium turnings and a solution of p-bromophenyl tetrahydro pyranyl ether (151.65 g; 0.59 moles) in 400 ml THF was added dropwise to the stirred mixture while cooling with a water bath. The remaining p-bromophenyl-pyranylether was washed in with 75 ml THF. The mixture stirred for three hours at room temperature and at the end of this time, only a trace of residual magnesium remained. Dichlorophenylphosphine oxide (41.1 ml; 0.29 moles) was introduced to the addition funnel along with 100 ml THF and the resulting solution was added dropwise to the Grignard reagent which had been cooled in an ice bath. After complete addition, the residual dichlorophenylphosphine oxide was rinsed in with 50 ml THF and the reaction was allowed to stir at room temperature for eight hours. The solution was then transferred to a 2000 ml round bottom flask and most of the THF was removed by rotary evaporation. Approximately 600 ml of methanol were introduced to the solution along with 20 ml of concentrated hydrochloric acid and allowed to stir for one hour to cleave the protecting group. The solvent and tetrahydropyranylmethylether were removed by rotary evaporation,

producing an oil that was dissolved in 10% sodium hydroxide solution and precipitated into 1M HCl. The tan solid was filtered, washed with water and dried overnight under vacuum. The crude material was then recrystallized twice from methanol to yield white crystals, m.p. 233.5 - 234.5° C (lit.15 m.p. 233 - 234° C).

Synthesis of phosphorus containing polycarbonate copolymers:

Copolymers of controlled composition were synthesized in 50 g batches. Calculated amounts of bis(4-hydroxyphenyl)phenylphosphine oxide were added along with bisphenol A to a 500ml, 5 neck round bottom flask equipped with a mechanical stirrer, condenser, phosgene dip tube, caustic addition funnel, and pH probe. 400 ml of water, triethylamine (16 mole %) as a phase transfer catalyst, and 400 ml of methylene chloride were added along with t-butylphenol to control the molecular weight. Phosgene (1.5 equivalents) was introduced to the rapidly stirred interfacial mixture at a rate of 0.36 g/min. while maintaining the pH at 11.0 through the metered addition of a 40% caustic solution. Work-up involved washing the polymer solution with 5% hydrochloric acid followed by multiple water washes. The polymer was isolated by flashing off the methylene chloride in rapidly stirred boiling water, followed by filtration and drying at 80°C under vacuum.

Characterization:

The monomers and polymers were analyzed by ¹H and ³¹P NMR on a Varian 400 MHz instrument. Differential scanning calorimetry and thermogravimetric analysis were performed on Perkin-Elmer 7 series instruments at a heating rate of 10°C per minute. Intrinsic viscosity values were determined in chloroform at 25°C. Cone calorimetry was conducted under a constant external radiant flux of 40 kw/M², in the horizontal configuration on 10cm by 10cm by 0.3cm compression molded films.

III-iii. Phosphorous Containing Polyarylethers

Polymer Synthesis

Bisphenol-A poly(arylene ether phosphine oxide) (Bis-A PEPO).

High molecular weight poly(arylene ether phosphine oxide)s (PEPO) were synthesized *via* a nucleophilic aromatic substitution (S_NAR) step growth polymerization of 4,4'-bis(fluorophenyl)methylphosphine oxide (BFPMPO) with 4,4'-bisphenol-A (Bis-A). Detailed description of monomer synthesis will be described elsewhere. A representative polymerization procedure is provided. To a 500 mL three neck flask equipped with a mechanical stirrer, nitrogen inlet, and a Dean-Stark trap was added equal molar amounts (0.05moles) of each monomer, followed by 0.058 mol (1.15 equivalents) of potassium carbonate (Fisher). Freshly dried and distilled N, N-dimethylacetamide (DMAc) (175 mL) was introduced to afford a mass fraction of

solids of 15%. Toluene (50 mL) was added as an azeotroping agent and the reaction was heated to reflux (135 °C to 140 °C). After four hours, the solution temperature was raised to 155 °C by the removal of toluene; a slight reflux was maintained to ensure anhydrous reaction conditions. This temperature was maintained for sixteen to eighteen hours to ensure very high conversion of the functional groups. After cooling, chloroform (35 mL) was added to dilute the mixture and the salts were vacuum filtered off with the aid of filter paper. Acetic acid (5 mL) was added and the polymer was then precipitated into a volume ratio of 80:20 methanol/water separated and dried in a vacuum oven at 150 °C for 12 h. The polymer was purified by redissolving in chloroform (20% solids), reprecipitating into stirred methanol and drying *in vacuo* at 170 °C for 12 h. The yield obtained for this polymer and all others described herein was >90%.

Synthesis of other poly(arylene ether phosphine oxide)s based on 4,4'-bis(fluorophenyl)methyl phosphine oxide (BFPMPO).

Similar reaction conditions were used as described for the synthesis of Bis-A PEPO above, except that different bisphenols were employed. These bisphenols include; 1,1-bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane (3F)¹⁰, phenolphthalein (PP)^{11,12}, hexafluoro bisphenol-A (6F) kindly provided by Dr. J. S. Senger, and hydroquinone (HQ) (Eastman Chemical).

BFPMPO and 4,4'-bis(fluorophenyl)phenylphosphine oxide (BFPPPO) were used to synthesize poly(arylene ether phosphine oxide sulfone)s which can be designed to have both the desirable phosphine oxide and sulfone moieties incorporated into the backbone of the polymer.

Poly(arylene ether methyl phosphine oxide sulfone) (BFPMPO-SO₂).

High molecular weight poly(arylene ether phosphine oxide sulfone) based of BFPMPO was synthesized as follows. To a 3-neck 250 mL high temperature reaction flask equipped with a mechanical stirrer, nitrogen inlet, and outlet, was added equal molar amounts (0.01 moles) on BFPMPO and 4,4'-bis(hydroxyphenyl)sulfone (Bis-S) monomer, followed by 0.015 moles (1.15 equivalents) of potassium carbonate, and a mass ratio of 150% of diphenyl sulfone as the solvent. The reaction was initially run at 135 °C for 1 hour and 170 °C for 4 hours, to dry the system. The temperature was then raised to 270 °C for 4 hours and finally to 320 °C for 20 minutes. The short time at 320 °C was necessary to complete the reaction of the functional groups necessary to reach high molecular weight. The reaction flask was then cooled, 100 mL of DMAc were added to lower the viscosity and the potassium salts were removed using vacuum filtration. After adding acetic acid (5 mL) to neutralize the pH, the polymer was precipitated into methanol and dried in a vacuum oven at 150°C overnight. It was redissolved in N-methyl pyrrolidone (NMP) reprecipitated into methanol and dried in a vacuum oven at 170 °C to 200 °C overnight.

Poly(arylene ether phenyl phosphine oxide sulfone) (BFPPSO-SO₂).

Similar conditions were used as described in the synthesis of poly(arylene ether methyl phosphine oxide sulfone). The only exception being that 4,4'-bis(fluorophenyl)phenylphosphine oxide (BFPPSO) was used at the activated dihalide instead of methyl analog (BFPMPO).

Poly(arylene ether methyl phosphine oxide) homopolymer (BFPMPO-BOHPMPO).

High molecular weight poly(arylene ether phosphine oxide) homopolymer based on BFPMPO was synthesized as follows: To a 3-neck 250 mL high temperature reaction flask equipped with mechanical stirrer, nitrogen inlet, and outlet, was added equal molar amounts (0.01 mol) of BFPMPO and 4,4'-bis(hydroxyphenyl)methylphosphine oxide (BOHPMPO) followed by 0.015 moles (1.15 equivalents) of potassium carbonate, and a mass ratio of 150% of diphenyl sulfone as the solvent. The same temperature-time procedure and work up as for the poly(arylene ether phosphine oxide sulfone)s was employed.

Poly(arylene ether phenyl phosphine oxide) homopolymer (BFPPSO-BOHPPO).

Similar conditions were used as described in the synthesis of poly(arylene ether methyl phosphine oxide) homopolymer. The only exception being that 4,4'-bis(fluorophenyl)phosphine oxide (BFPPSO) was the activated dihalide instead of BFPMPO and 4,4'-bis(hydroxyphenyl)phenylphosphine oxide (BOHPPO) was used as the bisphenol.

Poly(arylene ether methyl phosphine oxide phenyl phosphine oxide) alternating copolymer (BFPMPO-BOHPPO).

Similar conditions were used as described in the synthesis of poly(arylene ether methyl phosphine oxide) homopolymer, however, BOHPPO was employed as the bisphenol.

Acronyms

Figure 2 provides a reference to the backbone structure of polymers utilized in this study. The acronyms of the polymers are listed below their structure. For simplicity, the polymers will be described by these acronyms throughout this paper.

Characterization.

NMR

¹H and ³¹P NMR were used to confirm the polymer structure; spectra were obtained using a Varian Unity 400 spectrometer.

Intrinsic Viscosity

Intrinsic viscosity or limiting viscosity number measurements were performed in chloroform at 25 °C using a Cannon-Ubbelohde viscometer. The flow time was measured three times each per concentration and the average was used in the calculation.

Thermal analysis

Glass transition temperatures were determined by differential scanning calorimetry (DSC) using a Perkin Elmer DSC 7 Differential Scanning Calorimeter. Scans were run at a heating rate of 10 °C/minute; reported values were obtained from a second heat scan after quench cooling. Thermogravimetric analysis (TGA) were performed on a Perkin Elmer TGA 7 Thermogravimetric Analyzer at 10 °C/minute in air for dynamic scans. Experimental uncertainties were determined by averaging the values obtained in several runs.

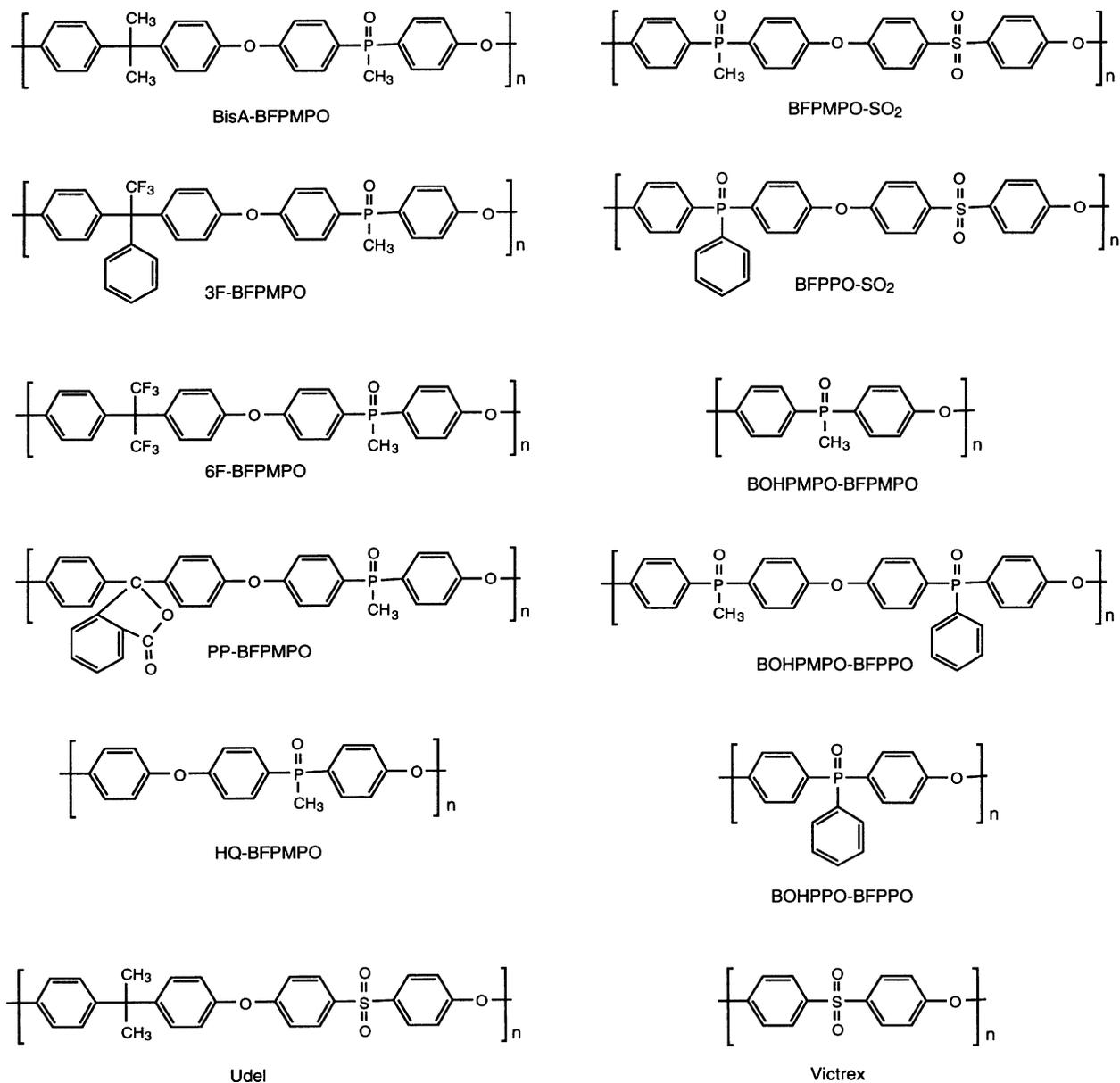


Figure 2 Structure and corresponding acronym of polymers utilized in this study.

Dynamic Mechanical Analysis

Dynamic mechanical analysis was conducted on compression molded specimen (15x6x3 mm) with a Perkin Elmer DMA 7, using a 3-point bending mode. The sample was heated from -150 °C to 50 °C at a rate of 2 °C/min.

Cone Calorimetry Analysis

Polymer samples with dimensions of 10 cm x 10 cm x 3 mm were compression molded and evaluated at the Fire Research Laboratory of the National Institute of Standards and Technology (NIST) using cone calorimetry at a constant heat flux of 40 kW/m². The instrument was run in the standard mode of ASTM E 1354, except that the sample was not mounted on the standard metal holder, but rather placed on a silicate board.

GPC

Molecular weights were analyzed on a Waters 150C ALC/GPC chromatograph equipped with a differential refractive index detector and a Viscotek Mode 100 viscosity detector connected in parallel.¹³ N-methyl pyrrolidone (HPLC grade) containing 0.06M LiBr filtered through 0.5 mm Teflon filter served as a mobile phase. The chromatography conditions were as follows: two stainless steel columns (7.8 mm x 300 mm) packed with Waters mStyragel HT 10³ Å and 10⁴ Å, mean particle diameter 10 mm, flow rate 1.0 mL/min, injection volume 200 mL, and a temperature of 60 °C for both GPC and detectors. Samples prepared to known concentrations (approx. 3 mg/mL) were dissolved in the mobile phase and filtered through 0.2 mm PTFE disposable filters prior to analysis. The uncertainties were obtained from an estimate of the error in the analysis based on previous experiences.

Mechanical behavior

The mechanical properties of the poly(arylene ether)s were measured at room temperature using tensile tests on an Instron 1123 equipped with a strain gauge extensometer (Instron 2630-013). The dog-bone shape samples (ASTM D-638 #5) were cut from a compression molded plaque with thicknesses ranging from 0.016-0.025 cm (0.0064-0.010 inches). The samples were tested at room temperature at a cross head speed of 1.27 cm/minute (ASTM D-638). Eight samples were tested and the mean was calculated. The uncertainties were obtained by calculating the standard deviation of all samples analyzed.

IV. Results and Discussion

IV-i. Polyamides

The synthesis of the monomers and copolymers are described in figures 3 and 4, respectively. The incorporation of the triarylphosphine oxide comonomer was controlled from 0-30 mole%, since higher levels were not expected to produce crystallizable, fiber forming copolymers.

