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PREPARATION OF PHOSPHORUS-CONTAINING POLYMERS—XXVI

DIBENZOPHOSPHOLE-CONTAINING POLYESTERS

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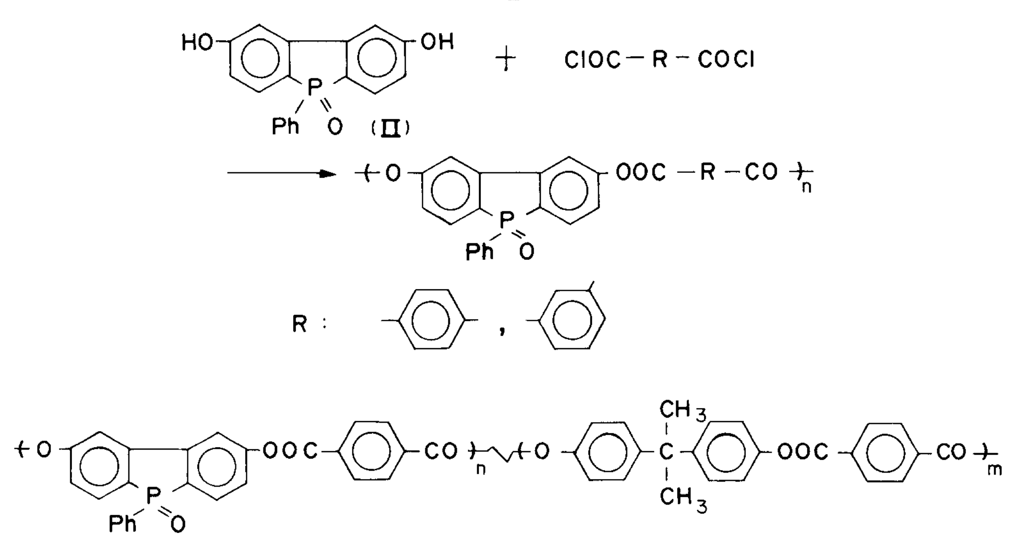
Abstract—New phosphorus-containing homo- and copolyesters were prepared from 2,8-dihydroxy-5-phenyl-5H-dibenzophosphole 5-oxide, bisphenol A and diacid chlorides, and their solubility, thermal stability, flame resistance and photochemical stability were investigated. Most of the polyesters were obtained at relatively low viscosities. Incorporation of the dibenzophosphole ring into the polymer backbone was found to improve solubility in polar aprotic solvents, flame resistance, and stability to u.v. light. The dibenzophosphole-containing homo- and copolyesters had initial decomposition temperatures comparable to those of phosphorus-free polyarylates.

INTRODUCTION

Numerous phosphorus-containing polymers have been synthesized and their properties described. The authors have also prepared single-stranded phosphorus-containing polymers containing C—P bonds [1–3], which are especially stable to hydrolysis. The C—P polymers also have good flame resistance, but their thermal stability was less than that of similar phosphorus-free polymers. In our later papers, the preparation and properties of double-stranded phenoxaphosphine-containing polymers were discussed [4–6], and their thermal stability was shown to be nearly comparable to that of phosphorus-free polymers. It was found that incorporation of ring structures, such as the phenoxaphosphine ring, into such polymers improved their thermal stability in comparison with the single-stranded phosphorus-containing polymers prepared previously. This led us to prepare other kinds of phosphorus-containing polymers with phosphorus atoms in ring systems.

In this work, new double-stranded phosphorus-containing homo- and copolyesters were synthesized from dihydroxydibenzophosphole derivatives, having diphenyl linkages instead of the diphenyl ether linkages of the phenoxaphosphine ring, and their properties were investigated.



EXPERIMENTAL

Materials and solvents

Bisphenol A, and tere- and isophthaloyl chlorides were used after recrystallization. Chloroform, *N,N*-dimethylacetamide (DMA) and the other solvents were purified in the usual manner. A solution of butyl lithium (BuLi) in hexane (10 w/v%) was commercially available.

Dibenzophosphole derivatives

2,8-Dimethoxy-5-phenyl-5H-dibenzophosphole 5-oxide (**I**). That part of the procedure which was concerned with the organometallic compound was carried out under nitrogen.

2,2′-Dibromo-5,5′-dimethoxydiphenyl was prepared as described in the literature [7, 8]. To a solution of the 2,2′-dibromo-compound (0.03 mol) in benzene (85 ml) in an ice-water bath, a solution of BuLi in hexane (39 ml) and 85 ml of ethyl ether were added rapidly. The reaction mixture was refluxed for 2 hr and cooled in an ice-water bath. Phenylphosphonic dichloride (0.03 mol) in benzene (50 ml) was added dropwise to the mixture. After the addition, the mixture was refluxed again for 3 hr, cooled and poured into ice-water. A solid was obtained at the interface between the organic and aqueous layers. After filtration, the solid was washed with water and recrystallized from acetone. In addition, the solvent was removed from the organic layer and the residue was also recrystallized from acetone. The 2,8-dimethoxy derivative was obtained in 31% yield.

2,8-Dihydroxy-5-phenyl-5H-dibenzophosphole 5-oxide (**II**). The 2,8-dimethoxy derivative (I) was refluxed in conc HBr for 9 hr and a white solid was obtained. The solid was dissolved in dilute NaOH solution and precipitated by acidification with acetic acid. Recrystallization from ethanol gave 95% of the 2,8-dihydroxy-compound, m.p. 336° (DTA method). Further recrystallization raised the melting point to 338°.

