

## Chapter 3

# Copolyarbonates and Poly(arylates) Derived from Hydrolytically Stable Phosphine Oxide Comonomers

D. M. Knauss<sup>1</sup>, J. E. McGrath<sup>1,3</sup>, and Takashi Kashiwagi<sup>2</sup>

<sup>1</sup>Department of Chemistry and National Science Foundation Science and Technology Center, High Performance Polymeric Adhesives and Composites, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0344

<sup>2</sup>Building and Fire Research Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899-0001

Hydrolytically stable bis(4-hydroxyphenyl) phenyl phosphine oxide was synthesized and utilized to produce high molecular weight polycarbonate and aromatic polyester copolymers. The glass transition temperature increased from about 150°C for the control bisphenol-A polycarbonate system to 186°C for the 50 wt. percent copolymer. The char yield via dynamic TGA in air increased from 0% for the control to 30% at 700°C for the 50% copolymer. The homopolymer had a Tg of 202°C, but only low molecular weight was achieved. In contrast, tough, transparent, high Tg polyarylates were prepared with terephthaloyl chloride that had a high char yield in air. Transparency and toughness were maintained in the copolymers, and the char yield in air increased significantly with phosphorus concentration. The materials are being characterized as improved fire resistant transparent systems and initial cone calorimetry studies do show that the heat release rate is significantly decreased. The residual carbon monoxide concentration does increase, which is consistent with the incomplete combustion.

The introduction of phosphorus compounds as flame retardants in polymers is well known (1). Most flame retardants are introduced as physically blended additives and are not chemically bonded to the polymer. Such additives can potentially be leached out of the material, which may introduce loss of protection and/or undesired hazards. Phosphorus containing comonomer flame retardants incorporated into the polymer backbone may overcome this problem. The incorporation of functionalized derivatives of triphenylphosphine oxide into a variety of polymers has recently been investigated (2-8). For example, the polycarbonate derived from bisphenol A and phosgene is an important engineering thermoplastic (9) and incorporation of various phosphorus compounds into the backbone have been examined. Some hydrolytically stable materials have been reported,<sup>10-15</sup> but more often incorporation of phosphorus compounds has usually created hydrolytically unstable phosphate linkages (16-23). Our objective was to

<sup>3</sup>Corresponding author

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 (15). Our goal was to investigate the effect of comonomer concentration on copolymer properties, including fire resistance. Some initial results of this cooperative effort are described in this paper.

## Experimental

**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.<sup>23</sup> 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 I<sub>2</sub> 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.<sup>15</sup> m.p. 233 - 234° C).

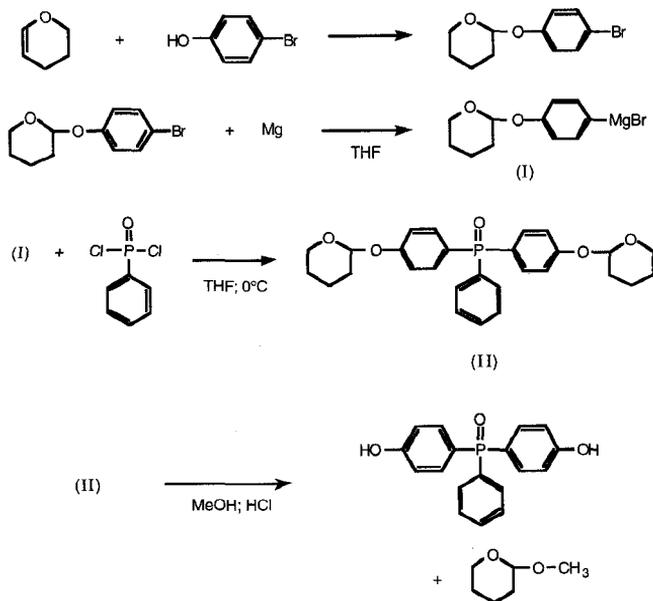
**Synthesis of phosphorus containing polycarbonate copolymers:** Copolymers of controlled composition were synthesized in 50 g batches. Calculated amounts of bis(4-hydroxyphenyl)phenylphosphine oxide were added along with bisphenol A to a 500ml, 5 neck round bottom flask equipped with a mechanical stirrer, 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  $^1\text{H}$  and  $^{31}\text{P}$  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/M<sup>2</sup>, in the horizontal configuration on 10cm by 10cm by 0.3cm compression molded films.

