

## Chapter 2

# Triarylphosphine Oxide Containing Nylon 6,6 Copolymers

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A hydrolytically stable triarylphosphine oxide containing dicarboxylic acid monomer, bis(4-carboxyphenyl) phenyl phosphine oxide  $P(O)(Ph)(C_6H_4COOH)_2$ , was synthesized via Friedel-Crafts reactions and chemically incorporated into the poly(hexamethylene adipamide) backbone to produce melt processible, improved flame-resistant copolymers. The content of triarylphosphine oxide comonomer in the melt synthesized copolymers was controlled from 0-30 mole%. The copolymers were crystallizable at 10 and 20 mole% incorporation of the phosphine oxide comonomer and produced tough solvent resistant films. The crystallinity was totally disrupted at 30 mole%, but the Tg values systematically increased from 58°C to 89°C. Dynamic TGA results in air at 10°C/minute showed that the char yield increased with phosphine oxide content. Cone calorimetric tests in a constant heat environment (40 kW/m<sup>2</sup>) were employed to investigate the fundamental flame retardancy behavior of the copolymers. Significantly depressed heat release rates were observed for the copolymers containing phosphine oxide, although carbon monoxide values appeared to increase. ESCA studies of the char show that the phosphorus surface concentration was significantly increased relative to copolymer composition. It was concluded that the triaryl phosphine oxide containing nylon 6,6 copolymers had improved flame resistance and that tough melt processible films and fibers could be produced from these modified polyamides.

Phosphorus compounds are known fire retardants (1-4), which are most commonly introduced to polymers as additives. Although economically attractive, phosphorus additives may detract from the polymers in terms of stability and performance. For example, the additives can potentially be extracted from the polymer matrix, especially in textile fiber applications (4). Such problems can be avoided by chemical incorporation of reactive phosphorus comonomers into the polymer

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backbone. It has been reported that phosphorus containing aliphatic diamines and dicarboxylic acids have been successfully incorporated into polyamides to improve flame resistance (5,6).

The utilization of triaryl phosphine oxide monomer in demonstrably high molecular weight homo- or co-polymeric 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 (7), poly(arylene ether)s (8-10), epoxies (11), polycarbonates (12) and polyamides (13, 14). 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 (10). 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. These initial results are provided in this paper.

## EXPERIMENTAL

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 sulfide 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 (BMPPPO) resulted.

The next step was to oxidize the methyl groups to carboxylic acid groups by using potassium permanganate (15). 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 (KMnO<sub>4</sub>) (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 KMnO<sub>4</sub> 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 KMnO<sub>4</sub> 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.

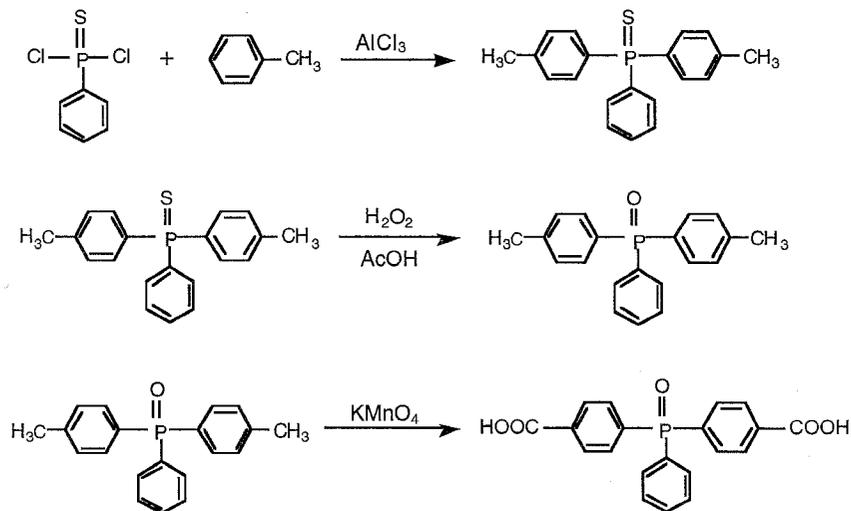
**Characterization:** The purity of the monomers were analyzed by <sup>1</sup>H and <sup>31</sup>P-NMR. Intrinsic viscosity values of the copolymers were determined in m-cresol at 25°C. Differential scanning calorimetry (DSC) and dynamic thermal gravimetric analysis (TGA) were performed by using Perkin-Elmer 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/m<sup>2</sup>. The sample used was a compression molded film with a size of 10cm x 10cm x 0.3cm.

