

# Synthesis, Thermal Properties, and Flame Retardancy of Phosphorus Containing Polyimides

YING-LING, LIU,<sup>1</sup> GING-HO HSIUE,<sup>1,2</sup> CHIH-WEIN LAN,<sup>1</sup> JEN-KWAN KUO,<sup>1</sup> RU-JONG JENG,<sup>2</sup> YIE-SHUN CHIU<sup>3</sup>

<sup>1</sup>Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan, Republic of China

<sup>2</sup>Department of Chemical Engineering, National Chung Hsing University, Taichung, Taiwan, Republic of China

<sup>3</sup>Chung-San Institute of Science and Technology, Lungtan, Taoyuan, Taiwan, Republic of China

Received 5 January 1996; accepted 31 May 1996

**ABSTRACT:** Phosphorus containing polyimides were prepared via phosphorylation of organosoluble polyimides. This was achieved by phenoxaphosphine oxide ring formation reaction or esterification with diethylchlorophosphate. The phosphorylation was confirmed by infrared, <sup>31</sup>P nuclear magnetic resonance, and elemental analysis for phosphorus. Polyimides containing phosphorus of 8.3 and 5.4% by weight were found. Thermal characteristics and decomposition behavior of the resulting polyimides were investigated by differential scanning calorimetry and thermogravimetric analysis. Introduction of phosphorus into polyimides slightly reduced their initial weight loss temperatures and led to high char yields at temperatures higher than 800°C. Limiting oxygen index values higher than 48 were found for the phosphorylated polyimides. Such properties make these polymers useful in flame retardant applications. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 875–882, 1997

**Key words:** polyimide; phosphorus; flame retardant; limiting oxygen index

## INTRODUCTION

Polyimides exhibit good thermal and oxidative stability as well as excellent mechanical properties. These outstanding characteristics make polyimides widely applicable in various fields, for example, in their use as matrix resins, adhesives, and coatings in the electronic industries in terms of high-performance application.<sup>1–4</sup> However, intractability of polyimides, such as insolubility in most organic solvents and poor processibility, still restrict their widespread applications. Therefore, much effort has been done to improve the polyim-

ides' intractability without sacrificing their high-temperature characteristics.<sup>5–9</sup> In addition to imparting solubility and processibility, phosphorus has been covalently incorporated into polyimides to bring about good fire resistance and ability to complex metals to the polyimides.<sup>10–14</sup> Furthermore, the solubility and processibility of the phosphorus-containing polyimides are also improved owing to the increase of the polymer's polarity.

One of the approaches to prepare phosphorus-containing polyimides was by means of copolymerization of difunctional phosphorus containing imido monomers with other common difunctional monomers.<sup>13–14</sup> Another approach was achieved via copolymerization of a difunctional bisimide monomer with a difunctional phosphorus containing monomer.<sup>10</sup> The rationale of the aforementioned approaches is to design and obtain a

---

Correspondence to: G.-H. Hsiue

Contract grant sponsor: National Science Council

Contract grant number: NSC-85-0210-D-007-020

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/070875-08

specific difunctional imido monomer and subsequently to copolymerize the imido monomer. Copolymerization would introduce different kind of linkages, such as esters and amides, into the resulting polyimide backbones. Recently, phosphorus containing diamine/dianhydrides were synthesized and utilized to form phosphorus containing polyimides.<sup>12</sup> This synthetic route avoided incorporating different linkages in the polyimides' backbones.

The above ways for phosphorylating polyimides, however, involved the shortcoming of complicated organic synthesis for obtaining the above-mentioned specific monomers. Furthermore, the introduction of different linkages, such as ester linkages, would reduce somewhat the mechanical property and thermal stability of polyimides. To avoid this shortcoming, a polymer reaction was utilized in this study to phosphorylate polyimides instead of copolymerization of phosphorus containing monomers. With respect to utilization in a polymer reaction, the organosoluble polyimides with high glass transition temperatures and good thermal stability were first synthesized. Two reactions were performed to phosphorylate the polyimides. A polyimide with phenylether groups was first phosphorylated via reacting with dichlorophenylphosphine to form phenoxaphosphine oxide rings in the polymer backbones, whereas the other polyimide with hydroxyl groups was phosphorylated via reacting with diethylchlorophosphate to form pendant phosphate ester groups. Both processes successfully resulted in phosphorus containing polyimides. Characterization, thermal properties, and flame retardance of these resulting polymers are discussed in the present work.