Characterization of the triarylphosphine oxide containing copolymers is summarized in table 1. The intrinsic viscosity of the copolymers was measured in m-cresol at 25°C and the data suggested that the copolymers have relatively high molecular weights. As shown in table 1 and in the DSC thermograms (figure 5), the copolymers exhibit a crystalline melting transition if the phosphine oxide comonomer is lower than 30 mole%. At 30 mole%, the copolymer is virtually amorphous. The crystallizable nature of the 0-20 mole% copolymers can also be seen from the DSC thermograms on cooling (figure 6). In general, the nylon 6,6 homopolymer has a very fast crystallization rate. However, once the triarylphosphine oxide comonomer is incorporated into the copolymer backbone, the crystallization rate is decreased (figure 6) and the crystal melting temperature (T_m) is depressed (Figure 5), as expected.

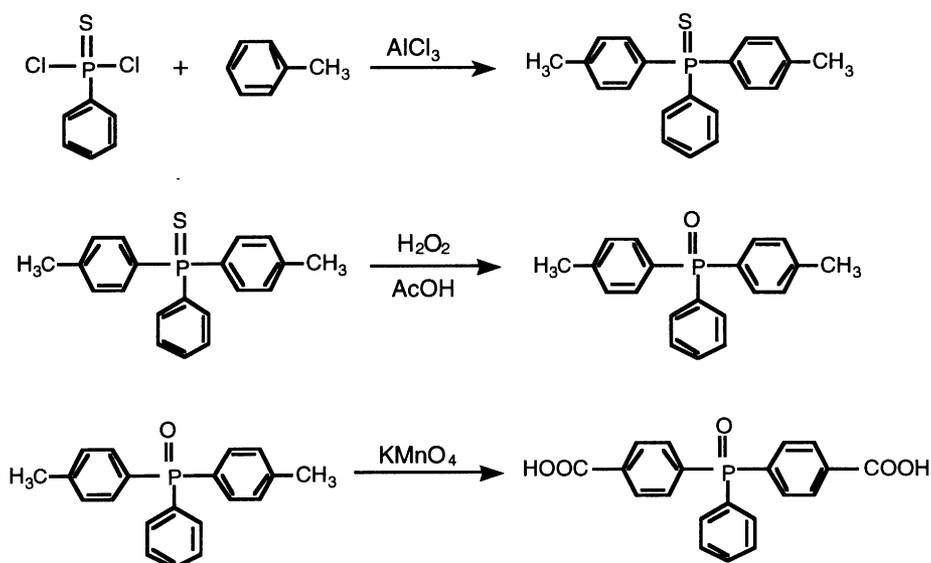


Figure 3. Synthesis of Bis(4-carboxyphenyl) Phenyl Phosphine Oxide

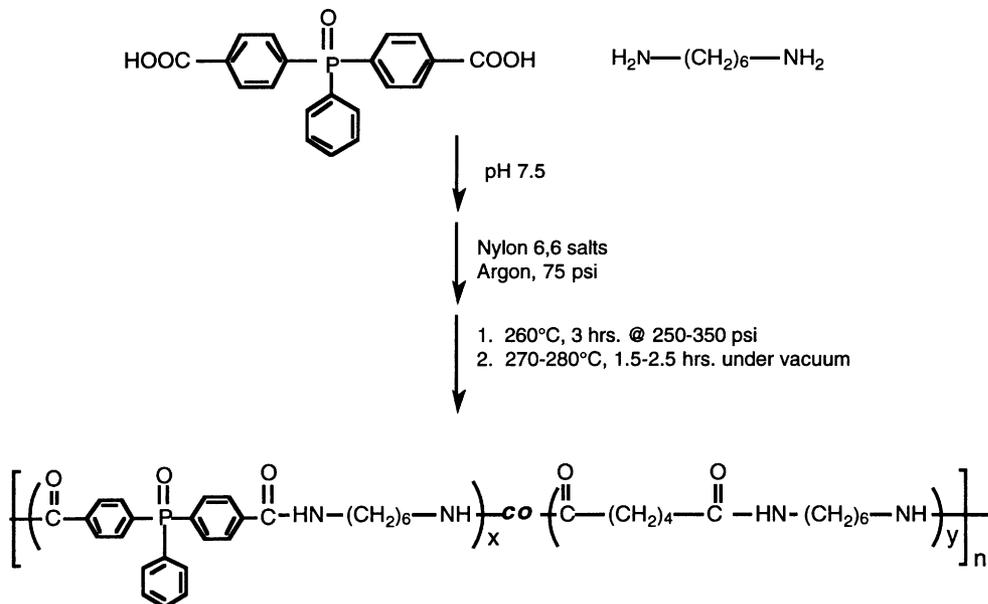


Figure 4. Synthesis of Triarylphosphine Oxide/Nylon 6,6 Copolymers

Table 1 Characterization of Triarylphosphine Oxide Containing Nylon 6,6 Copolymers

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

Note: 1. In m-cresol at 25°C, 2. DSC, 10°C/minute, 3. Air, 10°C/minute, 4. DMA, Loss Maxima

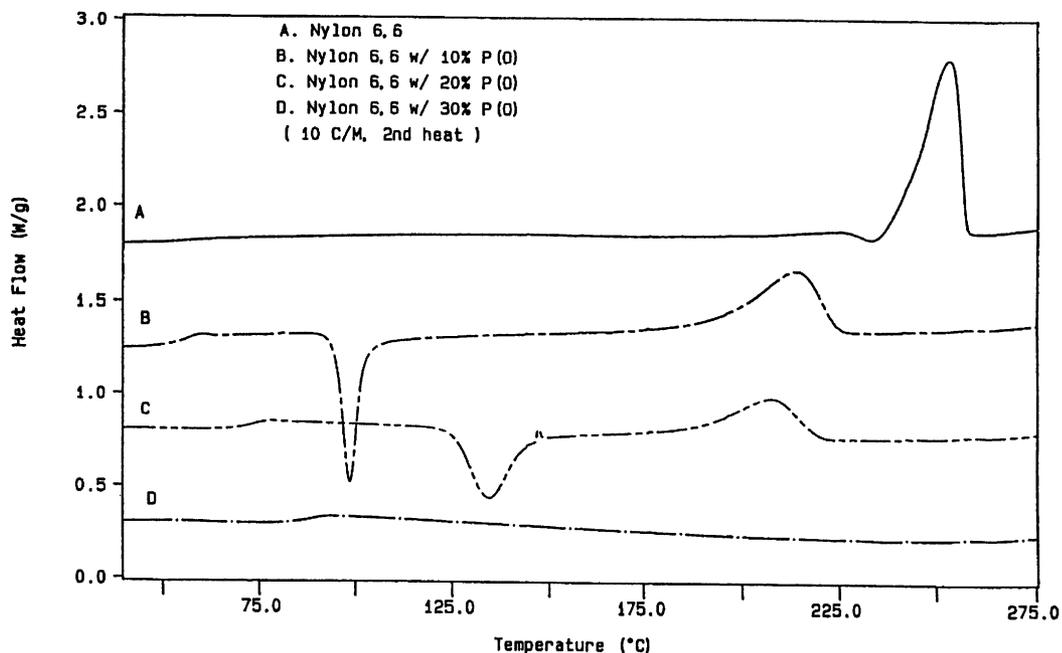


Figure 5 DSC of triarylphosphine oxide containing nylon 6,6 copolymers (heating curves)

Nevertheless, tough solvent resistant films were obtained by compression molding and preliminary efforts at drawing fibers from the melt appear to be successful. The glass transition temperatures (T_g) and the char yields of the copolymers increased as a function of the phosphine oxide content. The increased char yield of the copolymers is shown in the dynamic TGA thermograms (figure 7). The char yield in air is generally considered to strongly correlate with the flame retardancy of the material.

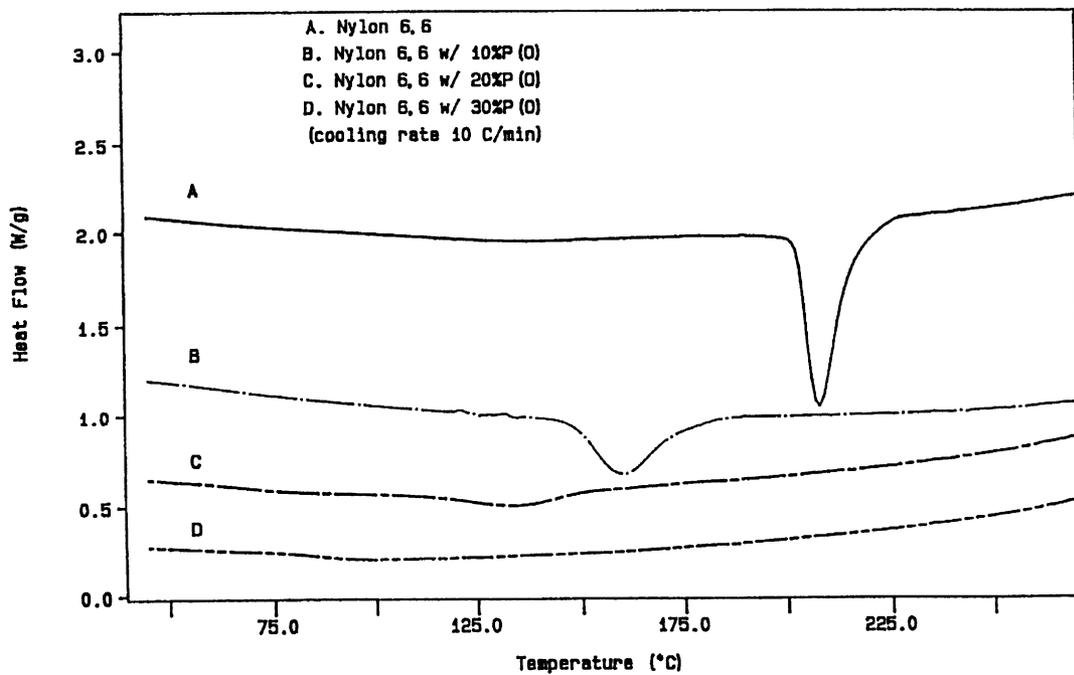


Figure 6. DSC of triarylphosphine oxide containing nylon 6,6 copolymers (cooling curves)

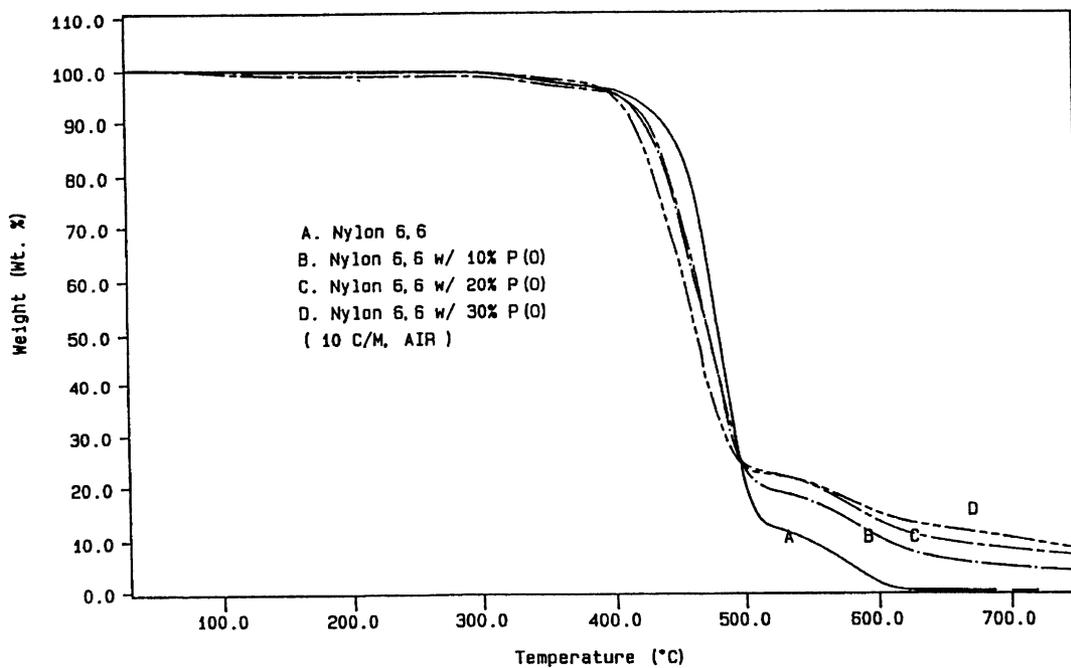


Figure 7. Dynamic TGA of triarylphosphine oxide containing nylon 6,6 copolymers in air

The DMA traces (figure 8), indicate that the storage modulus decreases as the temperature increases. The storage modulus dramatically decreased above the T_g of the copolymers, and then reached a plateau region due to the semi-crystalline nature of the 10 or 20% copolymers. Melt flow occurs as the temperature exceeds the crystal melting transition of the copolymers. From the DMA trace of the 30% copolymer, it was concluded that the copolymer was amorphous since flow occurred at temperatures above the T_g of the copolymer.

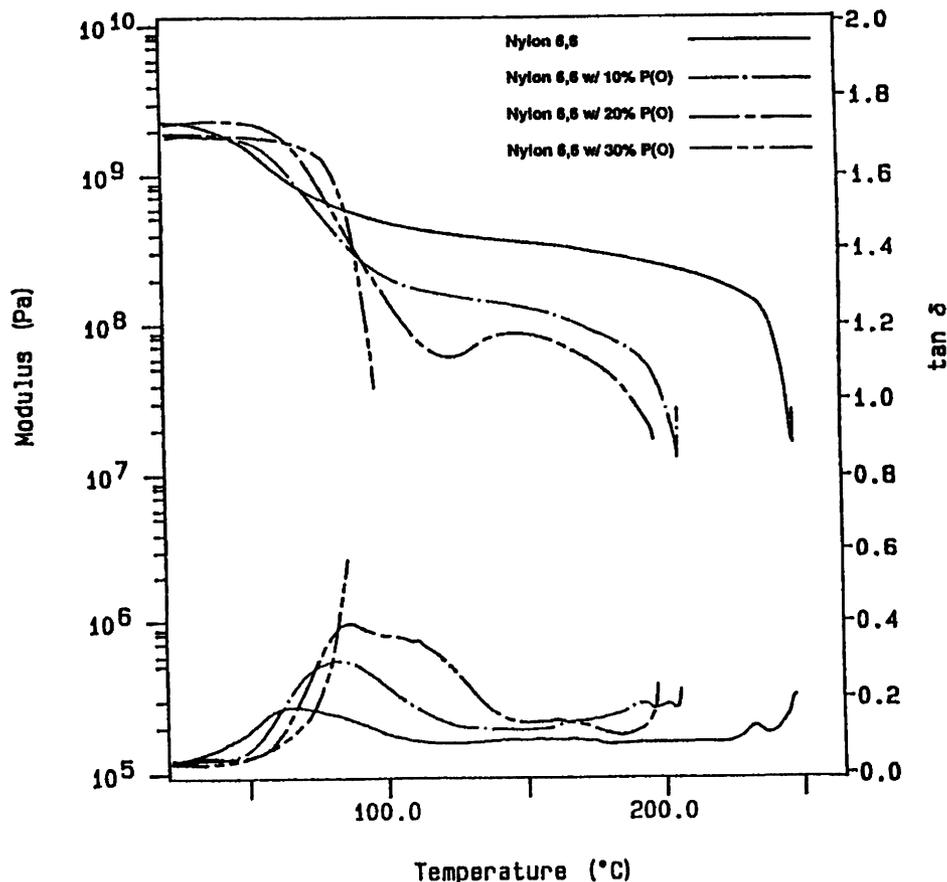


Figure 8. Dynamic mechanical behavior of compression molded triarylphosphine oxide containing nylon 6,6 copolymers (3 point bending)