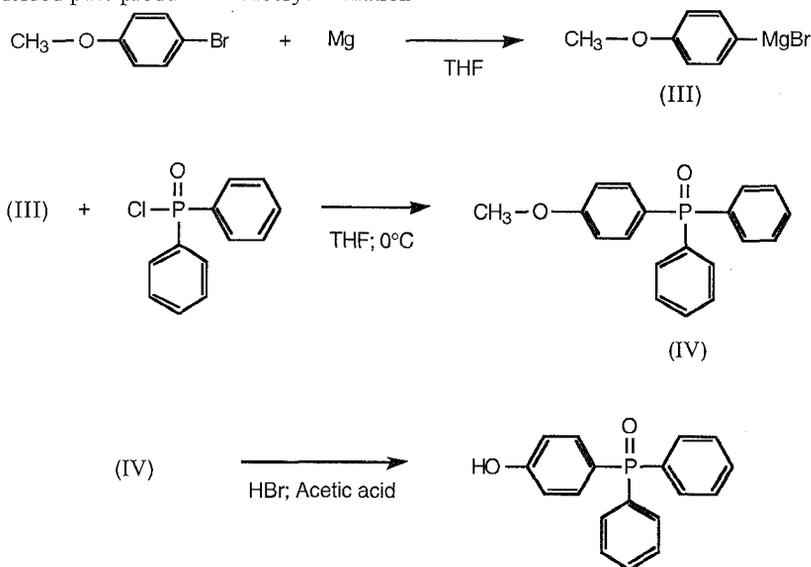
## Results and Discussion

**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 (Scheme 1). 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 (24).



**Scheme 1:** Synthesis of Bis(4-hydroxyphenyl)phenylphosphine Oxide

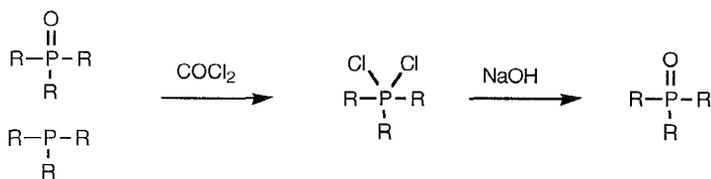
A monofunctional phenol derived from triphenylphosphine oxide was also synthesized as a model compound and endcapper. The 4-hydroxyphenyldiphenylphosphine oxide was synthesized from the reaction of the Grignard reagent obtained from 4-bromoanisole with diphenylphosphinic chloride, followed by cleavage of the methyl ether with HBr (Scheme 2). This method yielded pure product after recrystallization.



**Scheme 2:** 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 (Scheme 3). 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.



**Scheme 3:** 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  $^{31}\text{P}$  NMR. The intrinsic viscosity in chloroform was determined to be 1.45 dl/g, indicating that high molecular weight polymer was formed.  $^{31}\text{P}$  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  $^1\text{H}$  and  $^{31}\text{P}$  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.

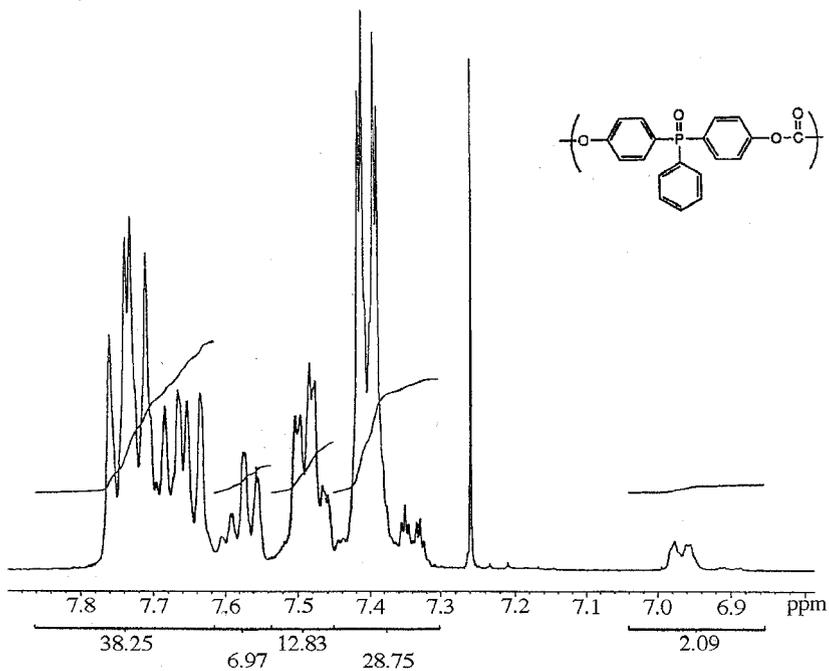
For comparison, bis(4-cumylphenyl) carbonate was synthesized under the same conditions. This compound was also formed in quantitative yield, with no detectable residual starting material observed by  $^1\text{H}$  NMR. This suggests that the reaction of the triphenylphosphine oxide phenolate with phosgene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