## EXPERIMENTAL

### Materials

Dichlorophenylphosphine (DCPP), diethylchlorophosphate (DECP), aluminum chloride, and copper(I) chloride from Aldrich Chem. Co. were used as received. Tetrahydrofuran (THF) was dried over sodium with benzophenone as an indicator and distilled prior to use. Triethyl amine (TEA) was dried over potassium hydroxide and distilled prior to use.

Polyimides (Fig. 1), with phenyl ether groups (PIA) or hydroxy groups (PIOH), were synthesized according to the literature.<sup>15-16</sup>

### Synthesis of Polyimide with Phenoxaphosphine Oxide Rings (PIA-PO)<sup>13,14,17-19</sup>

In a nitrogen atmosphere, 1 g of PIA, 10 g of dichlorophenylphosphine, and 1 g aluminum chloride were stirred at 130°C for 6 h. After cooling, the reaction mixture was poured into 400 g of crushed ice. The solid was filtered and washed with icy 10% sodium hydroxide aqueous solution and water. The product (PIA-P) was then dried under vacuum. PIA-P was then dissolved in THF and treated with aqueous H<sub>2</sub>O<sub>2</sub>. The product (PIA-PO) was obtained by reprecipitation from methanol.

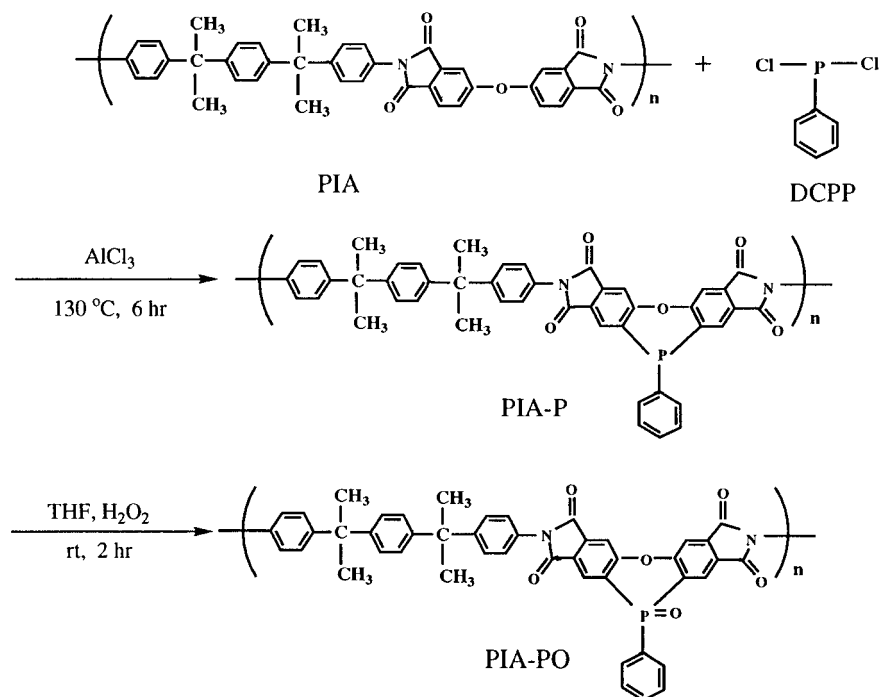
### Synthesis of Polyimide with Phosphate Groups (PIO-P)<sup>20-21</sup>

In a nitrogen atmosphere, 1 g of PIOH was dissolved in 30 mL of dry THF in a 150 mL round bottom flask fitted with a magnetic stirrer. Distilled dry TEA (3 mL) was added, and then the system was cooled to 0°C. After adding 0.1 g of Cu<sub>2</sub>Cl<sub>2</sub>, a solution of diethylchlorophosphate (3 g) in 20 mL THF was added dropwise over a period of 20 min. The reaction system was maintained at 0°C for 2 h and then kept at room temperature overnight. The precipitant was filtered and washed with THF. The filtrate was washed with 2% aqueous solution of NaOH. It was then concentrated and precipitated from methanol. The obtained product was dried under vacuum.