Cone calorimetry results for the triarylphosphine oxide containing copolymers show that the 10% copolymer had a similar weight loss versus time profile as the nylon 6,6 and that the 20 and 30% copolymers had reduced weight loss rates (figure 9). However, both the heat release rate and heat of combustion of the copolymers were significantly reduced compared to nylon 6,6 (figure 10, 11). These results indicated that the flame resistant properties of the copolymers have been significantly improved. However, the generation of soot and carbon monoxide increased under the test condition (figure 12, 13). The phosphine oxide moiety may act as a flame retardant in both the condensed and gas phase. ESCA results (figure 14a & 14b), show that the

phosphorus concentration on the surface of the 20% copolymer at room temperature is low but it is significantly increased after it was exposed to air at 550°C (i.e., close to the cone calorimetric

40 kW/m²

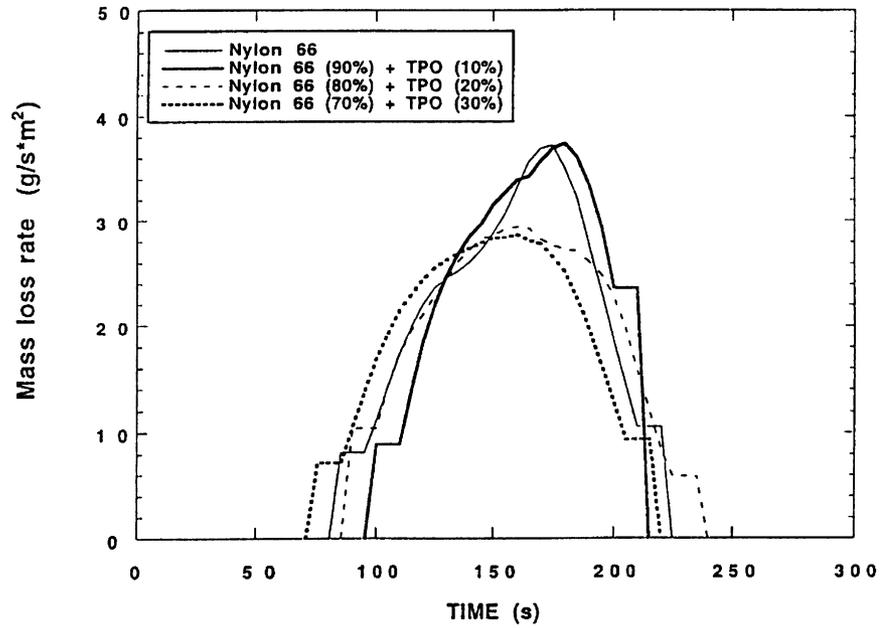


Figure 9. Weight loss versus time of triarylphosphine oxide containing nylon 6,6 copolymers at 40 kW/m²

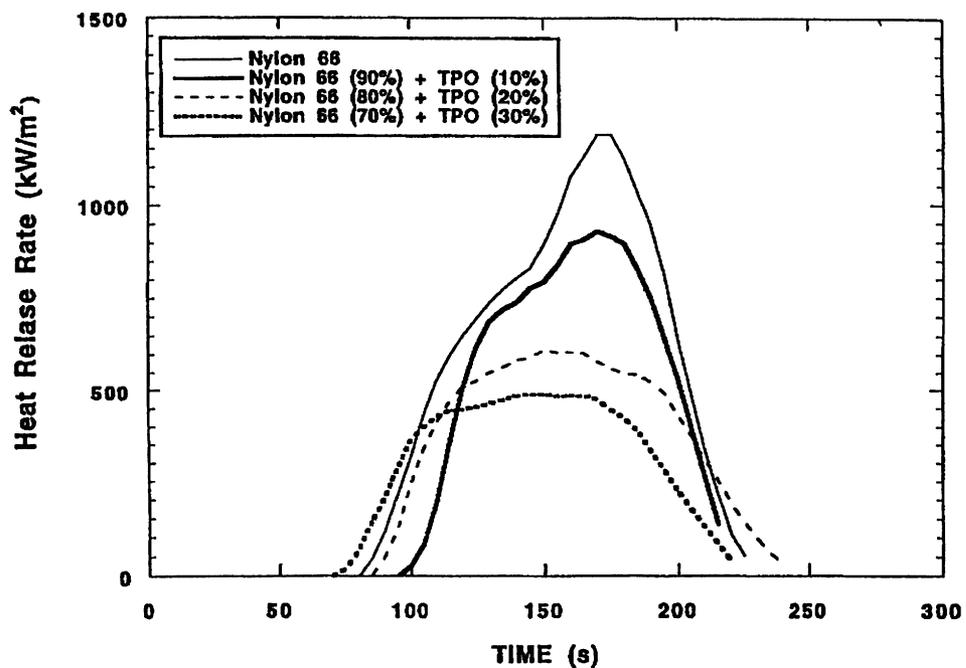


Figure 10. Heat release rate of triarylphosphine oxide containing nylon 6,6 copolymers

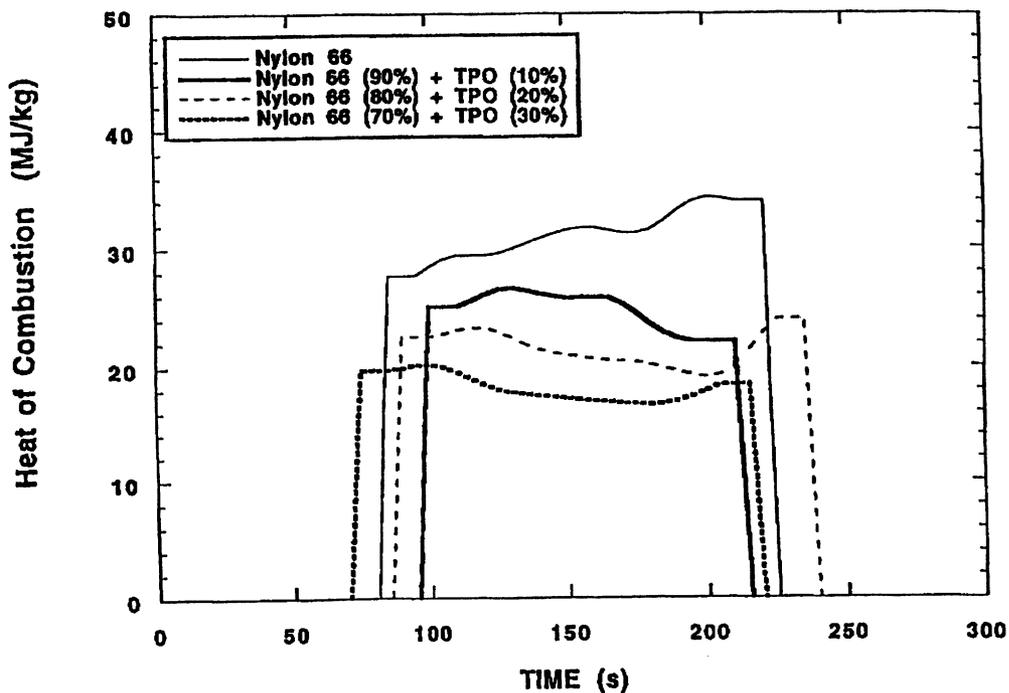


Figure 11. Heat of combustion of triarylphosphine oxide containing nylon 6,6 copolymers

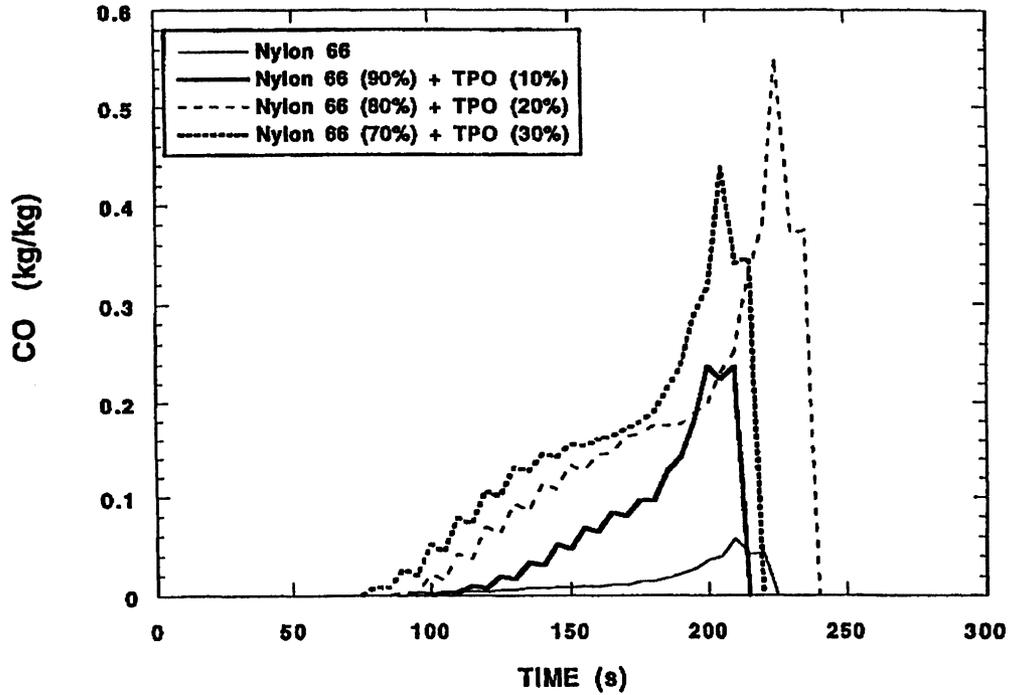


Figure 12. Carbon monoxide generation from the incomplete combustion of phosphine oxide containing nylon 6,6 copolymers

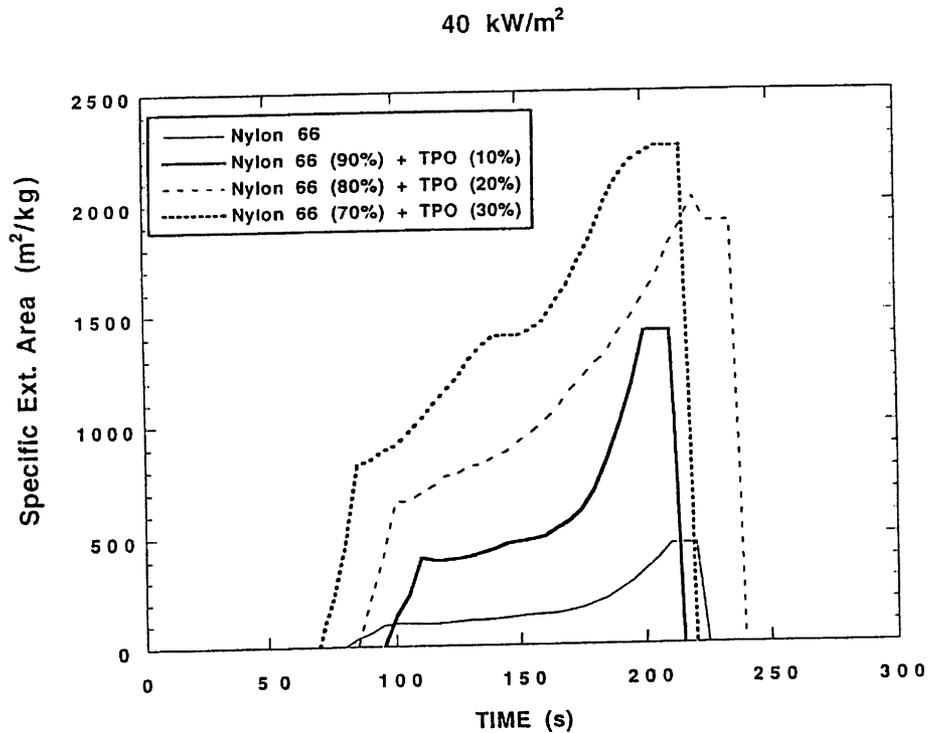


Figure 13. Specific extinction area of triarylphosphine oxide containing nylon 6,6 copolymers

test temperature) for 5 minutes. This result suggests that the phosphorus content played a role in the condensed phase. (The fluorine peaks in figure 10a were contamination from the Teflon sheet which was used to mold the samples.) Similar results have been reported from our laboratory by Webster et al. from ESCA results¹⁴ and Grubbs et al. by pyrolysis GC-MS data^{10,15} of triarylphosphine oxide containing poly(arylene ethers). They found that the most of the phosphorus content stayed in the condensed phase as char, probably in the form of phosphate, while only relatively small portions of phosphorus went to the gas phase. For a flame retardant system, large amounts of energy required for bond breakage to occur in the condensed phase (high Q_1 value) and low amounts of flammable gases evolved in the gas phase (low Q_2 value) may be desirable. Under these test conditions, the nylon 6,6 copolymers were decomposed and generated small particles. Since the phosphorus concentration on the surface was significantly increased after they were exposed to high temperature, this result strongly suggests that the chemically incorporated triaryl phosphine oxide moiety at least partially functions in the condensed phase. Detailed studies are in progress to further clarify this issue.

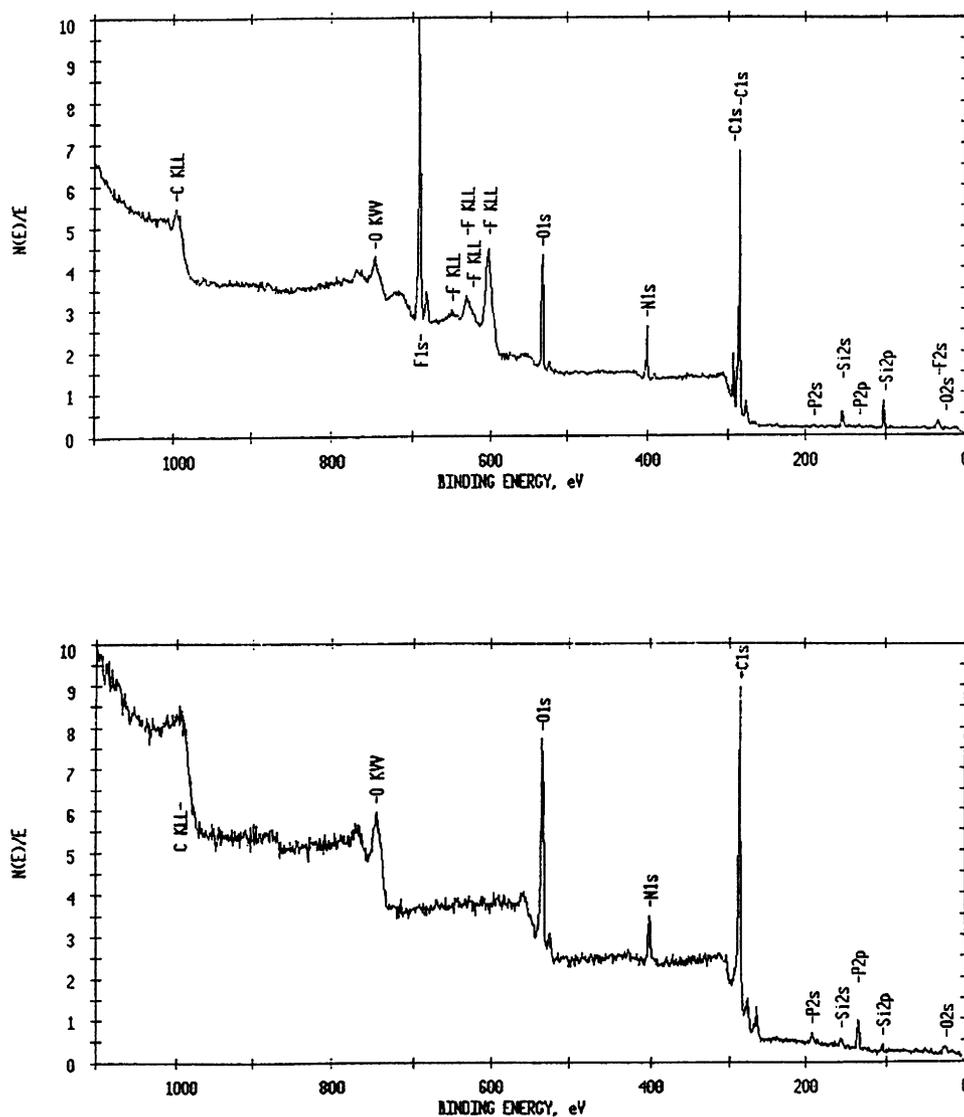


Figure 14. ESCA of 20% triarylphosphine oxide containing nylon 6, 6 copolymers: a.) room temperature b.) exposed in air at 540°C for 5 minutes

IV-ii. Polycarbonates

Monomer synthesis:

Bis(4-hydroxyphenyl)phenylphosphine oxide was synthesized by the reaction of the Grignard reagent derived from 2-(4-bromophenoxy)tetrahydropyran with phenylphosphonic dichloride, followed by acid catalyzed cleavage of the tetrahydropyranyl ether (figure 15). The bisphenol could be obtained in high purity by this method. Alternatively, a similar synthesis

utilizing the Grignard reagent obtained from 4-bromoanisole and subsequent acid cleavage of the methyl ether yielded a highly colored product which could not be decolorized. More recently, it has also been possible to avoid Grignard chemistry via utilizing hydrolysis of activated aryl halide precursors.

