

# Preparation of Phosphorus-Containing Polymers.

## XXVIII. Synthesis and Flame Resistance of Phenoxaphosphine-Containing Copolyesters

MORIYUKI SATO, HITOSHI KONDO, and MASAACKI YOKOYAMA,  
*Department of Industrial Chemistry, Kogakuin University, Nishishinjuku,  
Shinjuku-ku, Tokyo 160, Japan*

### Synopsis

Copolyesters containing phenoxaphosphine rings were prepared from 2,8-dichloroformyl-10-phenylphenoxaphosphine 10-oxide and isophthaloyl chloride and three bisphenols (bisphenol A, tetrabromobisphenol A, and tetrachlorobisphenol A) by interfacial polycondensation, and the flame resistance of the resulting copolyesters was investigated by measuring limiting oxygen index (LOI) values. Most of the copolyesters had good solubilities in *N*-methyl-2-pyrrolidone and chloroform and gave the films from the chloroform solutions. The relationship between the melting temperature of copolyesters and phenoxaphosphine content held for the Flory's equation for random copolymers over 20–30% of phenoxaphosphine content. The halogen-free copolyesters with phenoxaphosphine rings showed not only good thermostability but also good flame resistance. In contrast with these copolymers the halogen-containing copolyesters with phenoxaphosphine rings had very high LOI values and exhibited excellent flame-retardant property, but their thermostability was poor and the copolymers began to decompose at lower temperatures in comparison with the halogen-free copolyesters. The mode of action of the halogen-free copolyesters containing phenoxaphosphine rings was based on the effect of phosphorus in the solid phase, whereas the action of the copolyesters with both halogen and phenoxaphosphine ring was due to the additive effect of the solid-phase and the gas-phase mechanisms.

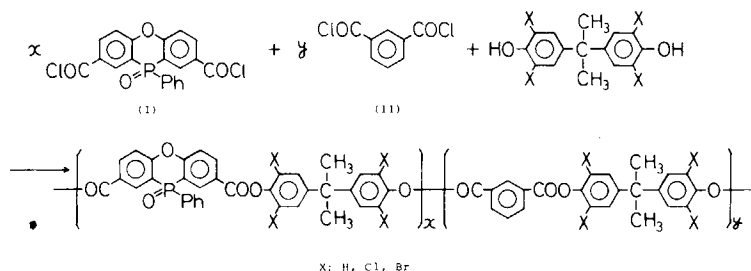
### INTRODUCTION

Phosphorus-containing polymers are known to have flame-retardant property.<sup>1</sup> Most of them have a single-strand backbone and decompose at lower temperatures compared with analogous phosphorus-free polymers. It would be difficult to impart both flame- and heat-resistant properties to the phosphorus-containing single-strand polymers. On the other hand, double-strand polymers composed of heterocyclic units such as polyimides and polybenzimidazoles, which have high thermostability, have already been reported to show good flame resistance, and their limiting oxygen index (LOI) values are over 40.0.<sup>2</sup> It had been expected that double-strand phosphorus-containing polymers with phenoxaphosphine rings, which are tricyclic fused compounds having carbon-phosphorus bonds, had both good thermal and flame-resistant properties. We prepared a series of phenoxaphosphine-containing polymers and disclosed the properties.<sup>3–9</sup> The polymers exhibited good resistance to heat and combustion. Of these phenoxaphosphine-containing polymers, the polyester derived from bisphenol A showed the LOI value of 46.0.<sup>10</sup> This value is much higher than those of polybisphenol isophthalate and polybisphenol terephthalate (LOI = 25.5)<sup>11</sup> and also higher even in comparison with poly(vinyl chloride) or polyimide (LOI = 42.0) which are commercially used for fire-proofing materials.

The mode of action of phosphorus-containing flame retardants is still a subject of debate. The compounds are shown to act either in the solid phase or the gas phase to reduce the flammability.<sup>12</sup> Deshpande et al.<sup>13</sup> showed that modified polyethylene terephthalate (PET) with phosphorus in the main chain afforded a higher LOI than PET blended volatile organophosphorus additives such as triphenylphosphine oxide and concluded that in these kinds of phosphorus-containing polymers the solid phase mechanism was more effective than the gas phase mechanism.