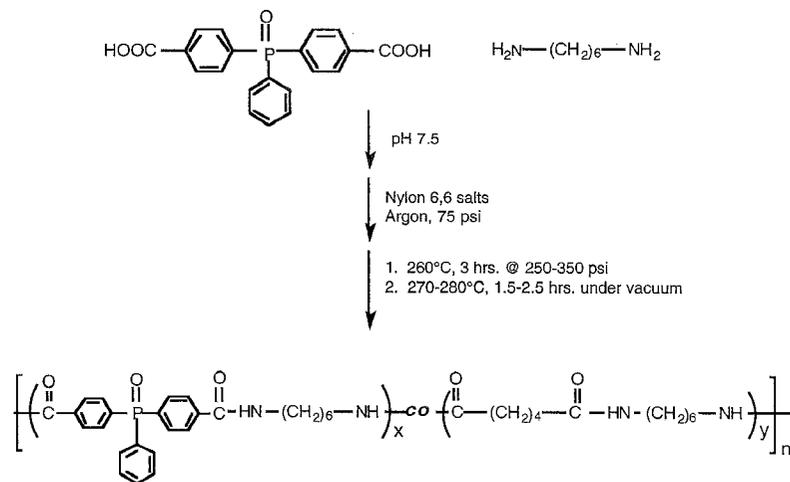
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## RESULTS AND DISCUSSION

The synthesis of the monomers and copolymers are described in Scheme 1 and 2, 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.



**Scheme 1** Synthesis of Bis(4-carboxyphenyl) Phenyl Phosphine Oxide



**Scheme 2** Synthesis of Triarylphosphine Oxide/Nylon 6,6 Copolymers

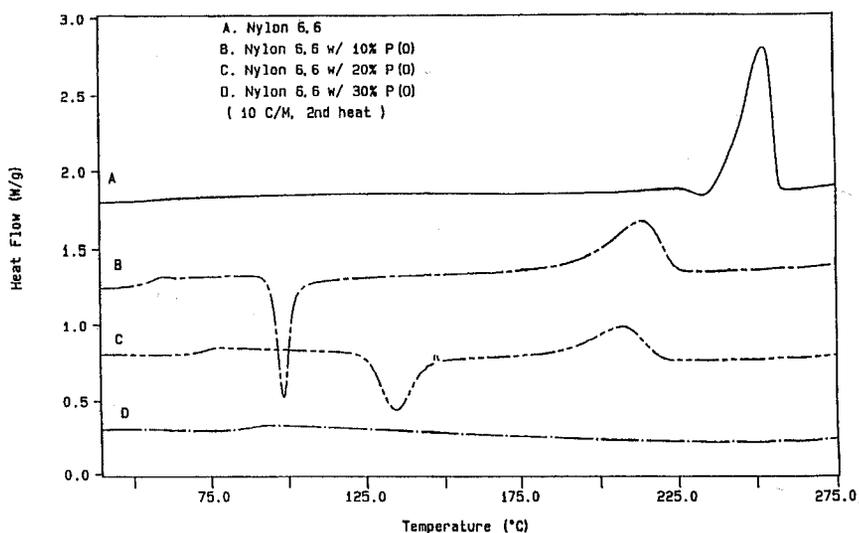
Characterization of the triarylphosphine oxide containing copolymers is summarized in Table 1. The intrinsic viscosity of the copolymers was measured in *m*-cresol at 25°C and the data suggested that the copolymers have relatively high molecular weights.

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

P(O)% in N66	$[\eta]^1$	T <sub>g</sub> <sup>2</sup> (°C)	T <sub>m</sub> <sup>3</sup> (°C)	TGA <sup>3</sup> (°C)	Char % (750°C)	T <sub>g</sub> <sup>4</sup> (°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	--