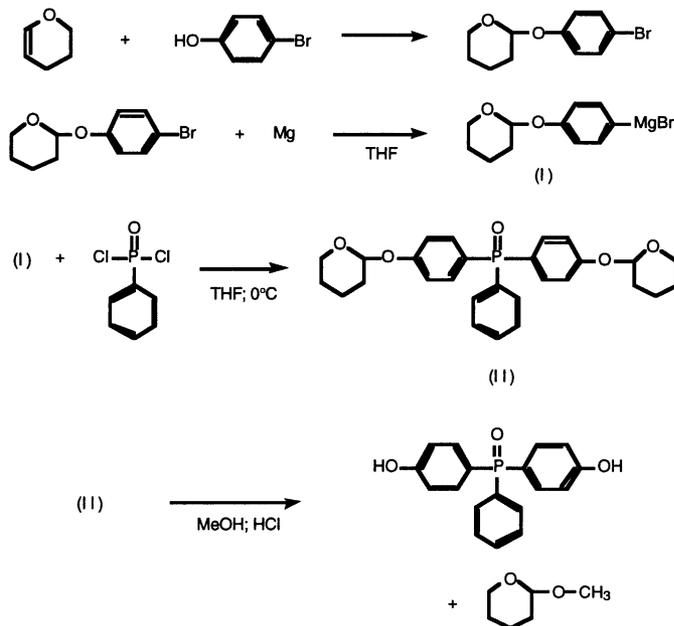


Figure 15. Synthesis of Bis(4-hydroxyphenyl)phenylphosphine Oxide

A monofunctional phenol derived from triphenylphosphine oxide was also synthesized as a model compound and endcapper. The 4-hydroxyphenyldiphenylphosphine oxide was synthesized from the reaction of the Grignard reagent obtained from 4-bromoanisole with diphenylphosphinic chloride, followed by cleavage of the methyl ether with HBr (figure 16). This method yielded pure product after recrystallization.

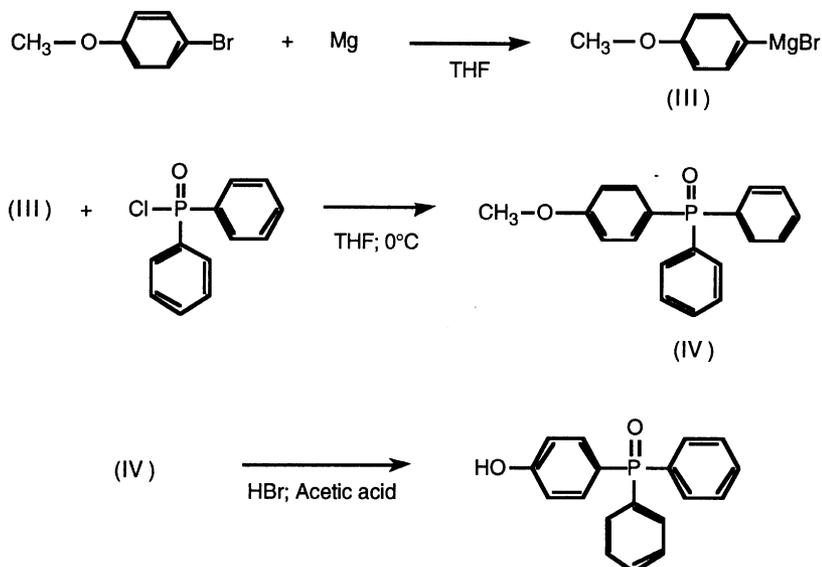


Figure 16. Synthesis of 4-Hydroxyphenyldiphenylphosphine Oxide

Model Reactions

Some model reactions were performed in order to determine the feasibility of forming polycarbonates. It has been reported in the literature that tertiary phosphine oxide (or phosphine) compounds can react with phosgene to form tertiary phosphine dichlorides. These halogenated compounds are unstable and can be easily hydrolyzed to the tertiary phosphine oxide (Figure 17). This reaction, if significant, could be competitive with the formation of the polycarbonate. Model reactions were performed in order to determine to what extent, if any, this might interfere with the polymerization.

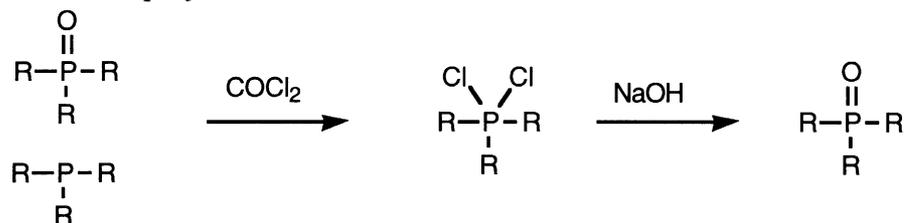


Figure 17. Possible Formation and Hydrolysis of Tertiary Phosphine Dichloride

Under interfacial polymerization conditions, the intermediate formed from phosgenation should be quickly hydrolyzed back to the phosphine oxide. In order to model these possible reactions, triphenylphosphine oxide and triphenylphosphine were phosgenated under conditions similar to those of an interfacial polycarbonate polymerization. Under these conditions, only unreacted triphenylphosphine oxide could be isolated from the reaction mixture. Since the triphenylphosphine quantitatively yielded triphenylphosphine oxide, the hydrolysis of any triphenylphosphine dihalide generated would rapidly occur under these conditions.

It was of interest whether high molecular weight bisphenol A polycarbonate could be formed in the presence of triphenylphosphine oxide. Interfacial polymerization was conducted in the

presence of a stoichiometric amount of triphenylphosphine oxide, utilizing a slight excess (1.5 equivalents) of phosgene. The polycarbonate obtained was isolated and examined by intrinsic viscosity and ^{31}P NMR. The intrinsic viscosity in chloroform was determined to be 1.45 dl/g, indicating that high molecular weight polymer was formed. ^{31}P NMR showed that no phosphorus compound was incorporated into the backbone of the polymer.

This model polymerization indicates that the reaction of phosgene with the phenolate of bisphenol A is faster than any possible reaction with triphenylphosphine oxide, but the reaction kinetics of the phenolate of the bis(4-hydroxyphenyl) phenyl phosphine oxide may not be as competitive.

The reaction of the bis(4-hydroxyphenyl) phenyl phosphine oxide with phosgene to form a polycarbonate was modeled by the synthesis of bis(triphenylphosphine oxide) carbonate from 4-hydroxyphenyldiphenylphosphine oxide. The monophenol was reacted with phosgene under the interfacial polymerization conditions, isolated from the reaction, and examined by ^1H and ^{31}P NMR. NMR analysis determined that the expected carbonate product was synthesized in approximately 98 percent purity, with the only impurity being residual starting material. This indicates that the reaction to form carbonate is indeed faster than the formation of any tertiary phosphorus dichloride side reaction product.

For comparison, bis(4-cumylphenyl) carbonate was synthesized under the same conditions. This compound was also formed in quantitative yield, with no detectable residual starting material observed by ^1H NMR. This suggests that the reaction of the triphenylphosphine oxide phenolate with phosgene may not be as fast as the reaction of phosgene with 4-cumylphenolate.

Homopolycarbonate Synthesis and Characterization

The synthesis of the homopolycarbonate of bis(4-hydroxyphenyl) phenylphosphine oxide was only partially successful. Interfacial and solution reactions were attempted, but only low molecular weight material was recovered in each case. The material was analyzed for intrinsic viscosity and by ^1H and ^{31}P NMR spectroscopy, DSC, and TGA.

The intrinsic viscosities in chloroform at 25°C ranged from 0.14 to 0.18 dl/g, while the ^1H NMR analysis (figure 18) indicated residual phenol end groups were present. The ^{31}P NMR spectrum (figure 19), which should depict a single peak, showed multiple unidentified phosphorus peaks to be present.

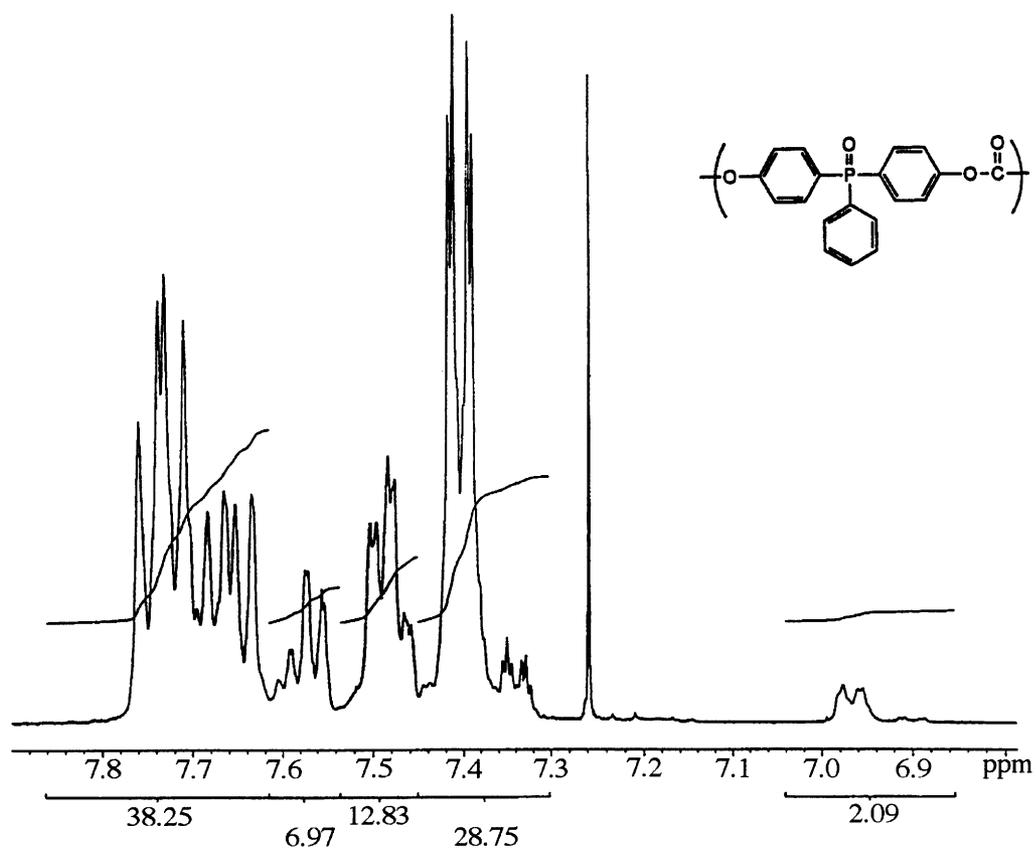


Figure 18. ¹H NMR Spectrum of the Polycarbonate Derived from Bis(4-hydroxyphenyl)phenylphosphine Oxide (400 MHz, CDCl₃)

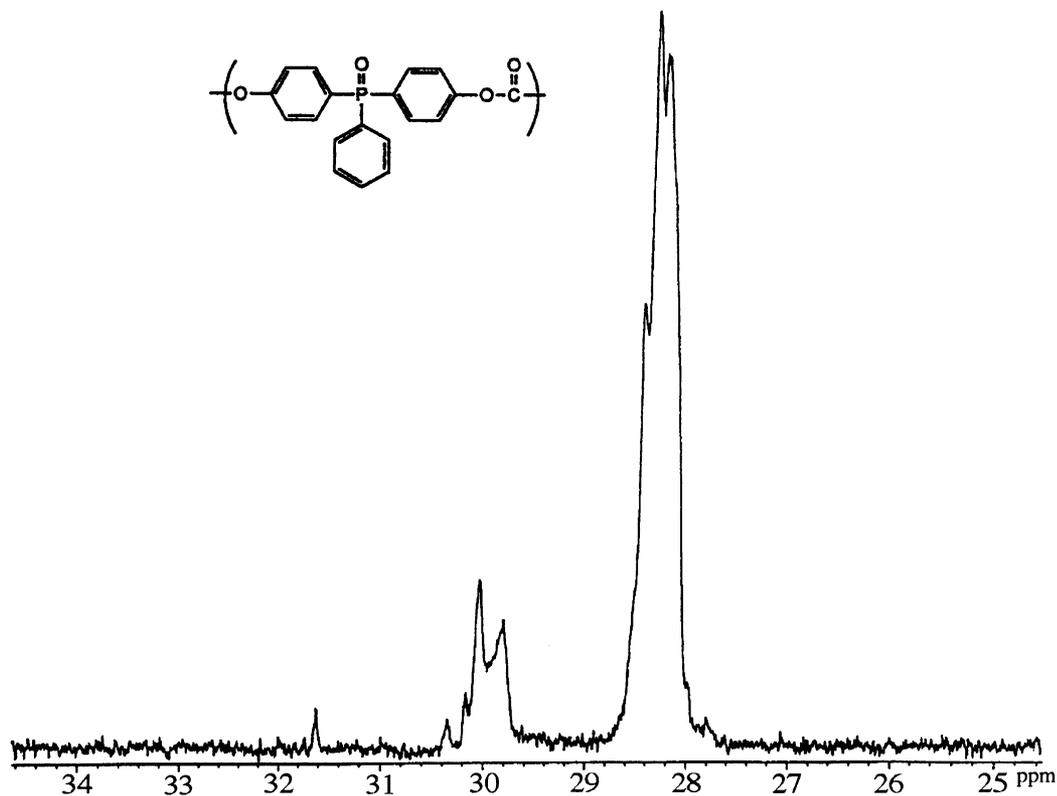


Figure 19. ^{31}P NMR Spectrum of the Polycarbonate Derived from Bis(4-hydroxyphenyl)phenylphosphine Oxide (400 MHz, CDCl_3)

Thermal analysis of the samples by DSC indicated a T_g of 202°C with no detectable T_m . In view of the modest molecular weight of the sample, it is expected that the T_g of high molecular weight polymer would be higher than this value. Thermogravimetric analysis in air demonstrated the decreased thermooxidative stability of this low molecular weight material compared to bisphenol A polycarbonate, but did demonstrate an increase in the char yield at elevated temperature (figure 20).

An attempt was also made to synthesize the homopolycarbonate by solution polymerization in anhydrous pyridine/methylene chloride. After 1 equivalent of phosgene was added, the reaction mixture formed an insoluble gel, which persisted as the phosgene addition was continued. Addition of water to the reaction mixture produced a solution.

Although the exact nature of the gel was not determined, perhaps the tertiary phosphine dihalide was formed under the anhydrous conditions. Such linkages would be hydrolytically unstable, and could explain why the addition of water produced a solution.