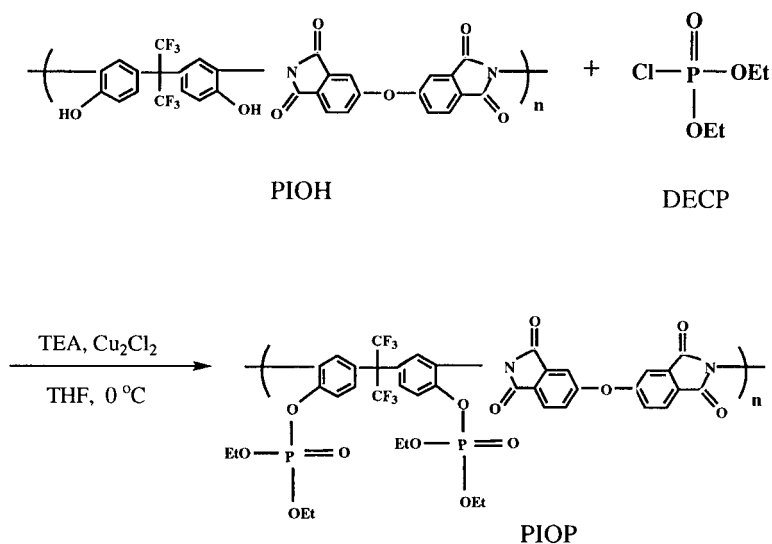
### Instrumental Analysis

Infrared (IR) spectra were obtained by using a Perkin-Elmer 842 infrared spectrophotometer. <sup>1</sup>H NMR (nuclear magnetic resonance) and <sup>31</sup>P NMR spectra were recorded with a Bruker MSL-300 (300 MHz) NMR spectrometer using CDCl<sub>3</sub> as a solvent. Differential scanning calorimeter (DSC) thermograms were recorded with a Seiko DSC 5200 at a heating rate of 10°C/min under nitrogen atmosphere. The phosphorus contents of the polymers were determined by a phosphorus elemental analysis via a micro digestion apparatus with a spectrophotometer. Thermogravimetric analysis (TGA) was performed by a DuPont 951 Thermogravimetric Analyzer at a heating rate of 10°C/

(A)



(B)



**Figure 1** Phosphorylation of (A) PIA and (B) PIOH.

min under nitrogen or air atmosphere. Limiting oxygen index (LOI) values were measured on a Stanton Redcroft flame meter by a modified method, as reported in the literature.<sup>22-23</sup> The percentage in the  $\text{O}_2\text{-N}_2$  mixture just sufficient to sustain the flame was taken as the LOI.

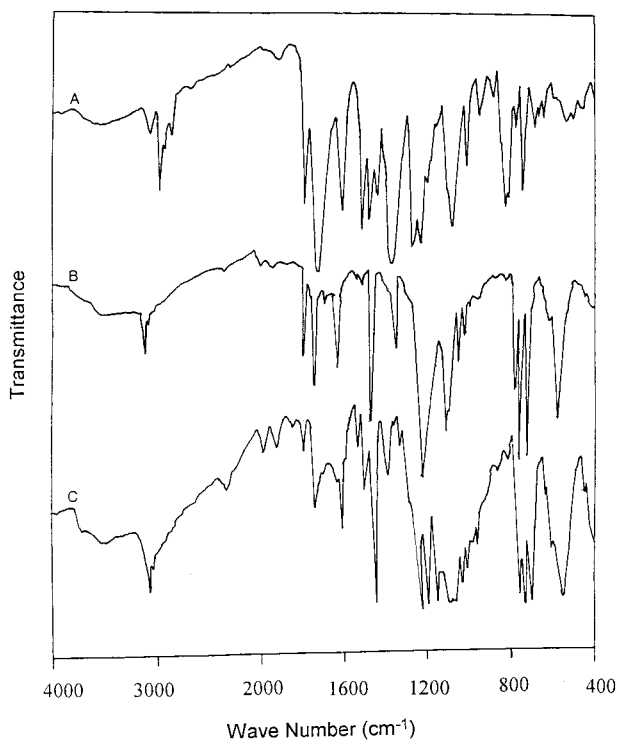
## RESULTS AND DISCUSSION

Polyimides (Table I) with phenyl ether groups/hydroxy groups were synthesized for further phosphorylation.<sup>15,16</sup> The reaction of phenyl ether and dichlorophenylphosphine was reported to