### Homopolycarbonate Synthesis and Characterization

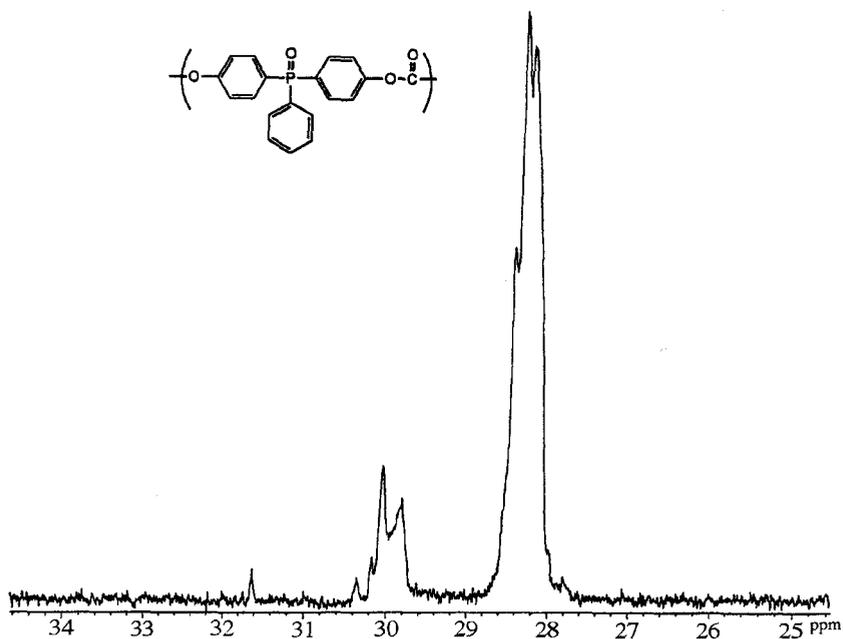
The synthesis of the homopolycarbonate of bis(4-hydroxyphenyl) phenylphosphine oxide was only partially successful. Interfacial and solution reactions were attempted, but only low molecular weight material was recovered in each case. The material was analyzed for intrinsic viscosity and by  $^1\text{H}$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

The intrinsic viscosities in chloroform at 25°C ranged from 0.14 to 0.18 dl/g, while the  $^1\text{H}$  NMR analysis (Figure 1) indicated residual phenol end groups were present. The  $^{31}\text{P}$  NMR spectrum (Figure 2), which should depict a single peak, showed multiple unidentified phosphorus peaks to be present.

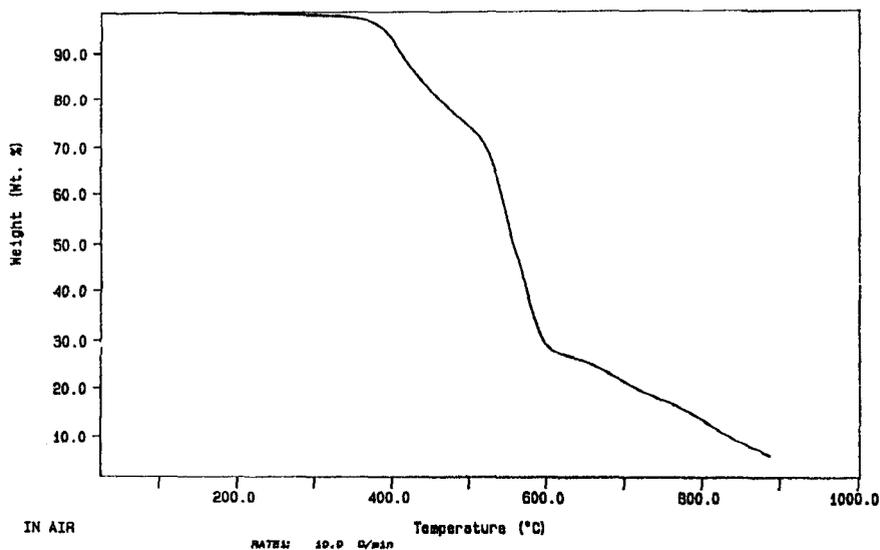
Thermal analysis of the samples by DSC indicated a  $T_g$  of 202°C with no detectable  $T_m$ . In view of the modest molecular weight of the sample, it is expected that the  $T_g$  of high molecular weight polymer would be higher than this value. Thermogravimetric analysis in air demonstrated the decreased 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 3).