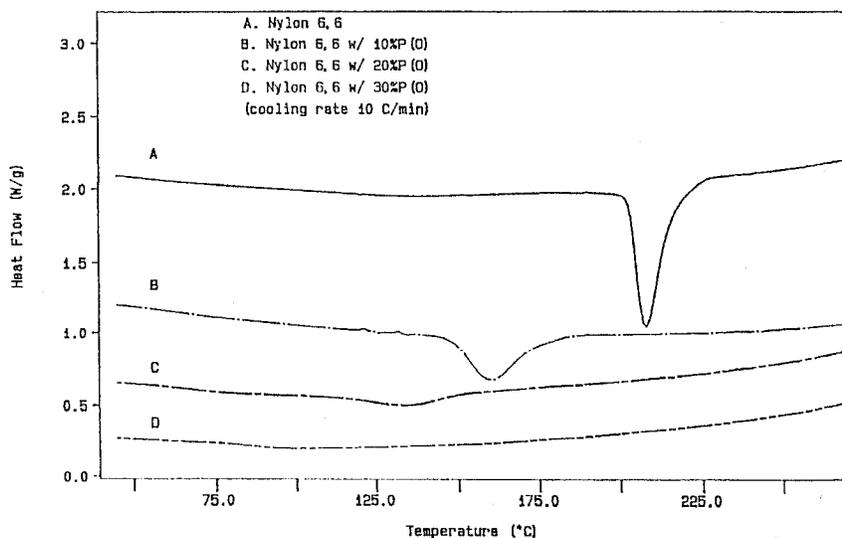
Note: 1. In *m*-cresol at 25°C  
 2. DSC, 10°C/minute  
 3. Air, 10°C/minute  
 4. DMA, Loss Maxima

As shown in Table 1 and in the DSC thermograms (Figure 1), 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



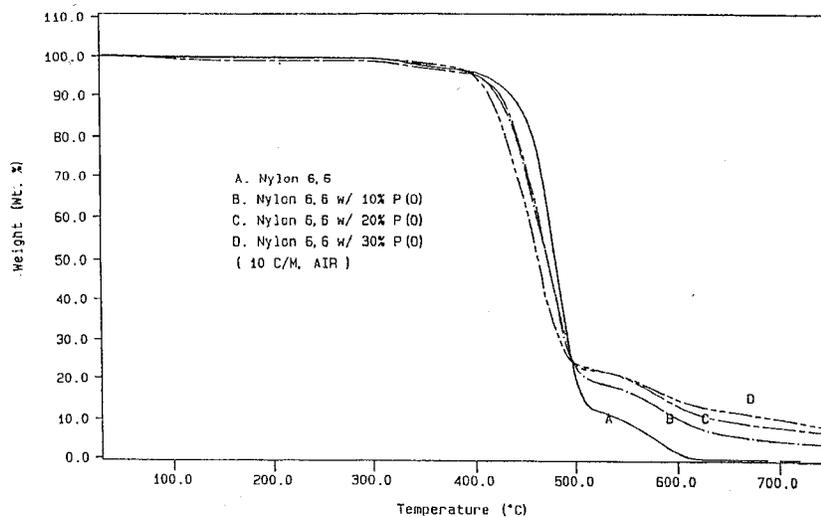
**Figure 1** DSC of triarylphosphine oxide containing nylon 6,6 copolymers (heating curves)

crystallizable nature of the 0-20 mole% copolymers can also be seen from the DSC thermograms on cooling (Figure 2). 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 2) and the crystal melting temperature (T<sub>m</sub>) is depressed (Figure 1), as expected.



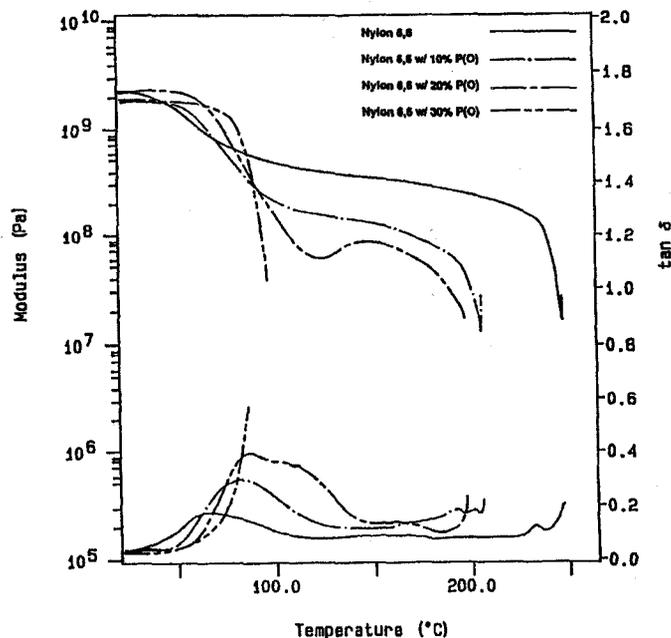
**Figure 2** DSC of triarylphosphine oxide containing nylon 6,6 copolymers (cooling curves)

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 3). The char yield in air is generally considered to strongly correlate with the flame retardancy of the material.