Synthesis and Characterization of a Phosphorus Containing Polyarylate

The polyarylate derived from bis(4-hydroxyphenyl) phenyl phosphine oxide and terephthaloyl chloride was synthesized by interfacial methods to determine if the monomer was of sufficient purity for the synthesis of high molecular weight material (figure 21). A highly viscous solution resulted and analysis after isolation of the polymer yielded an IV of 0.88 dl/g. A

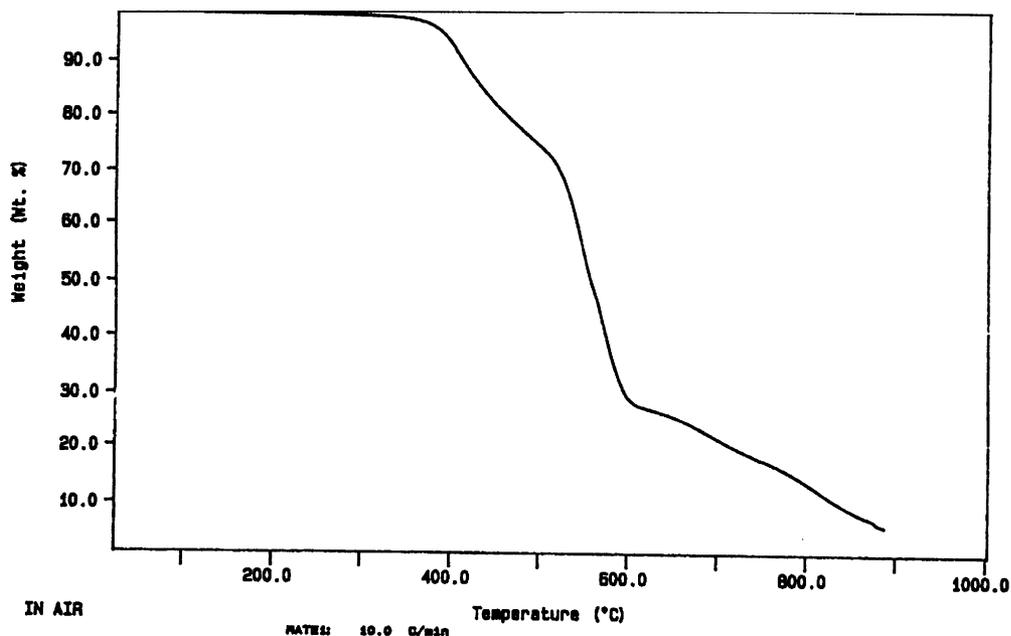


Figure 20. Thermogravimetric Analysis for the Homo-polycarbonate Derived from Bis(4-hydroxyphenyl)phenylphosphine Oxide (Air Atmosphere, 10°C/min)

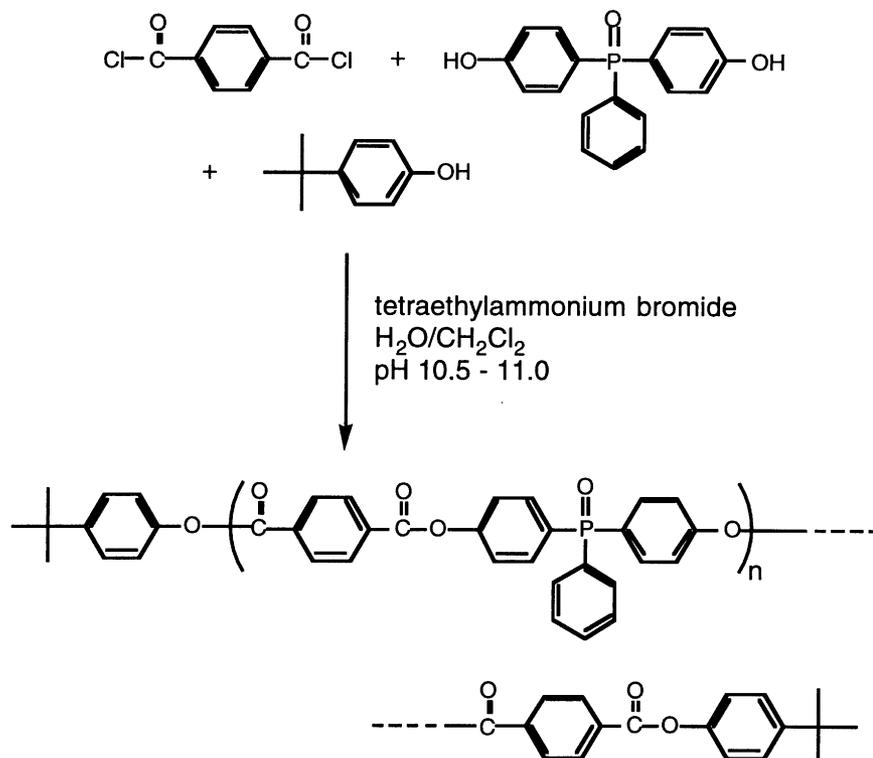


Figure 21. Synthesis of a Phosphorus Containing Polyarylate

second reaction was performed in which the molecular weight was controlled to an expected $\langle M_n \rangle$ of 40.0 kg/mole, by offsetting the stoichiometry and end capping with 4-*t*-butylphenol. The intrinsic viscosity of this sample was determined to be 0.46 dl/g.

The polyarylate was analyzed by ^1H and ^{31}P NMR, DSC, and TGA. The NMR spectra are depicted in figures 22 and 23. Thermal analysis data for the polymer are tabulated in table 2 and the dynamic TGA trace is depicted in figure 24.

The homo-polyarylate obtained with this bisphenol monomer proceeds to high molecular weight and produced a tough polymer with good mechanical properties. The very high char yield at 800°C is very interesting indeed.

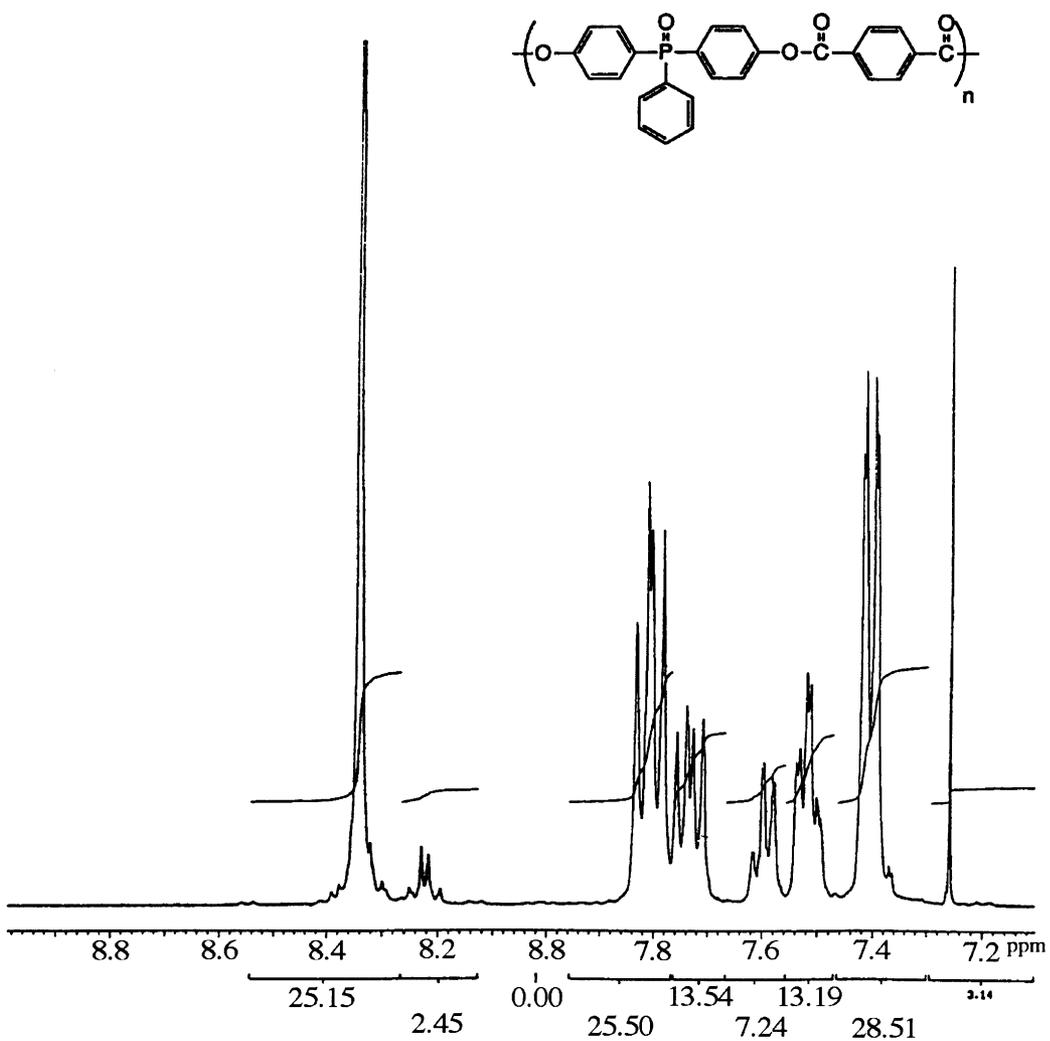


Figure 22. ^1H NMR Spectrum for the Polyarylate Derived from Bis(4-hydroxyphenyl)phenylphosphine Oxide and Terephthaloyl Chloride (400 MHz, CDCl_3)

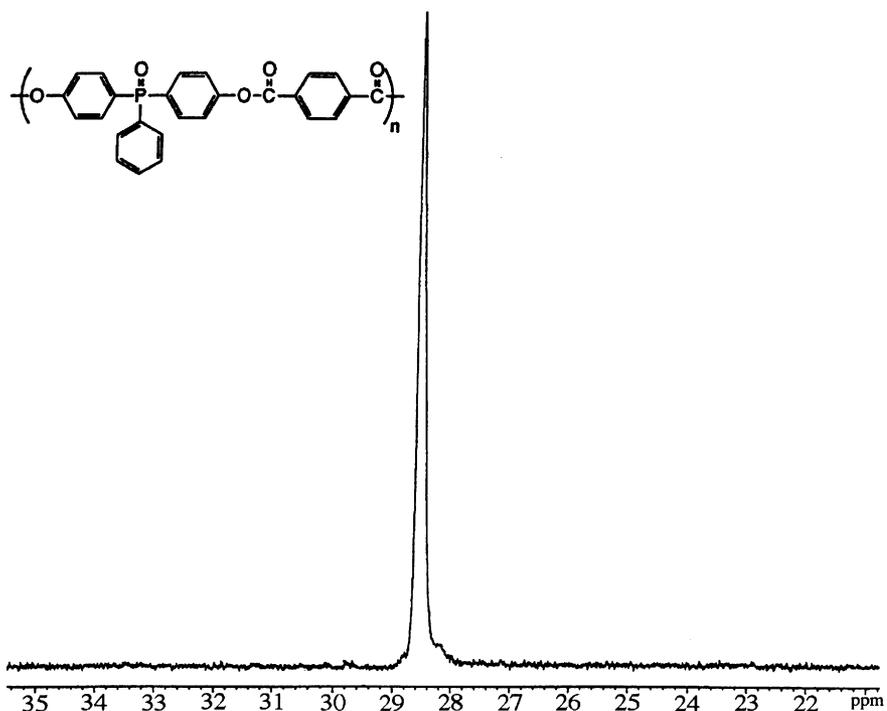


Figure 23. ^{31}P NMR Spectrum for the Polyarylate Derived from Bis(4-hydroxyphenyl)phenylphosphine Oxide and Terephthaloyl Chloride (400 MHz, CDCl_3)

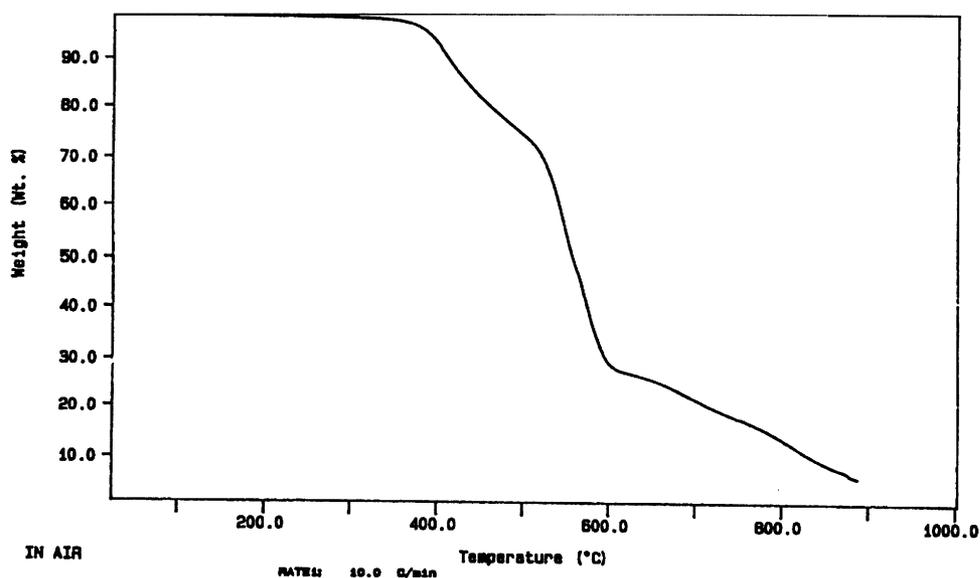


Figure 24. Thermogravimetric Analysis for the Polyarylate Derived from Bis(4-hydroxyphenyl)phenylphosphine Oxide and Terephthaloyl Chloride (Air Atmosphere, $10^\circ\text{C}/\text{min}$)

Table 2. Thermal Analysis Data for Phosphorus Containing Polyarylates

| T _g (°C) | 5% Weight Loss (°C) | Weight at 800°C in air (%) |
|---------------------|---------------------|----------------------------|
| 246 | 491 | 48% |

Synthesis of Polycarbonate Copolymers

The phosphorus containing bisphenol was reacted with phosgene and bisphenol A to afford polycarbonate statistical copolymers in varying amounts up to 50 weight percent. Copolymers were synthesized by interfacial techniques with 1, 5, 10, 25, and 50 weight percent of the repeat unit and it was possible to control the molecular weight by the addition of 4-*t*-butylphenol to the reaction mixture (figure 25). Bisphenol A polycarbonate homopolymers with triphenylphosphine oxide termination were also synthesized by the substitution of 4-hydroxyphenyldiphenylphosphine oxide for 4-*t*-butylphenol.