Halogen-containing polymers are also known to show flame resistance and have been prepared by many researchers.<sup>14-17</sup> Avondo et al.<sup>18</sup> have investigated the modes of action of halogen and/or phosphorus and disclosed that halogen is released in the gas phase to retard the flame, whereas phosphorus accelerates the char formation to increase the aromaticity in the residue. Coexistence of both phosphorus and halogen might enhance the resistance of polymers to combustion, and excellent flame-retardant property of polymers could be observed. The flame retardance based on both phosphorus and halogen can be explained from the combined or additive effect of phosphorus in the solid phase and halogen in the gas phase.<sup>18</sup> It is interesting to prepare phenoxaphosphine-containing or both phenoxaphosphine- and halogen-containing copolyesters and investigate their flame retardant properties.

In this article we prepare copolyesters by the reaction of 2,8-dichloroformyl-10-phenylphenoxaphosphine 10-oxide (I) and isophthaloyl chloride (II) with three bisphenols as shown in the scheme below and discuss the flame resistant properties of the resulting copolyesters:



## EXPERIMENTAL

**Reagents.** Chloroform was purified in the usual manner. Tetrabutylammonium chloride (TBAC) obtained commercially was used without further purification. Bisphenol A (mp 155–156°C), tetrachlorobisphenol A (mp 134°C), and tetrabromobisphenol A (mp 179–181°C) were commercially available and recrystallized from benzene. Isophthaloyl chloride (II) was vacuum-distilled before use, and (I) was prepared according to our method already reported.<sup>3</sup>

**Synthesis of Copolyesters.** A typical example for preparation of copolyesters is described. To a solution of tetrabromobisphenol A (8.02 mmol, 4.36 g) in aqueous NaOH of 40 mL (1N NaOH 16 mL and water 24 mL), TBAC (2 wt % of theoretical amount of polymer) was placed. Then a solution of (I) (4.81 mmol, 2.01 g) and (II) (3.21 mmol, 0.65 g) in chloroform (40 mL) was added to the mixture with vigorous stirring. After 15 min, the mixture was poured into a large quantity of acetone–water to precipitate the product. The white precipitate

was filtered off and washed thoroughly with water, acetone, and ethyl ether. The product was further purified by repeated precipitation from chloroform into acetone–water mixture and dried to constant weight *in vacuo* at 100°C. The yield was 99%.

**Characterization.** Reduced viscosities, infrared (IR) spectra, and thermogravimetry (TG) were examined by a known method.<sup>3–9</sup> As the char yield, the percentage of char residue at 700°C was taken. The LOI values of copolyesters were measured with the Suga Test Instruments Model ON-1 Type Flammability Test Kit. The test specimen (100 mm × 10 mm × 0.5 mm) was used by cutting a film cast from a solution of copolyester (2 g) in chloroform (15 mL). The LOI value was defined as the minimum oxygen concentration in an oxygen–nitrogen atmosphere at which the test sample burned to the distance more than 50 mm from the top.

## RESULTS AND DISCUSSION

### Synthesis of Copolyesters

Phenoxaphosphine-containing copolyesters were prepared from (I) and (II) taken in molar ratio in feed and three bisphenols (bisphenol A, tetrabromobisphenol A, and tetrachlorobisphenol A) by interfacial polycondensation under the reaction conditions reported previously.<sup>4</sup> The polycondensation was carried out in chloroform–water mixture in the presence of TBAC. The results are listed in Tables I–III. The copolyesters with reduced viscosities of 0.25–0.77 dL/g were obtained in quantitative yields. IR spectra of the copolyesters showed the characteristic band of ester carbonyl near 1750 cm<sup>-1</sup> in addition to the absorptions of phenoxaphosphine ring.<sup>3</sup> These copolyesters were soluble in dimethylformamide (DMF), dimethylacetamide (DMA), *N*-methyl-2-pyrrolidone (NMP), nitrobenzene, and chloroform, and the solubility tended to increase with increasing phenoxaphosphine content. The copolymers were insoluble in dimethyl sulfoxide (DMSO), formic acid, and *m*-cresol. The halogen-free copolyesters and the bromine-containing copolyesters had solubilities in phenol/tetrachloroethane (6:4 by weight), which is a good solvent for polyesters, but the chlorine-containing copolyesters were insoluble in the solvent. Most of the copolyesters gave films on casting from chloroform solutions.