**Figure 3** Dynamic TGA of triarylphosphine oxide containing nylon 6,6 copolymers in air

The DMA traces (Figure 4), 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 4** 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 5). However, both the heat release rate and heat of combustion of the copolymers were significantly reduced compared to nylon 6,6 (Figure 6,7). 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 8,9). The phosphine oxide moiety may act as a flame retardant in both the condensed and gas phase. ESCA results (Figure 10a & 10b), 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 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 results (16) and Grubbs et al. by pyrolysis GC-MS data (17) of triarylphosphine oxide containing poly(arylene ethers). They found that the most of the phosphorus content stayed in

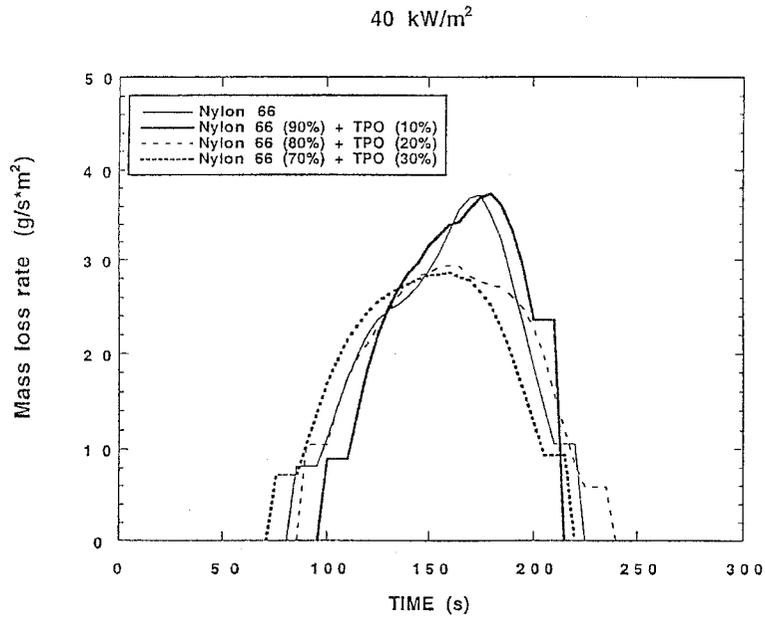


Figure 5 Weight loss versus time of triarylphosphine oxide containing nylon 6,6 copolymers at 40 kW/m<sup>2</sup>

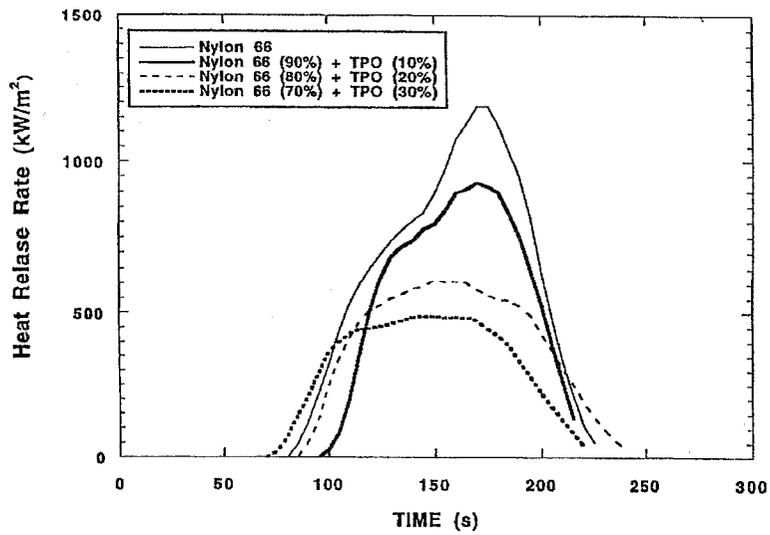


Figure 6 Heat release rate of triarylphosphine oxide containing nylon 6,6 copolymers