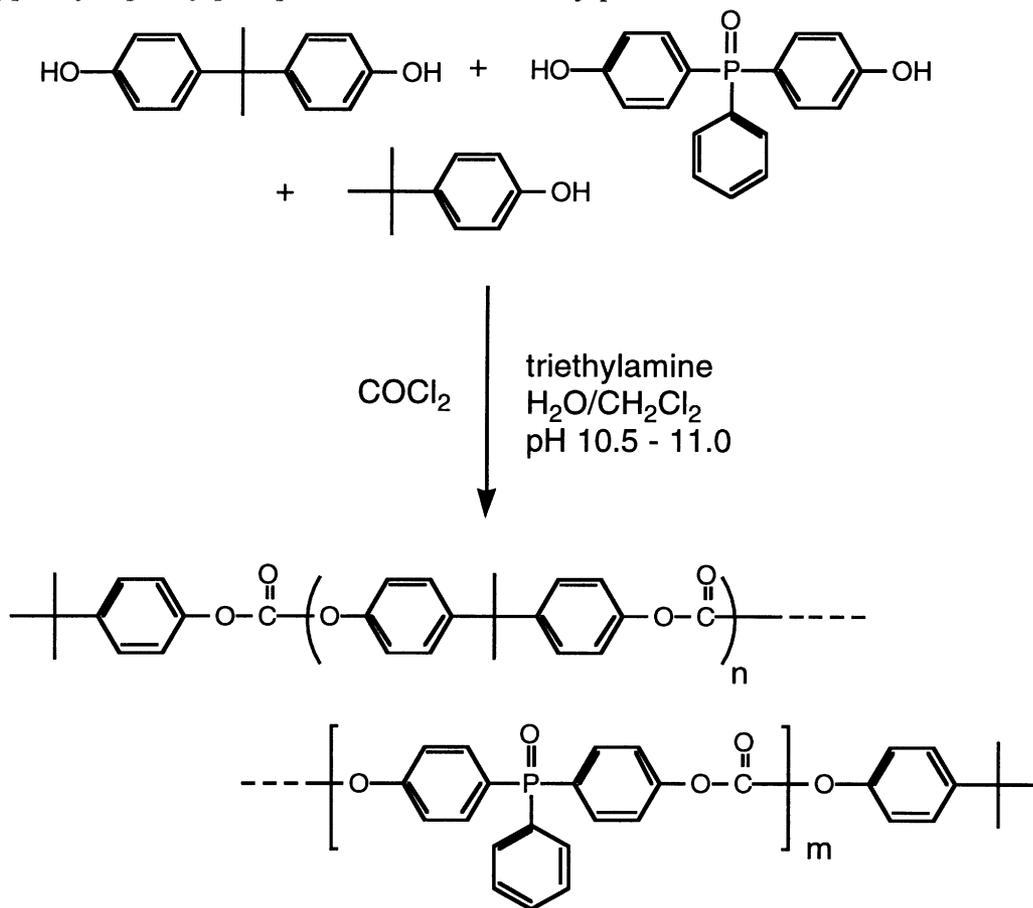


Figure 25. Synthesis of Phosphorus Containing Copolycarbonates

Characterization of Phosphorus Containing Polycarbonates

The relative molecular weight of the polymers and copolymers were estimated by intrinsic viscosity and GPC measurements relative to polystyrene standards and the composition was determined by ^1H NMR. (table 3). The molecular weight and end groups were controlled by the addition of a monofunctional phenol, either 4-*t*-butylphenol or 4-hydroxyphenyl-diphenylphosphine oxide. In the synthesis of the copolymers, 2.4 mole percent of 4-*t*-butylphenol relative to the total bisphenol present was used to control the molecular weight. The intrinsic viscosity of the copolymers was found to remain constant at this level of monofunctional phenol for the copolymer containing 10 weight percent of comonomer. However, a decrease in viscosity was observed for the 25 weight percent copolymer. Accordingly, the amount of monofunctional reagent was decreased to 1.6 mole percent for the synthesis of the 50/50 copolymer, which allowed for an intrinsic viscosity closer to the other materials.

Table 3. Characterization of Phosphorus Containing Copolycarbonates

| Sample | Incorporation (^1H NMR) (wt. %) | Intrinsic Viscosity (CHCl_3 ; 25° C) (dl/g) | T _g (°C) |
|-----------|-------------------------------------------------|----------------------------------------------------------------|------------------------|
| 1% PPO* | 1 | 0.75 | 154 |
| 5% PPO* | 5 | 0.75 | 156 |
| 10% PPO* | 9 | 0.72 | 159 |
| 25% PPO* | 24 | 0.49 | 166 |
| 50% PPO** | 48 | 0.69 | 186 |

* Molecular weight controlled with 2.6 mole percent 4-*t*-butylphenol

**Molecular weight controlled with 1.5 mole percent 4-*t*-butylphenol

The quantitative incorporation of bis(4-hydroxyphenyl)phenylphosphine oxide as a comonomer into bisphenol A polycarbonates proceeded very well and high molecular weight materials were synthesized as evidenced by the intrinsic viscosity and GPC values.

The T_g's of the copolymers were determined by DSC and are listed in table 3. An analysis of the trend in copolymer T_g's as a function of the weight fraction predicts that the high molecular weight homopolymer should have a T_g of about 224°C, as extrapolated from figure 26.

Dynamic thermogravimetric analysis (TGA) in an air atmosphere was performed on the samples in order to determine the relative thermooxidative stabilities of the copolymers (figure 27). The residual char weight remaining at high temperatures was also considered to be an indication of fire resistance. From the TGA, the copolymers were determined to be melt stable materials with nominal weight loss before 400°C, and demonstrated an observable increasing

trend in the char yield with increasing phosphorus content. In fact, the char yield in air at 700°C increases from 0 percent for commercial polycarbonate to approximately 30 percent for the 50/50 copolymer.

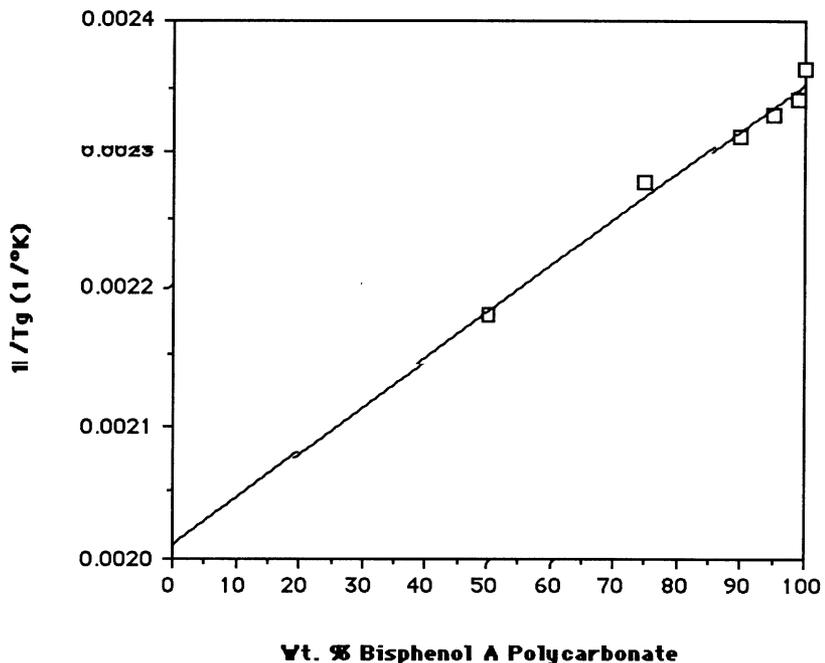


Figure 26. Linear Relationship of Copolymer Tg and Composition at 10°C/minute

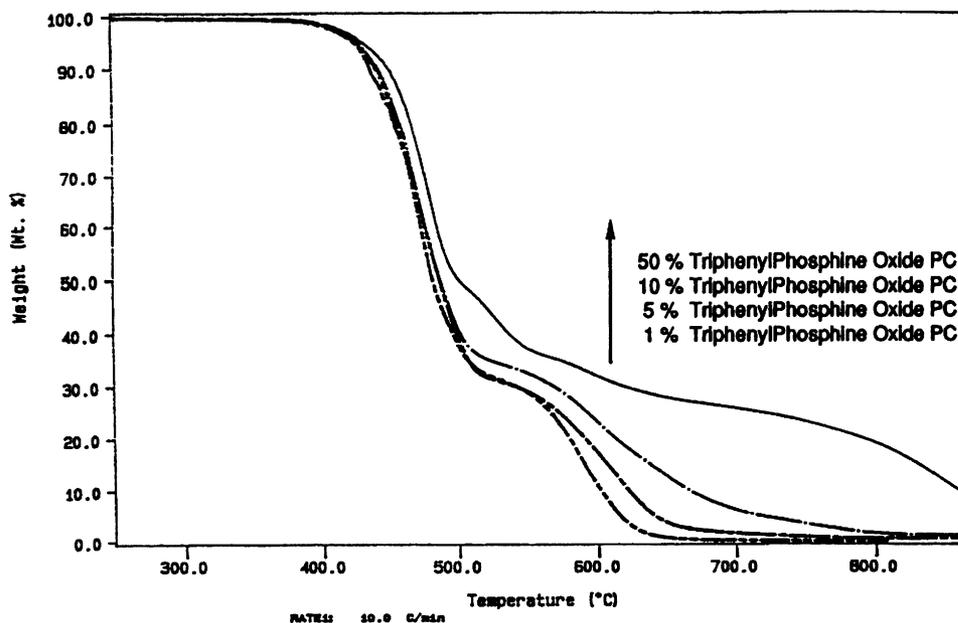


Figure 27. Thermogravimetric Analysis for Co-polycarbonates Derived from Bis(4-hydroxyphenyl) phenylphosphine Oxide and Bisphenol A (Air Atmosphere, 10°C/min)

The fire resistance of the novel copolymers has been preliminarily examined by cone calorimetry and results are graphically depicted in figure 28. Cone calorimetry data measures the heat release rate with time and a definite improvement can be detected for the copolymers over a bisphenol A polycarbonate control sample. An improvement in the peak heat release rate is observed with as little as 1% of the phosphorus unit incorporated. It is not clear yet whether the apparent decrease in initial time for heat release to begin is important and no explanation for this behavior can be offered.

The polycarbonate with only triphenylphosphine oxide termination was also examined in comparison to the control and copolymer samples. Again, an improvement can be detected with even the small amount of triphenyl phosphine oxide introduced at the chain ends of this polymer. Further work is needed to further quantify important parameters such as smoke and total heat release.

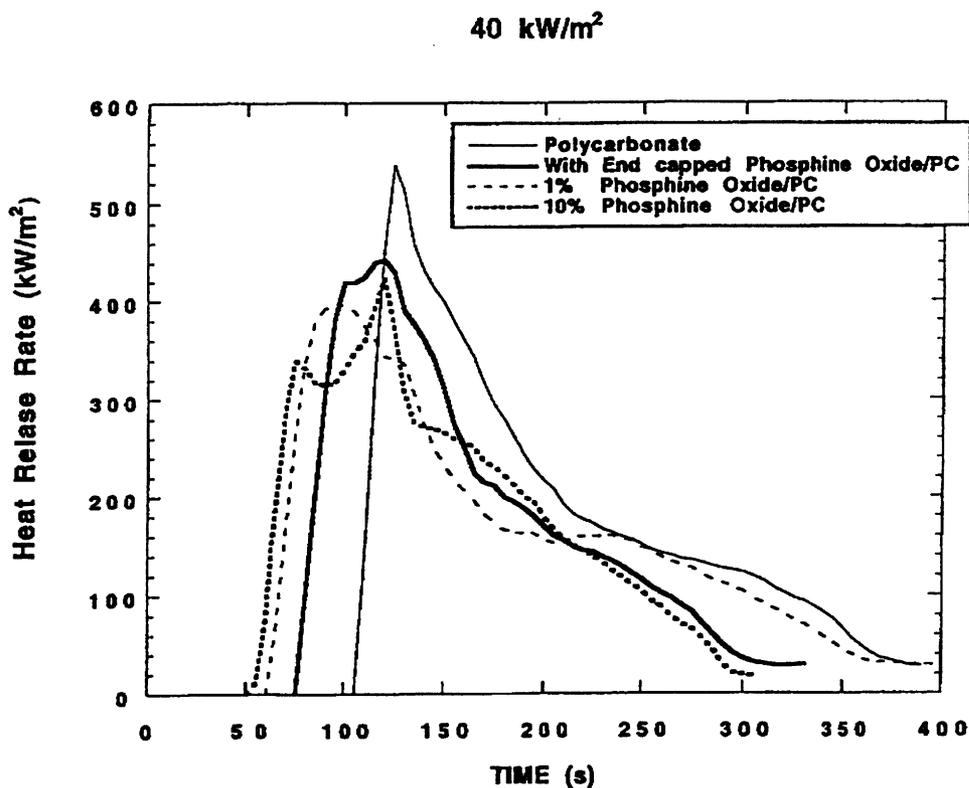


Figure 28. Cone Calorimetry Data for Phosphorus Containing Polycarbonates (10cm x 10cm x 0.3cm)

IV-iii. Poly(arylene ether)s

High molecular weight poly(arylene ether)s based on 4,4'-bis(fluorophenyl)methylphosphine oxide (BFPMPPO) were successfully synthesized *via*

nucleophilic aromatic substitution. Figure 29 illustrates the general synthetic procedure used for the poly(arylene ether phosphine oxide)s. High molecular weight poly(arylene ether phosphine oxide sulfone)s and poly(arylene ether)s with a high phosphorus content were also synthesized by the approaches described in the experimental section. High reaction temperatures were necessary as a consequence of the deactivating effect of the phosphine oxide moiety in the bisphenol monomers. Figures 30 and 31 illustrate the synthesis of these polymers.

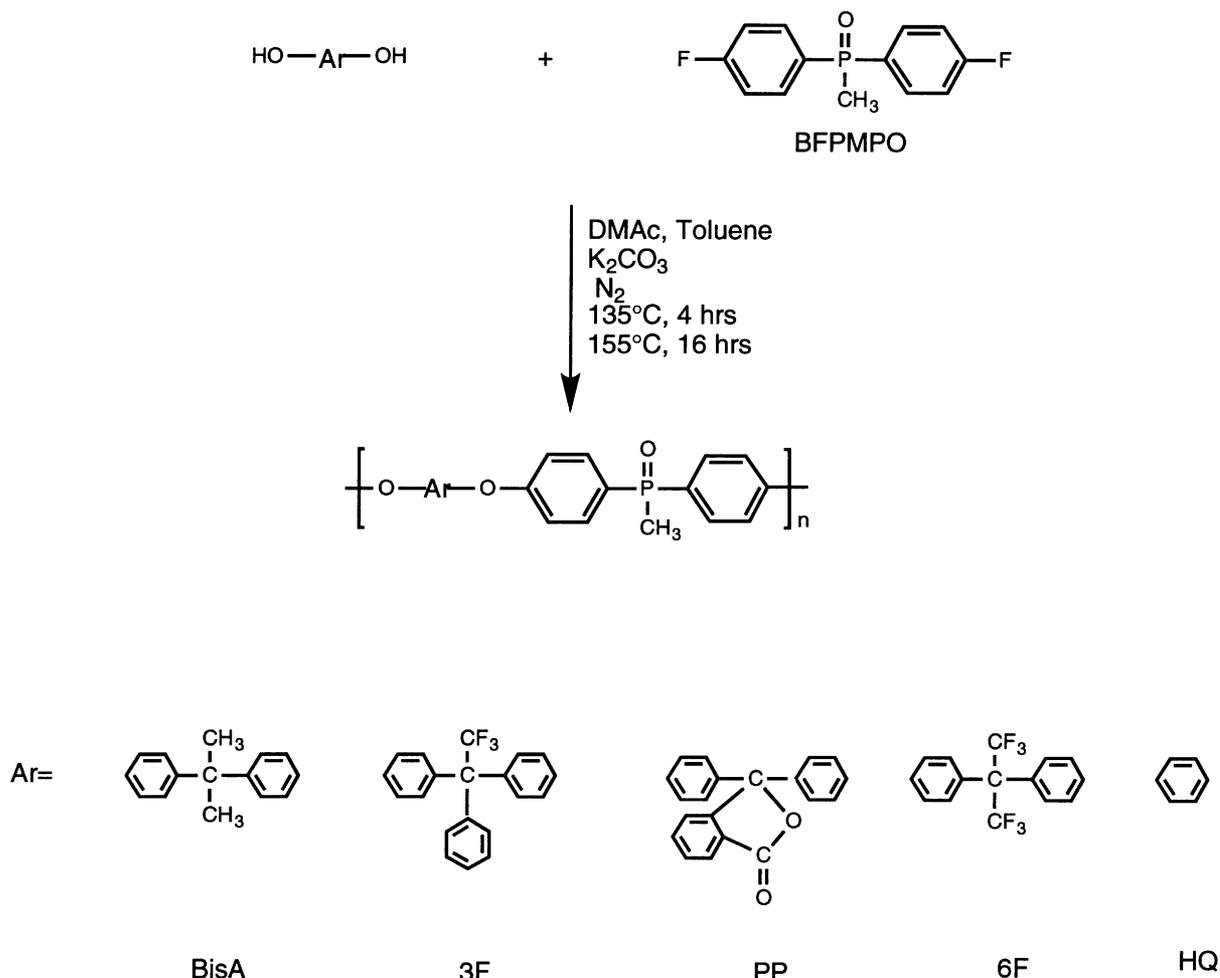
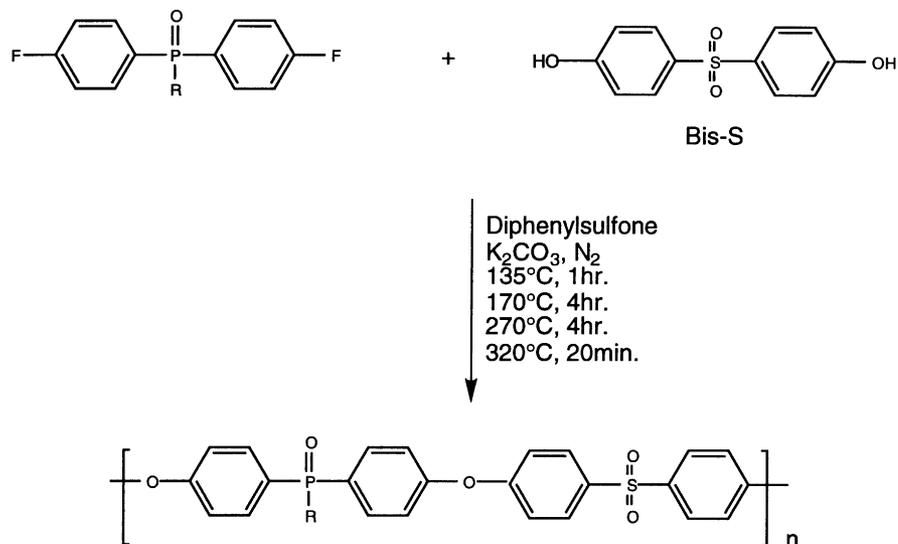