### Thermal Property

The melting temperatures ( $T_m$ ) of the copolyesters were measured, and the relationship between  $T_m$  and phenoxaphosphine content is illustrated in Figure 1. The  $T_m$ –phenoxaphosphine content curves showed the minimum temperatures at around 20–30% of phenoxaphosphine content. Beyond that content,  $T_m$  rose linearly as the phenoxaphosphine content increased. Analogous phenomena have also been observed in other copolyesters.<sup>19,20</sup> This relationship between  $T_m$  and phenoxaphosphine content held for the Flory's equation<sup>21</sup> for random copolymers at the phenoxaphosphine content more than 20–30%:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = - \left( \frac{R}{\Delta H_u} \right) \ln X \quad (1)$$

TABLE I  
Results for Halogen-Free Copolyesters with Phenoxaphosphine Rings

No.	Molar ratio		Yield (%)	$\eta_{red}^a$ (dL/g)	NMP	Solubility <sup>b</sup>	
	(I)	(II)				Chloroform	Phenol/tetrachloroethane (6:4)
1	0	1.0	98	0.52 <sup>c</sup>	-	±	+
2	0.2	0.8	97	0.50	+	+	+
3	0.4	0.6	94	0.64	+	+	+
4	0.6	0.4	95	0.58	+	+	+
5	0.8	0.2	99	0.46	+	+	+
6 <sup>d</sup>	1.0	0	92	0.95 <sup>e</sup>	+	+	+

<sup>a</sup> Measured at a concentration of 0.2 g/dL in chloroform at 30°C.

<sup>b</sup> +, soluble; ±, partly soluble; -, insoluble.

<sup>c</sup> In phenol/tetrachloroethane (6:4).

<sup>d</sup> Reported previously.<sup>4</sup>

<sup>e</sup> In DMA.

TABLE II  
Results for Bromine-Containing Copolyesters with Phenoxaphosphine Rings

No.	Molar ratio		Yield (%)	$\eta_{red}^a$ (dL/g)	Solubility		
	(I)	(II)			NMP	Chloroform	Pheno/tetrachloroethane (6:4)
7	0	1.0	99	0.43 <sup>b</sup>	+	-	±
8	0.2	0.8	100	0.46	+	+	+
9	0.4	0.6	99	0.25	+	+	+
10	0.6	0.4	99	0.39	+	+	+
11	0.8	0.2	100	0.40	+	+	+
12	1.0	0	92	0.34	+	+	+

<sup>a</sup> In chloroform.

<sup>b</sup> In NMP.

TABLE III  
Results for Chlorine-Containing Copolyesters with Phenoxaphosphine Rings

No.	Molar ratio		Yield (%)	$\eta_{red}^a$ (dL/g)	Solubility		
	(I)	(II)			NMP	Chloroform	Pheno/tetrachloroethane (6:4)
13	0	1.0	93	—	±	-	-
14	0.2	0.8	99	0.77	+	+	-
15	0.4	0.6	100	0.51	+	+	-
16	0.6	0.4	99	0.50	+	+	-
17	0.8	0.2	98	0.49	+	+	-
18	1.0	0	99	0.37	+	+	-

<sup>a</sup> In chloroform.

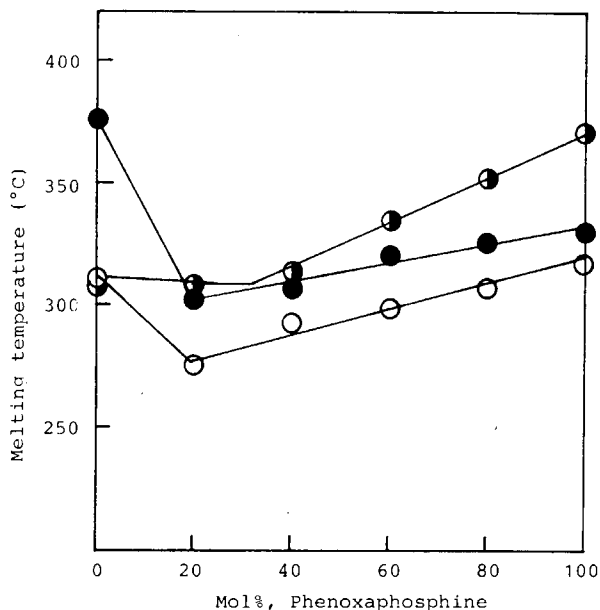


Fig. 1. Melting temperature of copolyesters versus polymer composition: (O) X = H; (●) X = Cl; (◐) X = Br.