**Table I Polyimides Before and After Phosphorylation**

Polyimides	Molecular Weight ( $\bar{M}_w$ )	Glass Transition Temperature ( $^{\circ}\text{C}$ )	Phosphorus Content (wt %)
PIA	6950	205	0
PIA-PO	8350	240	8.3
PI-OH	7360	200	0
PI-OP	9860	187	5.8

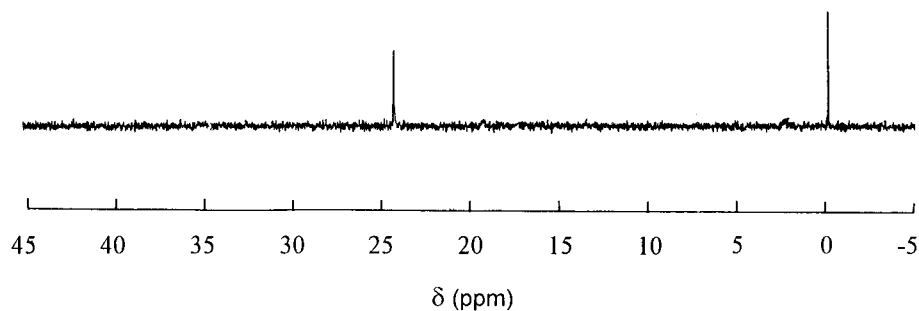
form phenoxaphosphine oxide rings with a high conversion.<sup>17-19</sup> Therefore, polyimide with phenyl ether groups (PIA) was phosphorylated by reacting with dichlorophenylphosphine [Fig. 1(a)]. Phenoxaphosphine rings were introduced into the polymer chains as a result. Furthermore, an oxidation was performed to introduce the phosphine oxide groups. Figure 2 shows the IR spectrum of the resulting phosphorylated polyimides. For PIA-P [Fig. 2(b)], the peaks at  $1435\text{ cm}^{-1}$  indicate the presence of P-Ph. This reveals the formation of phenoxaphosphine rings after the reaction. The absorption of Ph-O-Ph shifts from  $1165$  to  $1202\text{ cm}^{-1}$  after the phosphorylation.<sup>10,13,19</sup> Moreover,



**Figure 2** IR spectra of (A) PIA, (B) PIA-P, and (C) PIA-PO.

the characteristic absorptions attributed to imido carbonyl at  $1777$  and  $1723\text{ cm}^{-1}$ , and C—N of imide at  $1366\text{ cm}^{-1}$  are also observed.<sup>13</sup> The PIA-P was then oxidized to convert three-bonding phosphorus to five-bonding phosphorus, i.e., to introduce the P=O groups onto the polyimide. This oxidation was also confirmed by the IR spectrum. After oxidation, an absorption peak at  $1185\text{ cm}^{-1}$  corresponding to P=O absorption emerged, as shown in Figure 2(c). The introduction of phosphorus into the polyimide was then further confirmed by  $^{31}\text{P}$  NMR. Figure 3 shows the  $^{31}\text{P}$  NMR spectrum of PIA-PO. The peak at  $\delta = -0.48\text{ ppm}$  corresponds to the absorption of phenoxaphosphine oxide.<sup>24-25</sup> This confirms the formation of the phenoxaphosphine oxide rings after the reaction. However, another absorption peak at  $\delta = 24.04\text{ ppm}$  is also found. This absorption corresponds to the open-chained triphenylphosphine oxide,<sup>12,24</sup> therefore, implying that phosphorus was incorporated into polyimide PIA in the form of phenoxaphosphine oxide rings or triphenylphosphine oxide. The schematic for the formation of triphenylphosphine oxide is shown in Figure 4. However, cross-linking could occur via phenylphosphine formation between polymer chains. The solubility of PIA-PO in organic solvent was found to be poorer than that of PIA. This revealed somewhat the effect of the crosslinking structure of PIA-PO. Furthermore, the phosphorylation via formation of triphenylphosphine could also be read from the 8.3% phosphorus content of PIA-PO. The resulting PIA-PO should contain only 4.8% phosphorus if all phosphorus was incorporated onto the polyimide as phenoxaphosphine oxide rings. The proportions of these two types of phosphorus in the resulting polyimide determined via the peak integration of  $^{31}\text{P}$  NMR spectrum were found to be 59 and 41% for phenoxaphosphine oxide rings and triphenylphosphine, respectively.