**Figure 1:**  $^1\text{H}$  NMR Spectrum of the Polycarbonate Derived from Bis(4-hydroxyphenyl)phenylphosphine Oxide (400 MHz,  $\text{CDCl}_3$ )



**Figure 2:**  $^{31}\text{P}$  NMR Spectrum of the Polycarbonate Derived from Bis(4-hydroxyphenyl)phenylphosphine Oxide (400 MHz,  $\text{CDCl}_3$ )



**Figure 3:** Thermogravimetric Analysis for the Homo-polycarbonate Derived from Bis(4-hydroxyphenyl)phenylphosphine Oxide (Air Atmosphere,  $10^\circ\text{C}/\text{min}$ )

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.

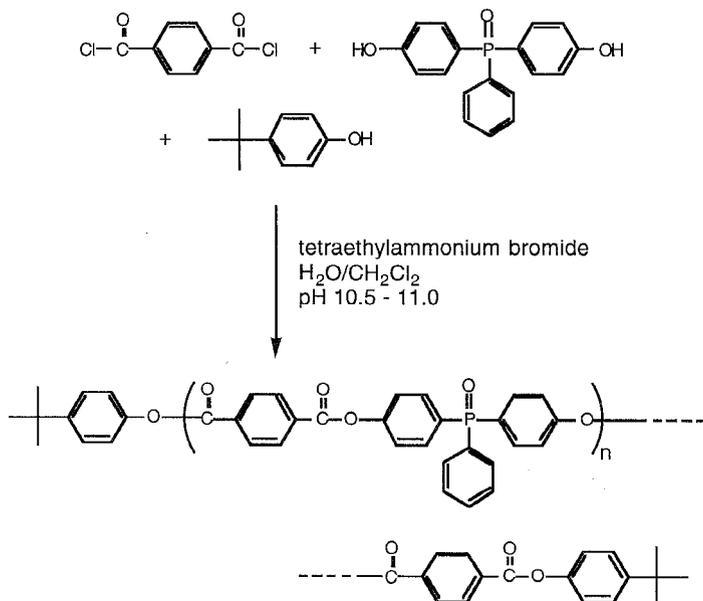
Although the exact nature of the gel was not determined, perhaps the tertiary phosphine dihalide was formed under the anhydrous conditions. Such linkages would be hydrolytically unstable, and could explain why the addition of water produced a solution.

### Synthesis and Characterization of a Phosphorus Containing Polyarylate

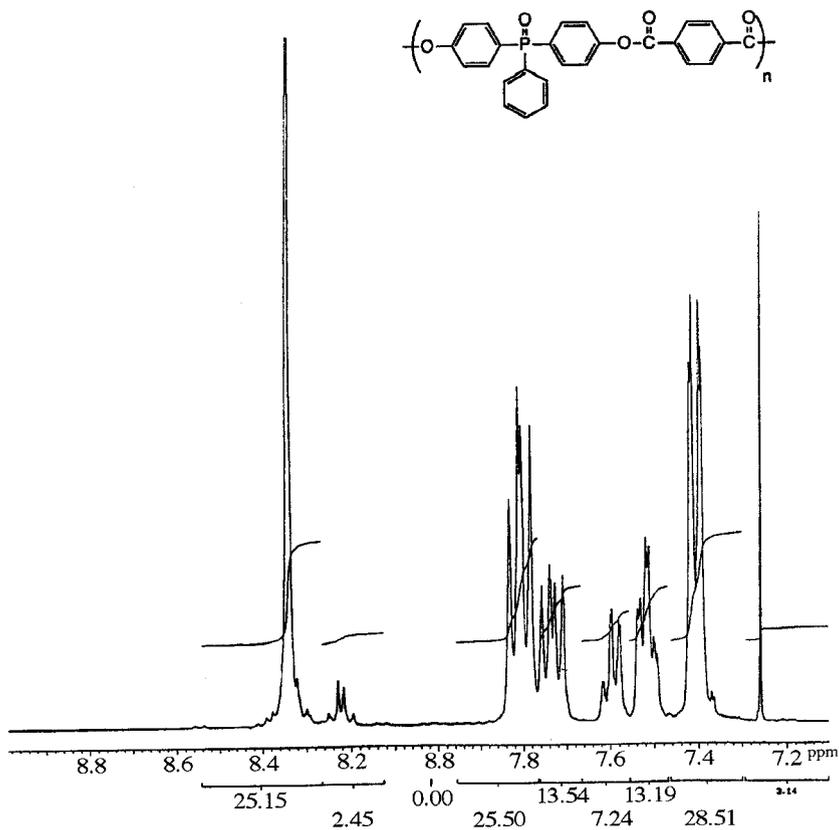
The polyarylate derived from bis(4-hydroxyphenyl) phenyl phosphine oxide and terephthaloyl chloride was synthesized by interfacial methods to determine if the monomer was of sufficient purity for the synthesis of high molecular weight material (Scheme 4). A highly viscous solution resulted and analysis after isolation of the polymer yielded an IV of 0.88 dl/g. A 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  $^1\text{H}$  and  $^{31}\text{P}$  NMR, DSC, and TGA. The NMR spectra are depicted in Figures 4, 5, and 6. Thermal analysis data for the polymer are tabulated in Table 1 and the dynamic TGA trace is depicted in Figure 6.