where  $T_m$  is the melting point of copolyesters,  $T_m^0$  is the melting point of the phenoxaphosphine-containing homopolyesters,  $\Delta H_u$  is the heat of fusion of per repeating unit of the homopolyesters (kcal/mol),  $X$  is the mole fraction of phenoxaphosphine-containing homopolyester in the copolyester, and  $R$  is the gas constant. The values of  $\Delta H_u$  were calculated from eq. (1). The values for halogen-free, bromine-containing, and chlorine-containing homopolyesters were 18.4 kcal/mol, 12.9 kcal/mol, and 48.6 kcal/mol, respectively. The chlorine-containing homopolyester shows the highest  $\Delta H_u$ . It is seen that these copolyesters have random sequences.

Thermal stabilities of the copolyesters in air and in nitrogen were evaluated by measuring TG at a heating rate of 10°C/min as shown in Tables IV–VI and Figure 2. In the halogen-free copolyesters the decomposition rate in the earlier stage was enhanced with the increase of phenoxaphosphine content in air, but the copolyesters showed little degradation below 400°C. The halogen-containing copolyesters started to decompose below 200°C, although they had higher melting temperatures than the halogen-free copolyesters. The halogen-containing copolyesters showed lower decomposition temperatures than the halogen-free copolyesters, and the former is less heat-resistant than the latter. This indicates that the incorporation of halogen atom into copolyesters results in decrease of the thermostability of the polymers. Similar results are also observed in other halogenated polymers,<sup>11</sup> and the resistance of the polymers to heat dropped with the increase of the halogen content.<sup>14–16</sup> The chlorine-containing copolyesters with phenoxaphosphine ring had better heat resistance than the bromine-containing copolyesters. Also in nitrogen the halogen-free copolyesters displayed better thermostability than the halogen-containing copolyesters. The resistance to heat reduced to the following sequence: the halogen-free copolyester > the

TABLE IV  
 Thermal and Flame-Retardant Properties of Halogen-Free Copolyesters with Phenoxaphosphine Ring

No.	Phosphorus content (%)	Melting temp (°C)	Decomposition temp <sup>a</sup> (°C)		Char yield at 700°C (%)		LOI
			In air	In nitrogen	In air	In nitrogen	
1	0	300-322	448	478	31	31	26.0
2	1.55	263-282	435	447	29	35	35.5
3	2.79	288-295	440	441	30	37	39.5
4	3.82	294-304	420	452	24	40	41.5
5	4.68	295-318	417	447	25	45	42.5
6	5.41	313-320	436	449	31	42	46.0

<sup>a</sup> A temperature at which 10% weight loss was observed in TG.

TABLE V  
Thermal and Flame-Retardant Properties of Bromine-Containing Copolyesters with Phenoxaphosphine Ring

No.	Phosphorus content (%)	Bromine content (%)	Melting temp (°C)	Decomposition temp (°C)		Char yield at 700°C (%)		LOI
				In air	In nitrogen	In air	In nitrogen	
7	0	49.0	298-318	398	417	5	36	58.5
8	0.89	46.0	297-317	380	413	11	39	61.0
9	1.68	43.4	301-325	363	398	10	39	63.0
10	2.38	41.0	323-345	372	403	14	43	64.5
11	3.01	38.8	340-362	372	406	21	46	66.0
12	3.58	37.0	350-390	359	396	18	48	59.5

TABLE VI  
Thermal and Flame-Retardant Properties of Chlorine-Containing Copolyesters with Phenoxaphosphine Ring

No.	Phosphorus content (%)	Chlorine content (%)	Melting temp (°C)	Decomposition temp (°C)		Char yield at 700°C (%)		LOI
				In air	In nitrogen	In air	In nitrogen	
13	0	29.0	370-382	399	459	10	41	47.5
14	1.16	26.6	307-317	404	433	12	41	53.5
15	2.15	24.7	310-324	409	432	9	43	55.0
16	3.01	22.9	310-330	413	437	25	47	55.5
17	3.75	21.5	318-334	407	437	33	50	57.5
18	4.40	20.2	320-338	401	438	31	52	54.5