Figure 29. Synthesis of Poly(arylene ether phosphine oxide)s

Molecular weight analysis

Determination of molecular weight and its distribution was accomplished using universal calibration GPC.¹³ Eighteen different polystyrene standards with low polydispersity indices were used to construct a calibration curve. The results for the aforementioned poly(arylene ether)s are listed in tables 4 and 5.

From tables 4 and 5, it is clear that the above materials are appropriately high molecular weight materials and appear to be well above the entanglement molecular weight. It is noted that the molecular weight of the experimental polymer samples is, in general considerably higher than that of the control poly(arylene ether sulfone)s utilized. The somewhat narrow molecular weight distribution may be due the fact that these polymers were reprecipitated twice and some of the low molecular weight fractions may remain in the precipitation medium. This would explain why the polydispersity index values deviate from the theoretical value of 2.0.



R = CH₃ or phenyl

Figure 30. Synthesis of Poly(arylene ether phosphine oxide sulfone)s

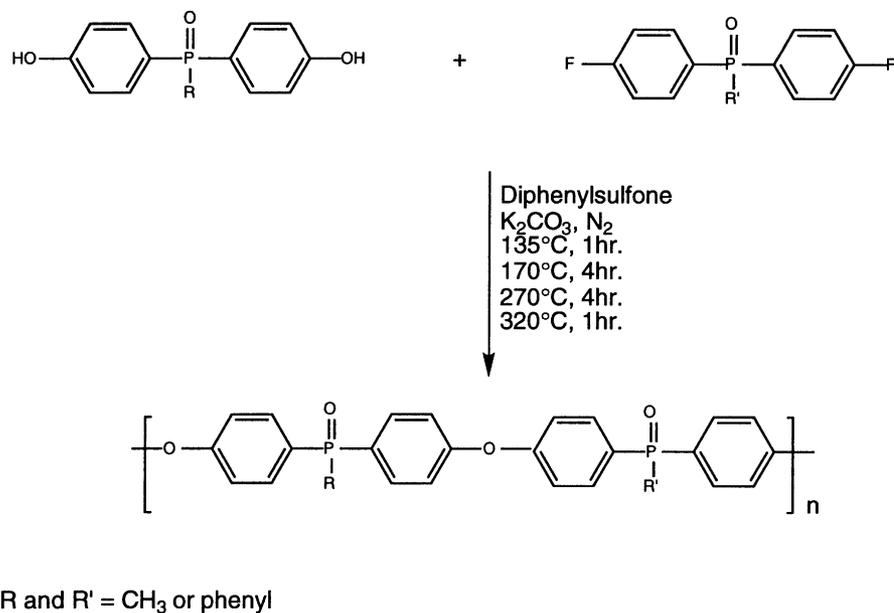


Figure 31. Synthesis of Poly(arylene ether phosphine oxide)s With A High Phosphorus Content

Table 4. Characterization of Poly(arylene ether phosphine oxide)s *via* Quantitative GPC Analysis*

| Polymer** | Mn (g/mole) | Mw (g/mole) | Mw/Mn |
|-------------|-------------|-------------|-------|
| BisA-BFPMPO | 27,000 | 47,000 | 1.7 |
| PP-BFPMPO | 41,000 | 72,000 | 1.7 |
| 3F-BFPMPO | 47,000 | 82,000 | 1.8 |
| 6F-BFPMPO | 21,000 | 33,000 | 1.6 |
| HQ-BFPMPO | 44,000 | 72,000 | 1.6 |
| Udel | 23,000 | 40,000 | 2.3 |

* Uncertainties based on experience of repeated measurements are $\pm 10\%$

** See Fig. 2

Table 5. Characterization of Poly(arylene ether phosphine oxide sulfone)s*

| Polymer** | Mn (g/mol) | Mw (g/mol) | Mw/Mn |
|------------------------|------------|------------|-------|
| BFPMPO-BOHPMPO*** | | | |
| BFPMPO-BOHPPO | 21,000 | 40,000 | 1.9 |
| BFPMPO-BOHPPO*** | | | |
| BFPMPO-SO ₂ | 29,000 | 45,000 | 1.6 |
| BFPMPO-SO ₂ | 24,000 | 35,000 | 1.5 |
| Victrex | 11,000 | 22,000 | 2.0 |

* Uncertainties based on experience of repeated measurements are $\pm 10\%$

** See Fig. 2

*** Insoluble in NMP 0.06M LiBr solution

Thermal and Mechanical Analysis

Differential scanning calorimetry (DSC) indicates that these polymers show glass transition temperatures as high as 260 °C and thermal gravimetric analysis shows that they are stable briefly in air over 500 °C. Table 6 demonstrates that PP-BFPMPO has a 71 °C increase in T_g when compared to its analogous BisA derivative. This may be due to the incorporation of the rigid pendant lactone heterocyclic unit on the polymeric backbone. These polymers show an increased char yield in air over similar ketone and sulfone derivatives. The phenolphthalein based PP-BFPMPO appears to have a higher than expected char yield based on the percent phosphorus within the polymer. Similar observations have been noted by Pearce *et.al*¹⁶ and others¹⁷ for of phenolphthalein based polycarbonates and polyesters and this increased char may indicate enhanced flame resistance, assuming that the surface residue inhibits oxygen from continuing to reach the fire front. The thermal analysis of these polymers are shown in Table 6.

Table 6. Thermal Analysis of High Molecular Weight Poly(arylene ether)s

| Polymer | 25°C [η] CHCl ₃ (dl/gm) | TGA ($\pm 5^\circ\text{C}$)* 5% mass loss in air | T _g ($\pm 3^\circ\text{C}$)** | Char yield*** (± 3 mass%) in air | %P**** |
|--------------|-------------------------------------------------|----------------------------------------------------------|--------------------------------------------|---------------------------------------------|--------|
| Bis A-BFPMPO | 0.45 | 500 | 192 | 16 | 7.0 |
| PP-BFPMPO | 0.51 | 477 | 263 | 14 | 5.8 |
| 3F-BFPMPO | 0.57 | 505 | 229 | 7 | 5.6 |
| 6F-BFPMPO | 0.37 | 530 | 208 | 5 | 5.7 |
| HQ-BFPMPO | 0.85 | 515 | 213 | 26 | 9.3 |
| Udel | 0.48 | 510 | 187 | 0 | 0 |

*Scan rate of 10°C/min

**Second heat rate of 10°C/min

***Scan rate of 10°C/min: Yield calculated at 700°C

****Calculated from polymer repeat unit

The phosphorus containing polymers also show an increase in the tensile modulus compared to poly(arylene ether sulfone) possibly due to enhanced intermolecular dipolar forces. For example, table 7 illustrates that the BisA-BFPMPO material shows a 15% increase in modulus when compared to the analogous poly(arylene ether sulfone) control. Furthermore, the rigid hydroquinone (HQ) unit and high concentration of polar phosphine oxide moieties may explain the increased modulus of the HQ-BFPMPO film.

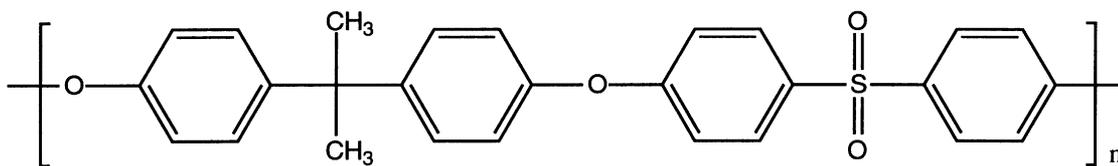
Polymers containing both the advantageous phosphine oxide and sulfone moieties were also examined. As can be seen in Table 6, these phosphine oxide-sulfone polymers have substantially improved properties such as: increased modulus, T_g, and char yield over the commercially available poly(arylene ether sulfone) 2. The moderate increase in T_g of these polymers is probably a function of the increased bulkiness and dipole moment of the phosphine oxide unit compared to the sulfone derivative. It is more important that incorporation of the phosphine oxide moiety within the polymeric backbone increased Young's modulus by over 25% relative to the polysulfone. In addition, as illustrated in table 8 and Figures 32-34 the dynamic and isothermal TGA char yields of these phosphine oxide sulfones is substantially higher than the control. Under isothermal conditions the polysulfone was completely volatilized after a short exposure to 550 °C. However, the phosphine oxide containing polymers studied showed between a 9 to 18 percent char yield after isothermal exposure at 600 °C for three hours.

Table 7. Room Temperature Stress-Strain Behavior of Compression Molded High Molecular Weight Poly(arylene ether)s*

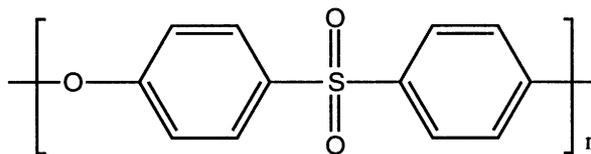
| Polymer | Youngs** Modulus (ksi) | Tensile** Strength (psi) | Strain** (%) |
|--------------|------------------------------|--------------------------------|-----------------|
| Bis A-BFPMPO | 420±45 | 12200±900 | >40 |
| 3F-BFPMPO | 420±7 | 13300±900 | 25±1 |
| 6F-BFPMPO | 350±14 | 11100±700 | 26±3 |
| HQ-BFPMPO | 510±35 | 12000±1200 | 38±3 |
| Udel | 360±38 | 10200±1000 | >40 |

* Uncertainties were obtained by calculating the standard deviation of all samples analyzed

**ASTM D638 (0.05 in/min)



1



2

Table 8. Thermal and Mechanical Properties of Phosphine Oxide-Sulfones

| Polymer | 25 °C [η] CHCl ₃ (dl/gm) | Char yield* (± 3 mass%) in air | TGA (± 5 °C)** 5% mass loss in air | Tg*** (± 3 °C) | Youngs**** Modulus (ksi) | Strain**** (%) |
|-------------------------|--------------------------------------------------|-------------------------------------------|-----------------------------------------------|------------------------|--------------------------------|-------------------|
| BOHPMPO-SO ₂ | 0.40 | 24 | 514 | 233 | 465 \pm 7 | 36 \pm 5 |
| BOHPPO-SO ₂ | 0.41 | 30 | 596 | 231 | 476 \pm 7.5 | 25 \pm 9 |
| Victrex 3600P | 0.41(NMP) | 15 | 561 | 222 | 374 \pm 16 | 25 \pm 3 |
| Victrex 4100G***** | | | | | 348 | |

* Scan rate of 10 °C/min: determined at 700 °C

** Scan rate of 10 °C/min

***Determined from second scan rate of 10 °C/min

****ASTM D638 (0.05 in/min)

*****Encyclopedia of Polymer science and Engineering 2nd ed.

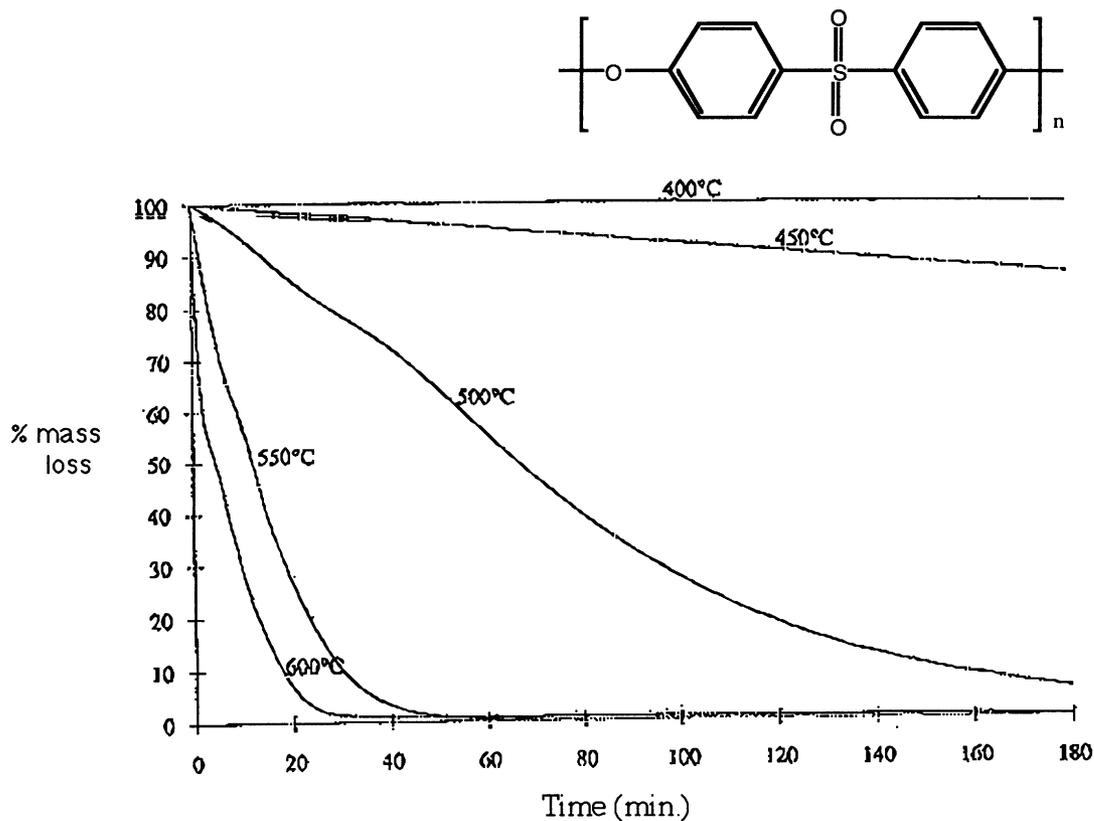


Figure 32. Isothermal TGA of Victrex in air for 3 hours at various temperatures.