Polyimide carrying hydroxyl pendant groups

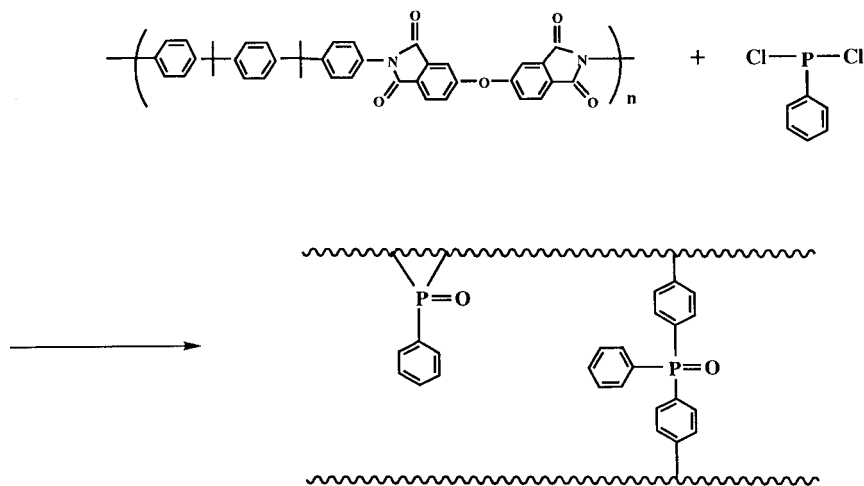


**Figure 3**  $^{31}\text{P}$  NMR spectrum of the phosphorylated PIA (PIA-PO).

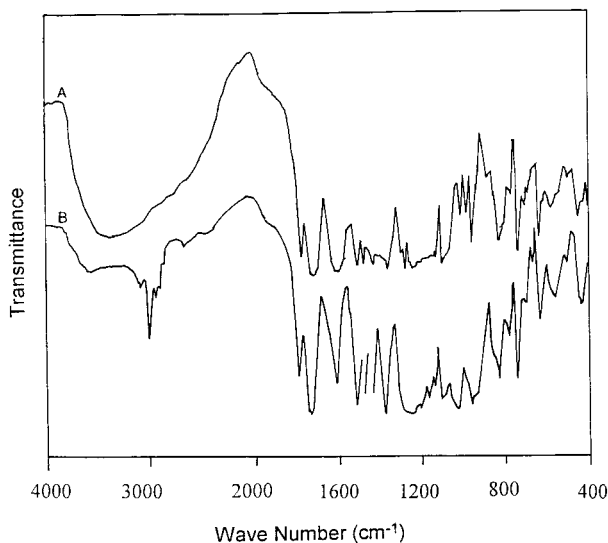
was phosphorylated via reacting with diethylchlorophosphate (DECP) [Fig. 1(b)]. DECP reacting with hydroxy groups to form phosphate groups has been reported to be with conversions higher than 95%.<sup>20–21</sup> This reaction was thus successfully performed in the present study for introducing phosphate groups into polyimides. Figure 5 shows the IR spectra of polyimides before (PIOH) and after (PIO-P) phosphorylation. The characteristic absorptions attributed from imido carbonyl at 1783 and 1720  $\text{cm}^{-1}$ , and C—N of imide at 1376  $\text{cm}^{-1}$  are observed for PIOH.<sup>13</sup> These characteristic absorption peaks of imido groups are also observed in the PIO-P spectrum. The Ph-OH absorption corresponding the broad peak at around 3200–3400  $\text{cm}^{-1}$  is eliminated after phosphorylation. Furthermore, some characteristic absorption at 1260  $\text{cm}^{-1}$  (—P=O), 1170 and 966  $\text{cm}^{-1}$  (—P—O—Ph), 1026  $\text{cm}^{-1}$  (—P—O—C), and

2987  $\text{cm}^{-1}$  (—CH<sub>3</sub>) are observed in PIO-P.<sup>21</sup> This reveals the formation of phosphate structure and subsequently confirms the phosphorylation of polyimide PIOH. The incorporation of phosphorus into PIOH was also examined by  $^{31}\text{P}$  NMR. Figure 6 shows the  $^{31}\text{P}$  NMR spectrum of PIO-P. A single peak of  $\delta = -5.20$  ppm was found.<sup>21,24–25</sup> The phosphorus absorption in  $^{31}\text{P}$  NMR analysis confirms the phosphorylation of the polyimide PIOH.