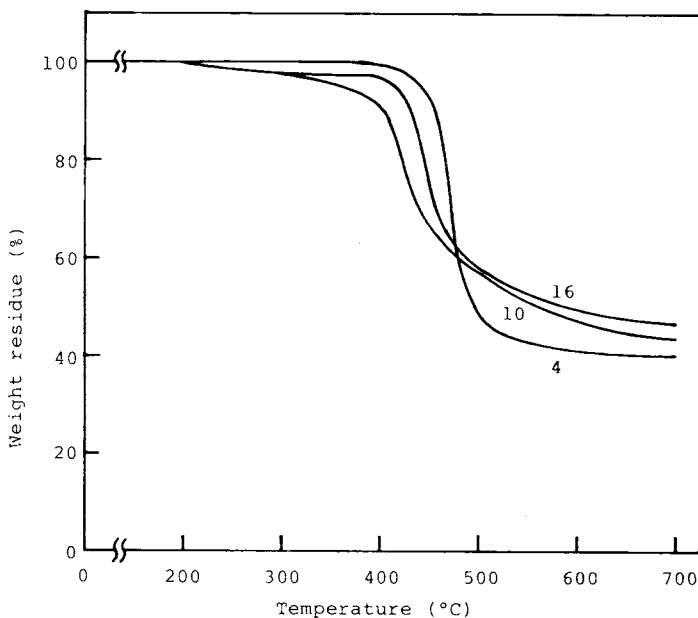


Fig. 2. TG curves of phenoxaphosphine-containing copolyesters in nitrogen (Polymers No. 4, 10 and 16).

chlorine-containing polyester > the bromine-containing copolyester. This sequence of thermal stability was the same as that expected from the values of the bond energy: C—H (99 kcal/mol) > C—Cl (79–81 kcal/mol) > C—Br (66–68 kcal/mol).

### Flame-Retardant Property

The flame retardance of the resulting copolyesters was evaluated by measuring the LOI values. These copolyesters showed considerably high LOI values and good flame resistance. The LOI values of the halogen-containing copolyesters were greater than those of the halogen-free copolyesters. The LOI's lowered in the sequence the bromine-containing copolyester > the chlorine-containing copolyester > the halogen-free copolyester. As shown in Figure 3, the LOI values of these copolyesters proportionally increase with the increment of phenoxaphosphine content, but the efficiency curves were nonlinear. With the increase of phenoxaphosphine content, the halogen-free copolyesters exhibited more rapidly increase of the LOI's than the halogen-containing copolyesters. The curve of the halogen-free copolyesters leveled off at high content of phenoxaphosphine ring, and the difference in the LOI values between the maximum and the minimum content of the phenoxaphosphine ring was 20.0. It is seen that the effect of the introduction of phenoxaphosphine ring into polymer backbone on flame resistance is great. The halogen-containing copolyesters exhibited convex curves and had the maximum LOI values near 80 mol % of the phenoxaphosphine content. Also the halogen-containing polyesters without phenoxaphosphine ring had considerably high LOI values. The difference in the LOI values of those halogen-containing copolyesters between the maximum and the

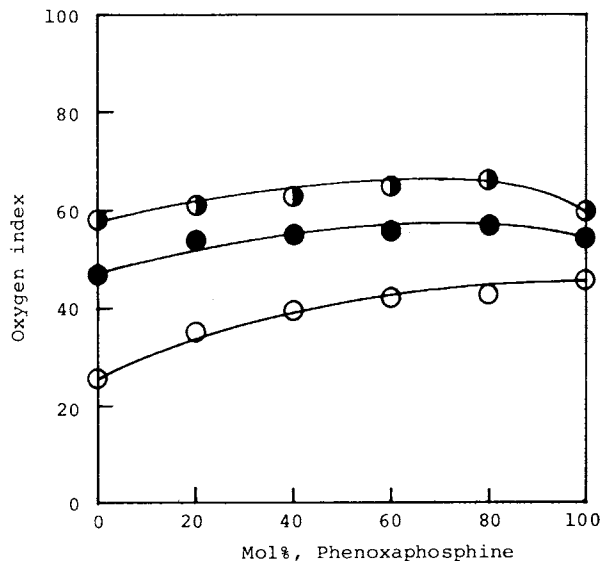


Fig. 3. Oxygen index versus polymer composition: (○) X = H; (●) X = Cl; (◐) X = Br.