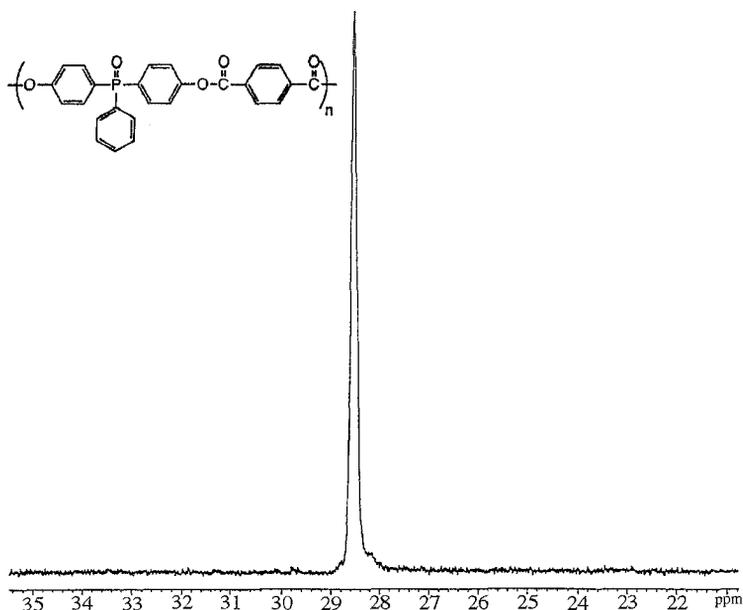
The homo-polyarylate obtained with this bisphenol monomer proceeds to high molecular weight and produced a tough polymer with good mechanical properties. The very high char yield at 800°C is very interesting indeed.



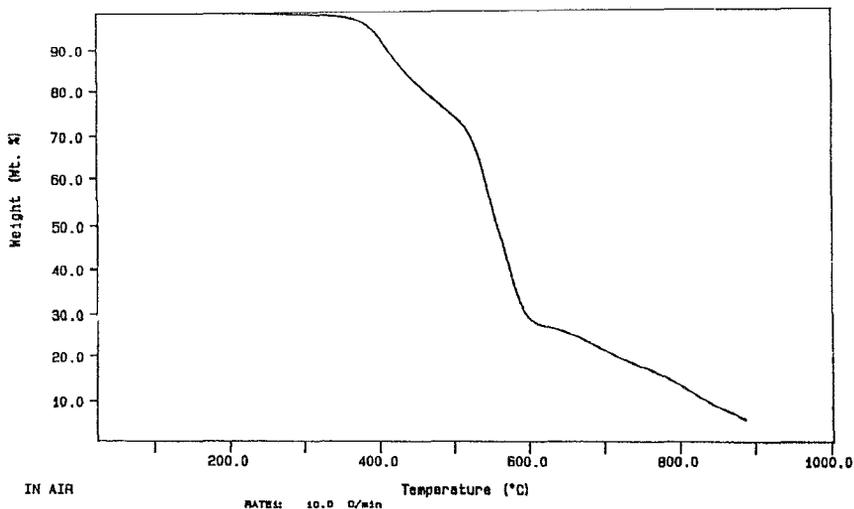
**Scheme 4:** Synthesis of a Phosphorus Containing Polyarylate