The glass transition temperatures ( $T_g$ ) of the polyimides were studied by DSC. PIA showed a  $T_g$  at around 205°C. The corresponding phosphorylated PIA-PO showed a  $T_g$  as high as 240°C. The high  $T_g$  for PIA-OP might result from the formation of additional phenoxaphosphine ring structure. Furthermore, formation of phosphine oxide structure could lead to a somewhat crosslinked structure, therefore, to increase the  $T_g$  of the polyimide. For PI-OH and PI-OP,  $T_g$ s of 200 and 187°C



**Figure 4** Cross-linking reaction in the phosphorylation of PIA.



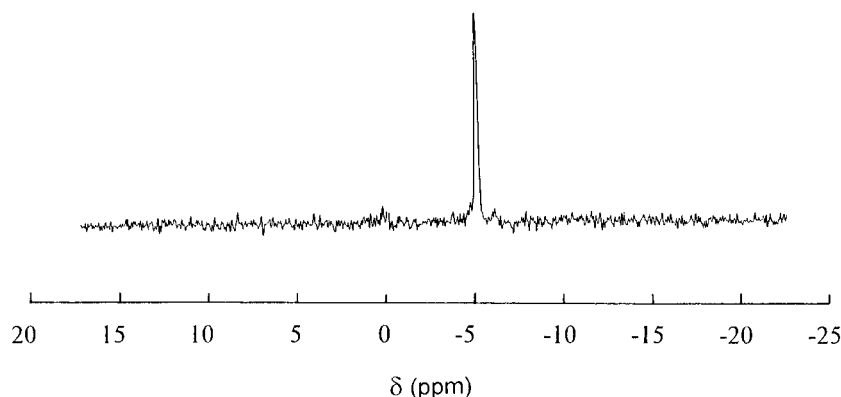
**Figure 5** IR spectra of (A) PIOH and (B) PIOP.

were found, respectively. It is noteworthy that the  $T_g$  of PI-OP was lower than that of PI-OH. The decrease in  $T_g$  should be due to the elimination of hydroxyl groups of PI-OH after phosphorylation. This elimination of hydroxyl groups decreased the density of hydrogen bonding and subsequently lowered the glass transition temperature of the polymer. The same phenomenon was also observed in phosphorylation of hydroxy containing polystyrene.<sup>21</sup>

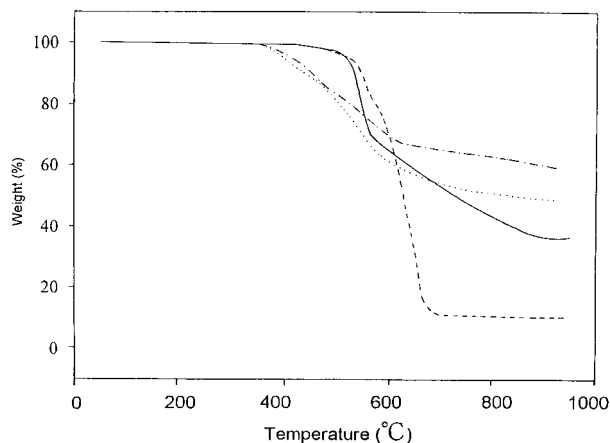
The TGA thermograms of PIA and PIA-PO are shown in Figure 7. PIA shows 1% weight loss at around 550°C (Table II). On the other hand, PIA-OP began to lose its weight at about 420°C. The decomposition temperature of PIA-OP is in good agreement with the decomposition temperatures

of other reported phenoxaphosine oxide rings containing polymers.<sup>18</sup> In spite of the fact that the introduction of phosphorus slightly reduced the thermal stability of the polyimide, PIA-OP still exhibits relatively good stability in heat resistance at temperatures lower than 420°C. While beginning to lose weight, PIA exhibited a rapid weight loss behavior under nitrogen or air. This rapid weight loss process was not observed in the PIA-OP thermograms. The weight loss of PIA-OP began at about 420°C and then gradually proceeded as temperature increased. The disappearance of rapid weight loss in TGA thermograms was also observed in other phenoxaphosphine oxide rings containing polymers.<sup>13,14,17</sup> This is different from the weight loss behavior of other open-chain phosphorus containing polymers. In other words, the polyimide containing phenoxaphosine rings is more thermally stable than the polyimide containing open-chain phosphorus. Further discussion related to the thermal behavior of PI-OP. PI-OP is an open-chain phosphorus containing polyimide. In the TGA thermograms of PI-OP (Fig. 8), rapid weight loss was observed both under nitrogen and air. Furthermore, the 1% weight loss occurred at about 220°C for PI-OP. This decomposition temperature was much lower than that of PIOH, whose 1% weight loss was observed at 408°C. It is evident that open-chain phosphorus containing polyimides are not as thermally stable as polyimides containing phenoxaphosphine rings.