minimum was small. As presented in Tables V and VI, the introduction of phenoxaphosphine ring into polymer backbones leads to a decrease of halogen content in halogen-containing polymers. It is generally anticipated that the decrease of halogen content would result in lowering LOI values of polymers. However, a slight increase of LOI's in halogen-containing copolyesters is observed with the increment of phenoxaphosphine content in comparison with halogen-containing polyesters without phenoxaphosphine ring. Therefore, these data indicate that the practical effect of phenoxaphosphine ring on the flame resistance is much higher than the apparent increase of LOI's in Figure 3. On the contrary, as shown in Figure 4, the char yields of these copolyesters increased linearly with increase of the phenoxaphosphine content and the halogen-containing copolyesters had higher char yields than the halogen-free copolyesters at the individual content. Even the char yields of halogen-containing polyesters without phenoxaphosphine ring were higher than that of halogen-free polyester without phenoxaphosphine ring. The char yields reduced to the sequence: the chlorine-containing copolyester > the bromine-containing copolyester > the halogen-free copolyester. These results describe that in these halogen-containing copolyesters the effect of halogen on flammability is very high even at phenoxaphosphine-free content. Although the gas-phase activity is considered to be the major factor in reducing the flammability of these halogen-containing copolyesters, the action is not only attributed to the gas phase, but also due to the solid phase because the char yields are relatively high. Avondo et al.<sup>18</sup> have indicated that the major mechanism of action in reducing the flammability of PET is a gas phase process, although some solid phase inhibition of flammability of PET by halogenated retardants have also been observed. The action of phenoxaphosphine-rich halogen-containing copolyesters might be due to the additive effect of the solid phase and the gas phase, but the solid-phase activity may be the major factor in inhibition of flammability of the copolymers. The

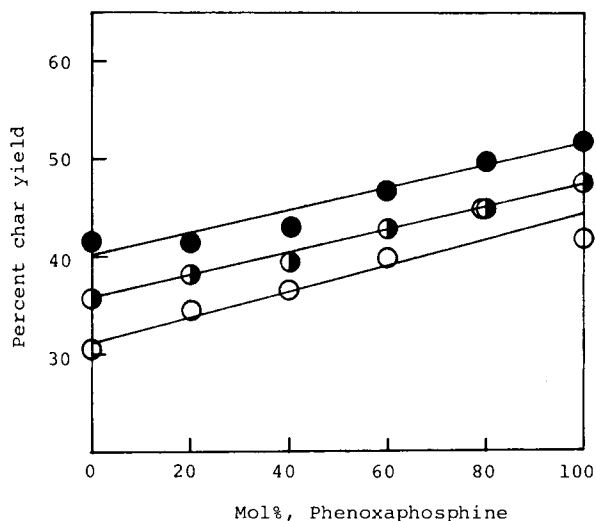


Fig. 4. Percent char yield versus polymer composition: (O) X = H; (●) X = Cl; (◐) X = Br.

mode of action of the halogen-free copolyesters may be based on the effect of phosphorus in the solid phase.

It has been reported that there is a linear relationship between char yield and LOI value for nonhalogenated polymers. The char yield and the LOI value are higher in polymers with multiple bonds and/or heterocyclic units.<sup>2,22</sup> The increase of char yield is reflected as improvement of flammability behavior of polymers.<sup>23</sup> For phosphorus-containing or both phosphorus- and halogen-containing polymers no relationship between char yield and LOI value has been reported to date. In this work the relationship between them was investigated by using the phenoxaphosphine-containing copolyesters. The correlation between char yield and LOI value is shown in Figure 5. The char yield–LOI curves of these copolyesters were convex, and there was a nonlinear relationship between char yield and LOI value. This might be that the phenoxaphosphine ring would accelerate the production of char, because of the effect of char formation of double-strand structure as well as that of phosphorus. Further, in the halogen-containing copolyesters, halogen may act also in the solid phase and affect the char formation as described by Avondo et al.<sup>18</sup> Phosphorus-containing or both phosphorus- and halogen-containing polymers with heterocyclic units such as phenoxaphosphine ring appear to have no first-order correlation between char yield and LOI value.