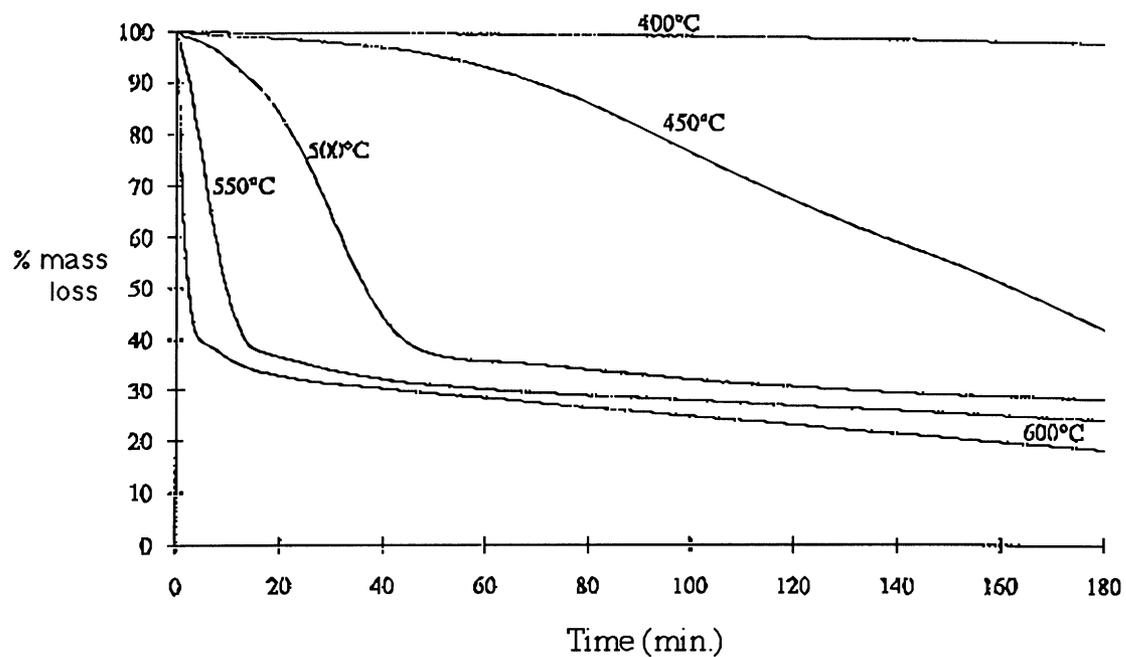
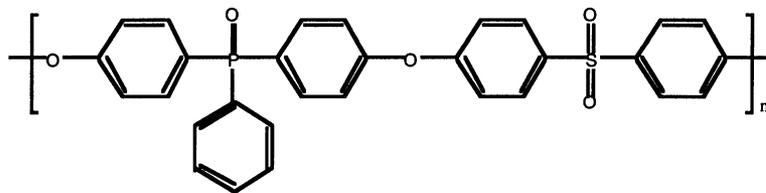


Figure 33. Isothermal TGA in air of BFPPO-SO₂ at various temperatures.

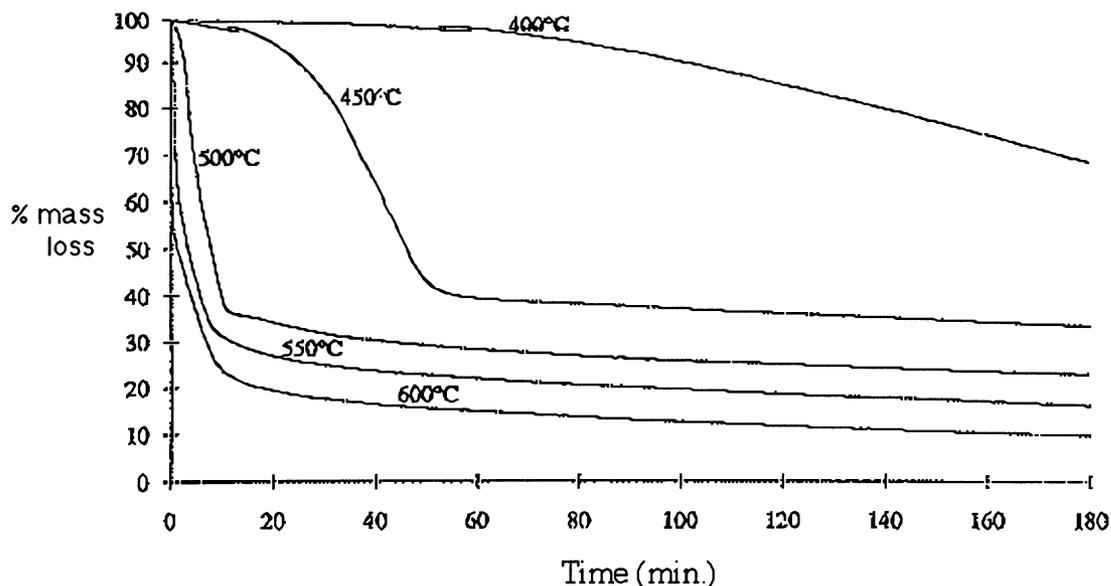
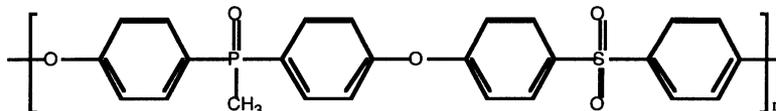


Figure 34. Isothermal TGA in air of BFPMPO-SO₂ at various temperatures mass percent phosphorus.

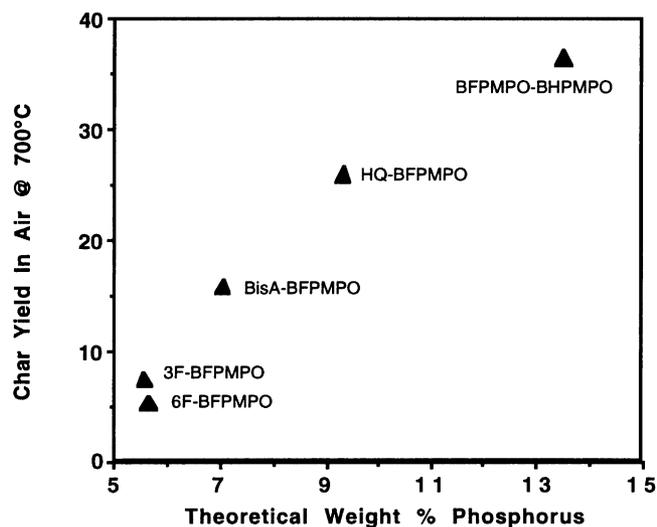
Since phosphorus appeared to have a direct influence upon the char yield it was decided to synthesize poly(arylene ether phosphine oxide) homopolymers that would contain up to 14 mass percent phosphorus. As shown in table 9, these polymers have substantially higher char yields and a slight increase in T_g over their phosphine oxide sulfone counterpart. This may be due to the high concentration of polar phosphine oxide moieties within the polymeric backbone. It may also be noted that the phosphine oxide homopolymer with a pendant aromatic ring has the highest char yield, which is consistent with results previously discussed by Lin and Pearce.¹⁸ A plot of char yield as a function of percent phosphorus in figure 35, demonstrates the influence of phosphorus content on the char yield. The polymer backbone is also a factor along with the percent phosphorus. For example, the concentration of aromatic rings has been noted to affect char yields, but nevertheless this is a significant correlation and demonstrates the direct influence that phosphorus has upon these char yields. Therefore, by invoking the generalization derived by van Krevelen¹⁹, that higher char yields produce higher limiting oxygen index values, one may conclude that the increased phosphorus content within the backbone of poly(arylene ether)s decreases their flammability.

Table 9. Thermal Properties of Poly(arylene ether phosphine oxide) homopolymers

| Polymer | $[\eta]$ _{25°C} CHCl ₃ (dl/gm) | Char Yield (±3 mass %) in air | TGA(±5 °C)* 5% Wt. loss in air | Tg(±3 °C)** |
|----------------|----------------------------------------------------------|-------------------------------------|--------------------------------------|-------------|
| BOHPMPO-BFPMPO | 0.32 | 30 | 518 | 238 |
| BOHPMPO-BFPPO | 0.33 | 30 | 530 | 238 |
| BOHPPO-BFPPO | 0.33 | 41 | 567 | 240 |

* Scan rate of 10 °C/min determined at 700 °C

**Determinet from second scan rate of 10 °C/min

**Figure 35. Influence of Percent Phosphorus On Char Yield AT 700 °C**

The flammability behavior studies of the phosphine oxide polymers has been initiated using cone calorimetry. The preliminary results are summarized in figure 36 and table 10.⁶⁻⁹

Table 10. Effect of Phosphine Oxide Upon the Peak Heat Release of Various Polymers*

| Polymer | Peak Heat Release Rate kW/m ² |
|-----------------------------------------------------|---------------------------------------------|
| Nylon 6,6 | 1200±180 |
| Nylon 6,6 30%PO (3.4 mass% Phosphorus) | 500±75 |
| BisA-polycarbonate | 540±75 |
| BisA-polycarbonate 10% PO (1.2 mass% Phosphorus) | 420±60 |
| Polysulfone (Udel) | 170 |
| Polyethersulfone (Viktrex) | 105±50 |
| BFPmPO-SO ₂ (6.7 mass% Phosphorus) | 105±50 |
| BFPPO-SO ₂ (5.9 mass% Phosphorus) | 85±40 |

* Samples tested using cone calorimetry at a flux of 40 kW/m²

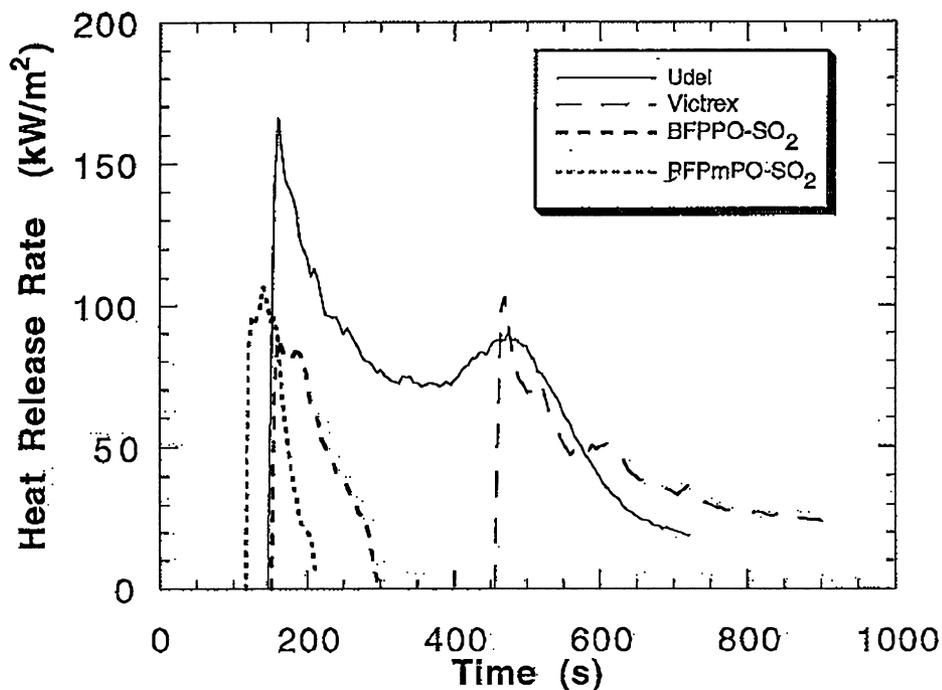


Figure 36. Cone calorimetry data for phosphorus containing poly(arylene ether)s obtained at a constant flux of 40 kW/m².

The commercial bisphenol-A based poly(arylene ether sulfone) 1 control had the highest heat release rate of the samples analyzed. This may reflect the aliphatic portion of the bisphenol-A monomer. The wholly aromatic poly(arylene ether sulfone) 2 ignited with a longer delay time and had a similar peak heat release to the phosphine oxide containing polymers. However, the phosphine oxide containing polymers did not generate a steady flame during combustion and extinguished shortly after ignition. Table 10 summarizes the effect upon the peak heat release rate by incorporating phosphorus within the backbone of various polymers ⁶⁻⁹

Although the phosphorus-containing polymer show different thermal, mechanical strength, and flammability, incorporation of a phenyl phosphine oxide unit does not appear to alter the sub-ambient relaxation behavior of the polymers relative to related materials studied earlier.^{12,20} Plots of Tan delta versus temperature shown in figure 37 indicates that low temperature relaxations often associated with ductility or toughness are essentially identical to the commercial control 2.

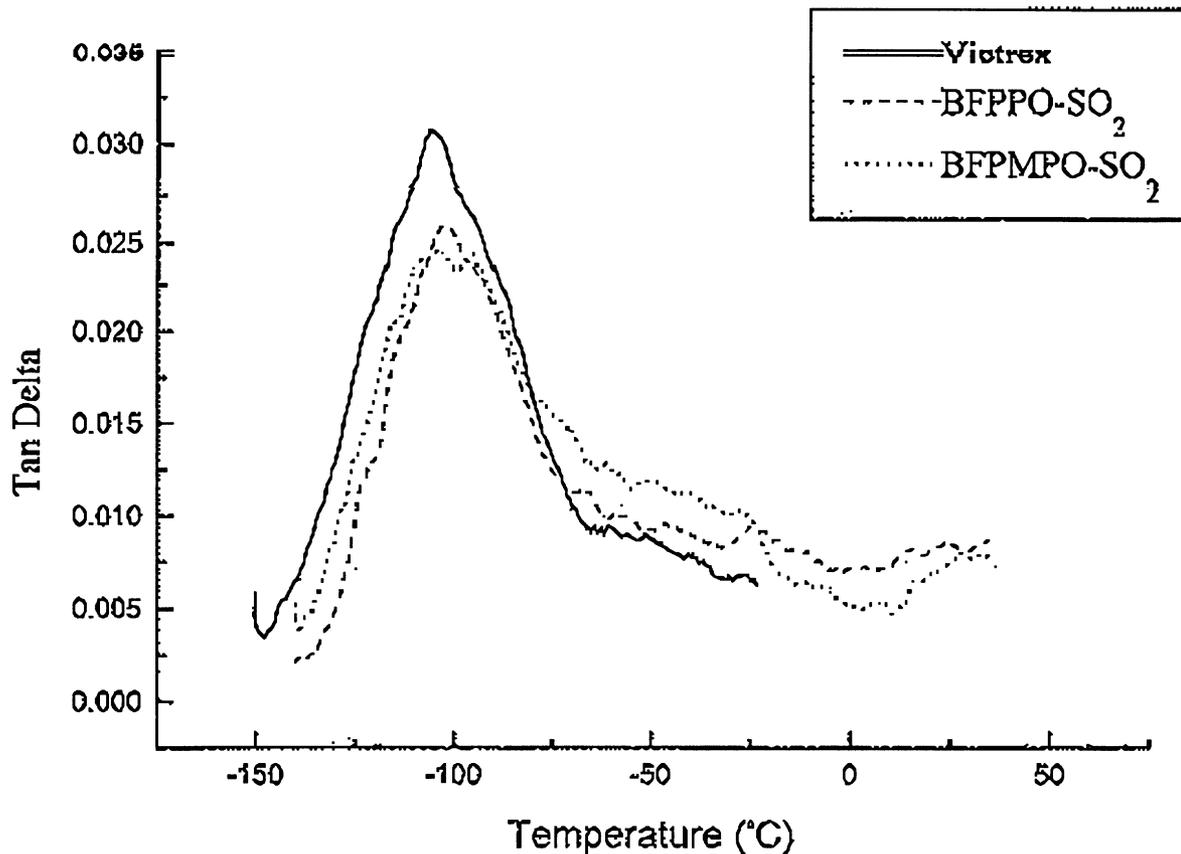


Figure 37. Effect of phosphorus upon the low temperature relaxation of poly(arylene ether)s.

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