**Figure 4:**  $^1\text{H}$  NMR Spectrum for the Polyarylate Derived from Bis(4-hydroxyphenyl)phenylphosphine Oxide and Terephthaloyl Chloride (400 MHz,  $\text{CDCl}_3$ )



**Figure 5:**  $^{31}\text{P}$  NMR Spectrum for the Polyarylate Derived from Bis(4-hydroxyphenyl)phenylphosphine Oxide and Terephthaloyl Chloride (400 MHz,  $\text{CDCl}_3$ )



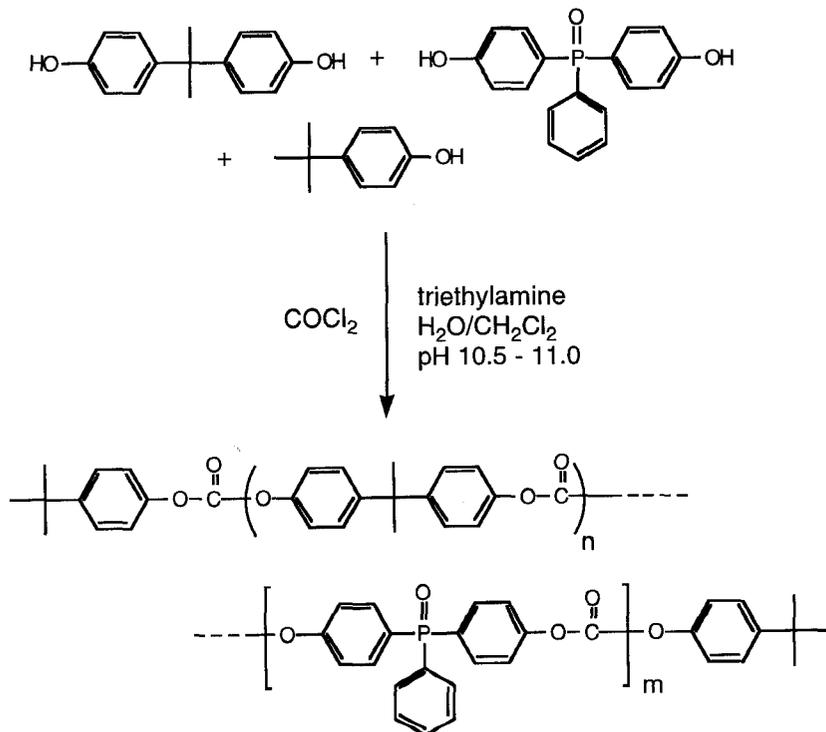
**Figure 6:** Thermogravimetric Analysis for the Polyarylate Derived from Bis(4-hydroxyphenyl)phenylphosphine Oxide and Terephthaloyl Chloride (Air Atmosphere,  $10^\circ\text{C}/\text{min}$ )

**Table 1:** Thermal Analysis Data for Phosphorus Containing Polyarylates

T <sub>g</sub> (°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 phosphene 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 (Scheme 5). Bisphenol A polycarbonate homopolymers with triphenylphosphine oxide termination were also synthesized by the substitution of 4-hydroxyphenyldiphenylphosphine oxide for 4-*t*-butylphenol.

**Scheme 5:** Synthesis of Phosphorus Containing Copolycarbonates

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## 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  $^1\text{H}$  NMR. (Table 2). The molecular weight and end groups were controlled by the addition of a monofunctional phenol, either 4-*t*-butylphenol or 4-hydroxyphenyldiphenylphosphine 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 2:** Characterization of Phosphorus Containing Copolycarbonates

Sample	Incorporation ( $^1\text{H}$ NMR) (wt. %)	Intrinsic Viscosity ( $\text{CHCl}_3$ ; 25° C) (dl/g)	T <sub>g</sub> (°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<sub>g</sub>'s of the copolymers were determined by DSC and are listed in Table 2. An analysis of the trend in copolymer T<sub>g</sub>'s as a function of the weight fraction predicts that the high molecular weight homopolymer should have a T<sub>g</sub> of about 224°C, as extrapolated from Figure 7.

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 8). 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.