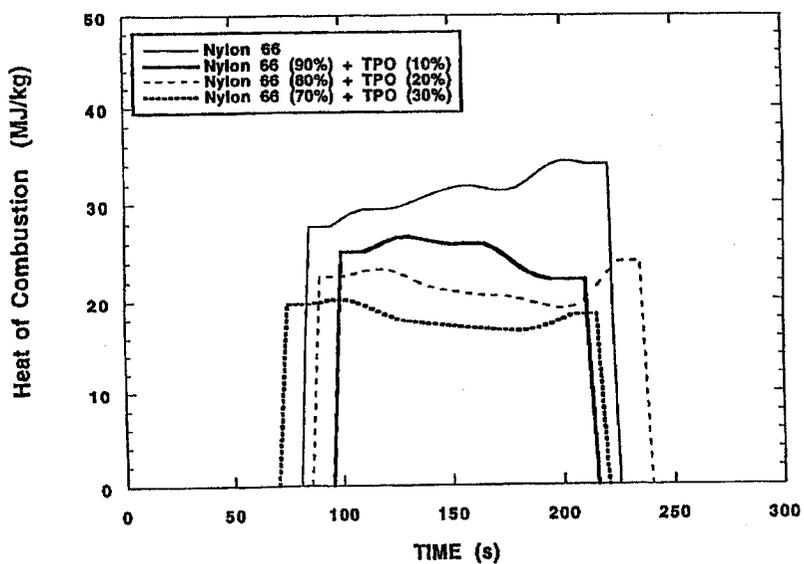


Figure 7 Heat of combustion of triarylphosphine oxide containing nylon 6,6 copolymers

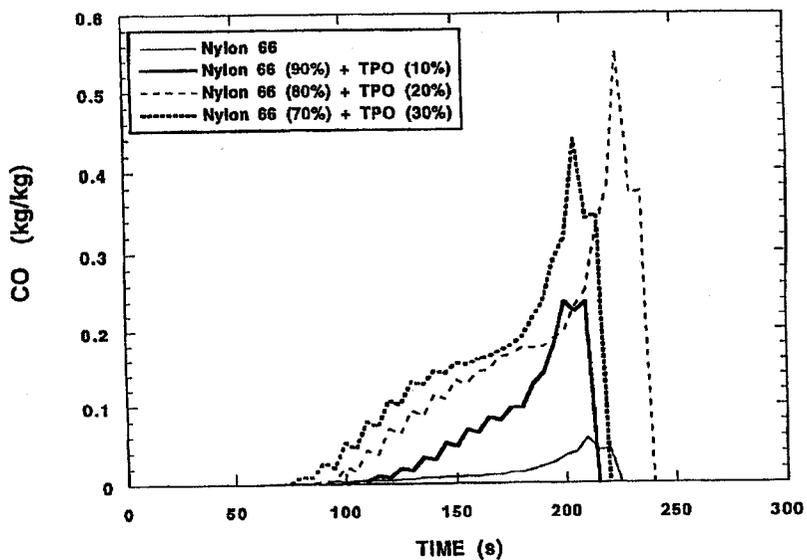
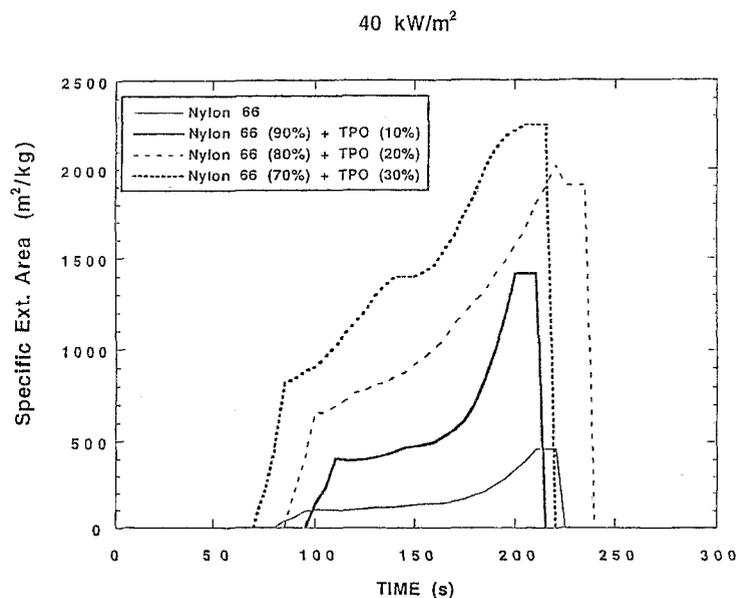


Figure 8 Carbon monoxide generation from the incomplete combustion of phosphine oxide containing nylon 6,6 copolymers

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.