In Figure 8, the first stage of weight loss might result from the decomposition of the pendant phosphate groups. The weight loss temperature of 284°C was almost of the same as the pendant phosphate decomposition temperature (280–



**Figure 6**  $^{31}\text{P}$  NMR spectrum of PIOP.



**Figure 7** TGA thermograms of PIA in N<sub>2</sub> (—), PIA in air (---), PIA-PO in N<sub>2</sub> (-·-), and PIA-OP in air (·····).

289°C) for polystyrene containing phosphate pendant groups.<sup>21</sup> The second stage of weight loss at 576°C involved the decomposition of the polyimide backbones. This high backbone decomposition temperature revealed that the phosphate pendant groups do not reduce the heat resistance of the polyimide. This phenomenon was also observed for the phosphorylated polystyrene.<sup>21</sup> On the other hand, polyimides containing phosphate in backbones were reported to exhibit a 10% weight loss at around 445°C.<sup>10</sup> Phosphate groups became more thermally stable while being incorporated into the polymer backbones.

The flame retardant properties of the phosphorus containing polyimides were studied in terms of char yields and LOI values (Table II). For PIA, the char yields at 800°C were 40 and 14% under nitrogen and air, respectively. The phosphorylated PIA-PO showed char yields of 54 and 68% under nitrogen and air, respectively. For PI-OH, after phosphorylation the char yields raised from

38 to 54% and from 16 to 31% under nitrogen and air, respectively. It has been reported that the weight of thermal residue up to 700°C is related to flame retardance.<sup>26</sup> The above-mentioned high char yields of PIA-PO and PI-OP imply that these polyimides are effective in flame retardancy. Furthermore, the flame retardance of the phosphorylated polyimides was evaluated by measuring the LOI values. LOI values of PIA-PO and PI-OP were found to be 52 and 48, respectively. These values are larger when compared to those of other reported phosphorus containing polyimides.<sup>10-13</sup>

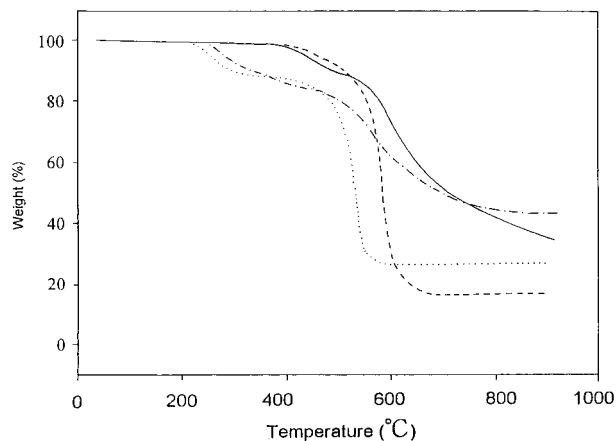
The phosphorus contents of polymers play an important role in flame retardance.<sup>18,21</sup> It is noteworthy that the phosphorus content of PIA-PO was almost double to that of PI-OP. However, the LOI values of both were similar. This could be understood by the synergistic effect of phosphorus and halogen (fluorine). The LOI values of the halogen containing phosphorylated polyester were reported to be greater than those of the halogen-free polyesters.<sup>18</sup>

## CONCLUSION

Phosphorus containing groups were introduced into polyimides via polymer modification. Polyimides bearing phenoxaphosphine oxide rings or pendant phosphate groups units were obtained. The introduction of phosphorus containing groups was found to slightly reduce the thermal stability of the polyimides and conspicuously increase their flame retardance. High char yields and LOI values confirmed the flame retardation of the polyimides via phosphorylation. The synergistic effects on flame retardance of phosphorus-nitrogen and phosphorus-halogen were found.