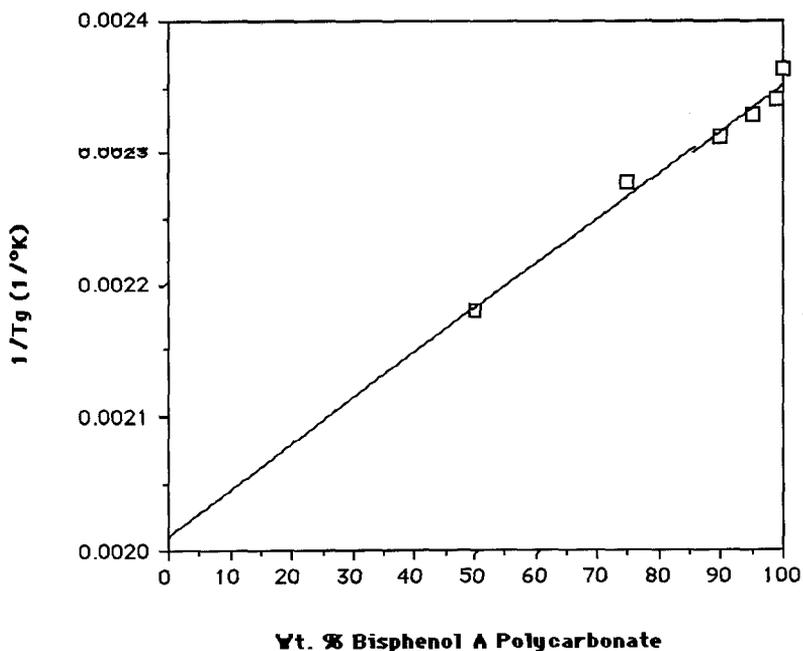


Figure 7: Linear Relationship of Copolymer Tg and Composition at 10°C/minute

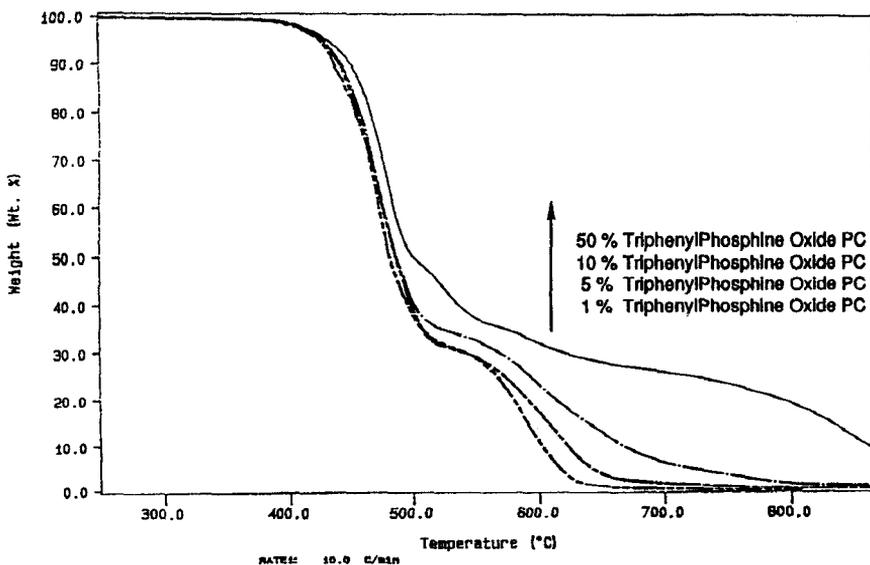
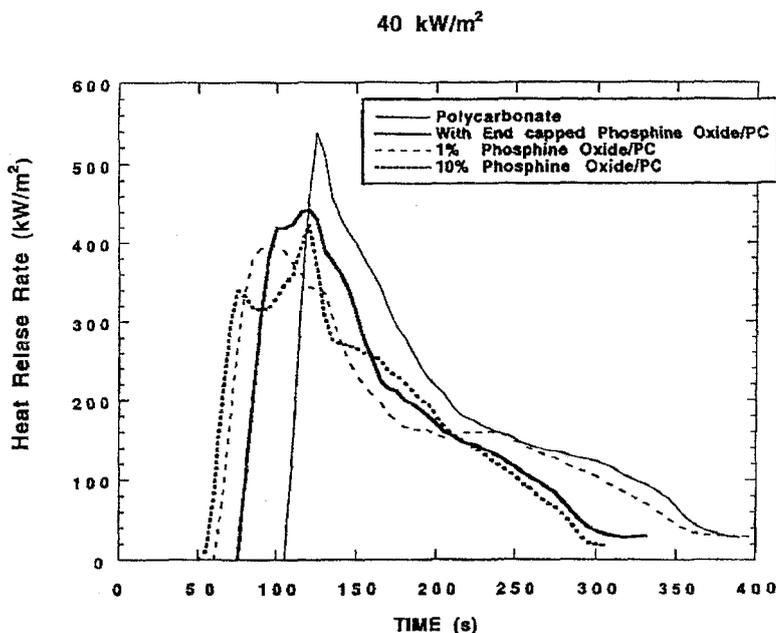