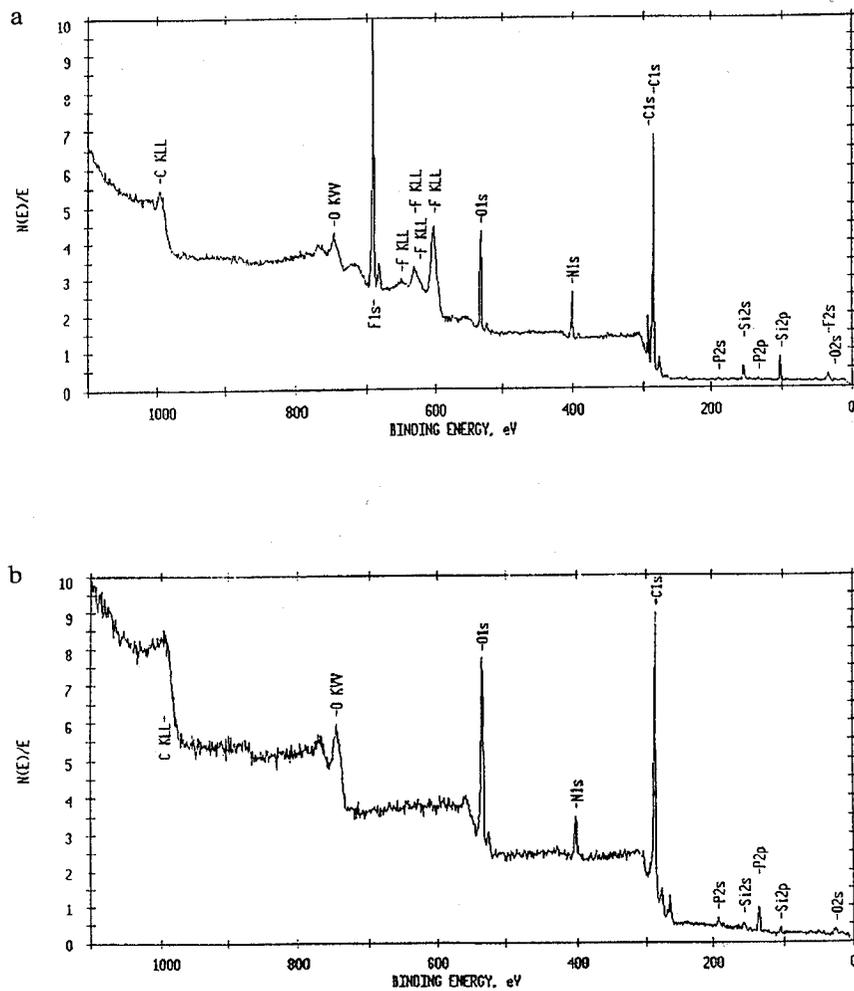


**Figure 9** Specific extinction area of triarylphosphine oxide containing nylon 6,6 copolymers

## CONCLUSIONS

Crystallizable triaryl phosphine oxide containing nylon 6,6 copolymers were successfully synthesized via melt polymerization in relatively high molecular weights at 10 or 20 mole%. Dynamic TGA results in air showed that the char yield increased with phosphine oxide content. Crystallinity was totally disrupted at 30 mole% incorporation, but the  $T_g$  values were systematically increased from 58°C to 89°C.

Cone calorimetric tests on the phosphorus containing polyamide copolymers exhibited significantly depressed heat release rates and heat of combustion. This property is very desirable and suggests that the copolymers are flame resistant



**Figure 10** ESCA of 20% triarylphosphine oxide containing nylon 6,6 copolymers: a.) room temperature b.) exposed in air at 540°C for 5 minutes

materials. On the other hand, initial results showed that the "soot" and carbon monoxide generated may be increased. ESCA results show that the phosphorus on the surface of the char is significantly increased.

#### ACKNOWLEDGMENTS

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