**Table II** Thermogravimetric Data and LOI Values of the Polyimides

Polyimides	Specific Temperatures of Weight Loss (°C)						Char% at 800°C		LOI
	1% Weight Loss		Rapid Weight Loss				Air	N <sub>2</sub>	
	Air	N <sub>2</sub>	Air		N <sub>2</sub>				
PIA	490	490	558	650	550	705	14	44	33
PIA-PO	325	330	504	705	560	—	54	68	52
PI-OH	402	408	433	610	450	590	16	36	32
PI-OP	221	225	284	537	301	576	31	51	48



**Figure 8** TGA thermograms of PIOH in N<sub>2</sub> (—), PIOH in air (---), PIOP in N<sub>2</sub> (- · -), and PIOP in air (·····).

## REFERENCES

1. C. E. Sroog, *J. Polym. Sci., Makromol. Rev.*, **11**, 161 (1976).
2. *Polyimides: Materials, Chemistry, and Characterization*, C. Feger, M. Khojasteh, and J. E. McGrath, Eds., Elsevier, London, 1989.
3. *Polyimides*, D. Wilson, P. Hergenrother, and H. Stenzenberger, Eds., Chapman and Hall, New York, 1990.
4. *Polyimides*, K. L. Mittal, Ed., Plenum Press, New York, 1984.
5. S. Maiti and B. Mandal, *Prog. Polym. Sci.*, **12**, 111 (1986).
6. S. Maiti and S. Das, *J. Appl. Polym. Sci.*, **26**, 957 (1981).
7. S. Maiti and A. Ray, *Makromol. Chem.*, **183**, 2949 (1982).
8. L. W. Frost and I. Kessa, *J. Appl. Polym. Sci.*, **8**, 1039 (1964).
9. J. P. Critchley and M. A. White, *J. Polym. Sci., Polym. Chem.*, **10**, 1809 (1972).
10. S. Banerjee, S. K. Palit, and S. Maiti, *J. Polym. Sci., Polym. Chem.*, **32**, 219 (1994).
11. S. Maiti, S. Banerjee, and S. K. Palit, *Prog. Polym. Sci.*, **18**, 227 (1993).
12. M. E. Martinez-Nunez, V. N. Sekharipuram, and J. E. McGrath, *Polym. Prepr.*, **35**, 709 (1994).
13. M. Sato, Y. Tada, and M. Yokoyama, *Eur. Polym. J.*, **16**, 671 (1980).
14. M. Sato, Y. Tada, and M. Yokoyama, *J. Polym. Sci., Polym. Chem.*, **19**, 1039 (1981).
15. G. H. Hsiue, J. K. Kuo, R. J. Jeng, T. H. Suen, R. J. Lee, J. T. Shy, and Y. L. Liu, *Mol. Cry. Liq. Cry., Sci. Tech., Sec. B: Nonlin. Optics*, **15**, 367 (1996).
16. P. Lakshmanan, S. Srinivasan, T. Moy, and J. E. McGrath, *Polym. Prepr.*, **34**(1), 707 (1993).
17. M. Sato and M. Yokoyama, *Eur. Polym. J.*, **15**, 733 (1979).
18. M. Sato and M. Yokoyama, *Eur. Polym. J.*, **15**, 75 (1979).
19. I. Ganath, A. Kalir, and I. Z. Pelah, *Isr. J. Chem.*, **6**, 651 (1968).
20. C. P. R. Nair, G. Glouet, and J. Brossas, *J. Polym. Sci., Polym. Chem.*, **26**, 1791 (1988).
21. Y. L. Liu, G. H. Hsiue, Y. S. Chiu, R. J. Jeng, and C. Ma, *J. Appl. Polym. Sci.*, **59**, 1619 (1996).
22. C. P. R. Nair, G. Glouet, and Y. Guilbert, *Poly. Deg. Stab.*, **26**, 305 (1989).
23. Y. L. Liu, G. H. Hsiue, Y. S. Chiu, R. J. Jeng, and L. H. Perng, *J. Appl. Polym. Sci.*, **61**, 613 (1996).
24. *Phosphorous-31 NMR; Principles and Applications*, D. G. Gorenstein, Ed., Academic Press, New York, 1984.
25. J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956).
26. D. W. van Krevelen, *Polymer*, **16**, 615 (1975).