Figure 8: Thermogravimetric Analysis for Co-polycarbonates Derived from Bis(4-hydroxyphenyl) phenylphosphine Oxide and Bisphenol A (Air Atmosphere, 10°C/min)

The fire resistance of the novel copolymers has been preliminarily examined by cone calorimetry and results are graphically depicted in Figure 9. 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 9:** Cone Calorimetry Data for Phosphorus Containing Polycarbonates (10cm x 10cm x 0.3cm)

## Conclusions

Phosgenation of the bis(4-hydroxyphenyl) phenyl phosphine oxide only produced low molecular weight homopolymers under the conditions investigated. However, synthesis of a series of high molecular weight copolycarbonates with bisphenol A was successfully accomplished via interfacial polymerization. Moreover, high molecular weight poly (arylates) were prepared, which showed high char yields. The copolymers were transparent, reasonably tough and were found to have high char yields and qualitatively good fire resistance. Initial results by cone calorimetry showed a decreased heat release rate and further suggest that these materials may have potential as flame retardants.

## Current and Future Studies

Additional studies are in progress to further confirm and expand the results herein.

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## References

1. E. D. Weil in, *Handbook of Organophosphorus Chemistry*, R. Engel, Ed., 1992, chapter 14.
2. Y. N. Lin, S. Joardar and J. E. McGrath, *Polym. Prepr.*, **34**(1), 515, 1993.
3. C. D. Smith, H. J. Grubbs, H. F. Webster, A. Gungor, J. P. Wightman and J. E. McGrath, *High Performance Polym.*, **4**, 211, 1991.
4. J. G. Smith Jr., J. W. Connell and P. M. Hergenrother, *Polym. Prepr.*, **33**(2), 24, 1992.
5. I-Y. Wan, D. B. Priddy, G. D. Lyle and J. E. McGrath, *Polym. Prepr.* **34**(1), 806, 1993.
6. S. Pak, G. D. Lyle, R. Mercier and J. E. McGrath, *Polymer*, **34**(4), 885, 1993.
7. Y. Delaviz, A. Gungor, J. E. McGrath and H. W. Gibson, *Polymer*, **34**(1), 210, 1993.
8. I-Y Wan, T. Kashiwagi, and J. E. McGrath, *Polymeric Materials: Science and Eng.*, **71**, 233, 1994.
9. D. Freitag, U. Grigo, P.R. Muller, W. Nouvertne, *Encyclopedia of Polymer Science and Engineering*; 2nd ed.; H.F. Mark, N.M. Bikales and C.G. Overberger, Ed.; John Wiley and Sons: New York, 1988; Vol. 11, pp 648-718.
10. P. Tacke, U. Westeppe, C. Casser, U. Leyer, and H. Waldmann, CA **119**(8), 73768s, 1992.
11. J. Green, CA **108**(20), 168658t, 1987.
12. M. Shinoki, T. Matsumoto, CA **108**(18), 151187r, 1987.
13. J. C. Williams, U. S. Patent 4,680,370 (to Dow Chemical Co.), 1987.
14. D. P. Braksmayer, U. S. Patent 4,556,698 (to FMC Corp.), 1985.
15. S. Hashimoto, I. Furukawa, T. Kondo, *J. Polym. Sci., Polym. Chem. Ed.*, **12**(10), 2357, 1974.
16. S. E. Bales, U. S. Patent 4,474,937 (to Dow Chemical Co.), 1984.
17. K. S. Kim, *J. Appl. Polym. Sci.*, **28**(7), 2439, 1983.
18. CA **94**(4) 16547, 1980.
19. F. Liberti, U. S. Patent 3,711,441 (to General Electric Co.), 1973.
20. C. A. Bialous and D. B. G. Jacquiss, CA **76**(6) 86580t, 1971.
21. G. S. Kolesnikov, O. V. Smirnova, and Sh. A. Samsoniya, CA **75**(8) 49698w, 1971.
22. H. Vernaleken in, *Interfacial Synthesis*, F. Millich and C. E. Carraher, Eds., 1977, chapter 13.
23. W. E. Parham and E. L. Anderson, *J. Am. Chem. Soc.*, **70**, 4187, 1948.
24. S. Srinivasan and J.E. McGrath, unpublished results.