It would be necessary to be further investigated on the mode of the action of phosphorus-containing or both phosphorus- and halogen-containing polymers in reducing the flammability.

## CONCLUSION

The phenoxaphosphine-containing copolyesters with or without halogen could be prepared by copolycondensation of 2,8-dichloroformyl-10-phenylphenoxaphosphine 10-oxide and isophthaloyl chloride with halogenated bisphenol A's or nonhalogenated bisphenol A. The introduction of phenoxaphosphine ring had remarkable effect on flammability. The halogen-free copolyesters exhibited

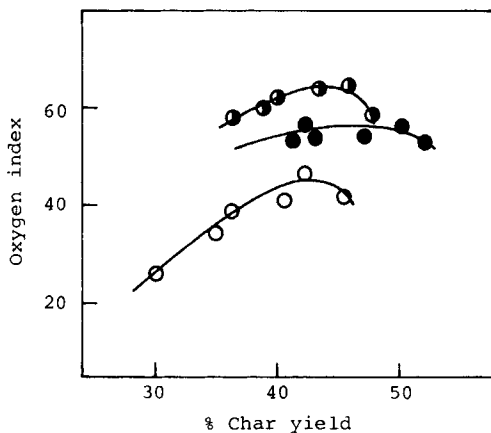


Fig. 5. Correlation between percent char yield and oxygen index.

high flame-proofing property without drastic decrease in thermal stability, although the halogen-containing copolyesters with higher flame-resistant property displayed lower thermal stability. The action of the copolyesters on combustion is based on the additive effect of the solid-phase and the gas-phase processes by phosphorus and halogen.

### References

1. S. R. Sandler and W. Karo, *Polymer Syntheses*, Academic, New York, 1974, Vol. I, p. 367.
2. D. W. van Krevelen, *Polymer*, **16**, 615 (1975).
3. M. Sato and M. Yokoyama, *Eur. Polym. J.*, **15**, 733 (1979).
4. M. Sato and M. Yokoyama, *Eur. Polym. J.*, **16**, 79 (1980).
5. M. Sato and M. Yokoyama, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 2751 (1980).
6. M. Sato, Y. Tada, and M. Yokoyama, *Eur. Polym. J.*, **16**, 671 (1980).
7. M. Sato and M. Yokoyama, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 591 (1981).
8. M. Sato, Y. Tada, and M. Yokoyama, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1037 (1981).
9. M. Sato, H. Kondo, and M. Yokoyama, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 335 (1982).
10. M. Sato, thesis, Nagoya University, 1981.
11. M. S. Lin and E. M. Pearce, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 2659 (1981).
12. M. Lewin, S. M. Atlas, and E. M. Pearce, *Flame-Retardant Polymeric Materials*, Plenum, New York, 1978, Vol. II, p. 123.
13. A. B. Deshpande, E. M. Pearce, H. S. Yoon, and R. Liepins, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **31**, 257 (1977).
14. M. Nagata, T. Kiyotsukuri, and N. Uchino, *Sen-i Gakkaishi*, **37**, T-369 (1981).
15. T. Kiyotsukuri, Y. Hashimoto, and M. Nagata, *Sen-i Gakkaishi*, **37**, T-97 (1981).
16. M. Nagata, T. Kiyotsukuri, and N. Uchino, *Sen-i Gakkaishi*, **36**, T-493 (1980).
17. F. R. Diaz, L. Gargallo, C. Lizana, and S. Gilbert, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2181 (1979).
18. G. Avondo, C. Vovelle, and R. Delbourgo, *Combust. Flame*, **31**, 7 (1978).
19. V. V. Korshak, *J. Polym. Sci.*, **31**, 319 (1958).
20. S. Hashimoto and Y. Nagasuna, *Kobunshi Kagaku*, **24**, 625 (1967).
21. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N.Y., 1953, Chap. XIII.
22. C. B. Quinn, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 2587 (1977).
23. M. S. Lin and E. M. Pearce, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 2151 (1981).

Received February 14, 1983

Accepted July 11, 1983