Model compound

2,8-*Bis*(benzoyloxy)-5-phenyl-5H-dibenzophosphole 5-oxide (**III**) was prepared from the monomer (**II**) and an excess of benzoyl chloride with triethylamine as acid acceptor in DMA at ambient temperature. The product was isolated by pouring the reaction mixture into water; the precipitate was recrystallized from benzene and dried *in vacuo*.

Instruments

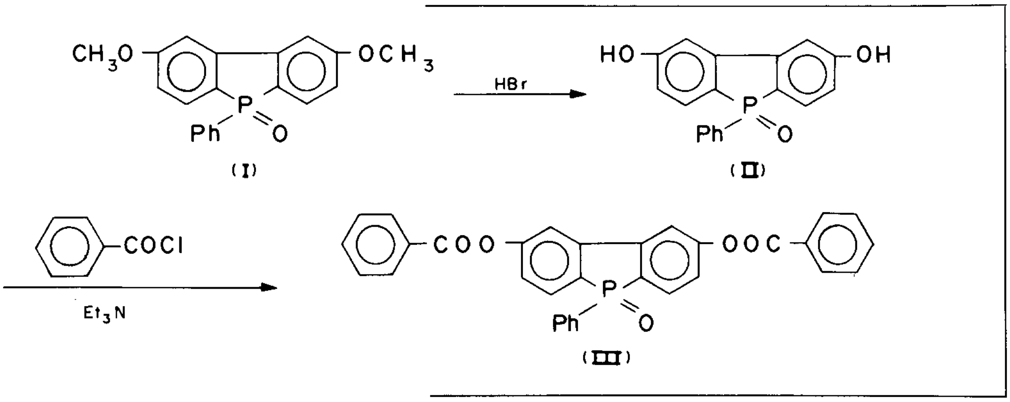
Differential thermal (DTA) and thermogravimetric analyses (TGA) were carried out as previously [4–6]. I.r. and u.v. spectra were obtained by JASCO Model A-102 i.r. spectrophotometer and Hitachi 101 u.v. spectrophotometer.

RESULTS AND DISCUSSION

Dibenzophosphole derivatives

2,8-Dimethoxy-5-phenyl-5H-dibenzophosphole 5-oxide (**I**) has already been prepared from 2,8-dimethoxy-5-phenyl-5H-dibenzophosphole by oxidation with styrene oxide. The tertiary dibenzophosphole was derived from phenylphosphonous dichloride and the dilithiated compound of 2,2′-dibromo-5,5′-dimethoxydiphenyl in 33% yield [8]. In this work, compound (**I**) was directly prepared from phenylphosphonic dichloride and 2,2′-dibromo-5,5′-dimethoxydiphenyl also in low yield (31%). This is likely to be due to a side reaction, i.e. hydrogen–lithium exchange, occurring together with halogen–lithium interconversion. The hydrogen–lithium exchange is known to occur on lithiation of *p*-bromoanisole. It might be that 2,2′-dibromo-5,5′-dimethoxydiphenyl also undergoes the side reaction and that the yields of dibenzophosphole derivatives consequently dropped.

2,8-Dihydroxy-5-phenyl-5H-dibenzophosphole 5-oxide (**II**) was easily obtained in high yield from 2,8-dimethoxy-compound (**I**) by treating with conc. HBr (48%) under reflux, and used as a monomer for preparation of dibenzophosphole-containing polyesters.



Homo- and copolyesters

Dibenzophosphole-containing homo- and copolyesters were prepared by interfacial polycondensation. To a solution of bisphenols (total 1 mmol) in aq. NaOH (1 N NaOH 2.2 ml and water 7.8 ml) and tetrabutylammonium chloride (2 wt% of theoretical yield of polymer), diacid chloride (1 mmol) in chloroform (10 ml) was added in one portion, and the mixture was vigorously stirred for 30 min. The reaction mixture was poured into acetone-water. The resulting solid was washed with water and acetone and dried under vacuum at 100°.

Photochemical reaction

A solution of polyester in chloroform was charged into a quartz cell. The atmosphere of the system was substituted by N_2 and the solution was irradiated by medium-pressure Hg lamp (made by Toshiba) at the distance of 20 cm.

To identify the polymer structure, 2,8-*bis*(benzoyloxy)-5-phenyl-5H-dibenzophosphole 5-oxide (**III**) was synthesized from (**II**) and benzoyl chloride in DMA at ambient temperature. The formation of these compounds was confirmed from i.r. spectra and elemental analyses. The characteristic i.r. bands of dibenzophosphole derivatives are as follows; 3050–3075 (aromatic C—H), 1595–1600 and 1575–1560 (Ph), 1435 (P—Ph), 1160–1170 (P=O) and 690–695 cm^{-1} (monosubstituted benzene). In addition, the spectrum of (**II**) exhibited an absorption at 1360 cm^{-1} attributed to C—O of phenol. (**III**) had a characteristic absorption band of ester carbonyl at 1730 cm^{-1}. Elemental analyses of these compounds were in good agreement with calculated values. Preparative results of the dibenzophosphole derivatives are listed in Table 1.

Table 1. Preparation of dibenzophosphole derivatives

	Yield	m.p.	Elemental analyses					
	(%)	(°C)	C Calc.	% Found	H Calc.	% Found	P Calc.	% Found
I	31	257–258*	71.43	71.62	5.06	5.26	9.23	9.25
II	95	338*	70.13	70.05	4.22	4.77	10.06	9.89
III	87	212–213	74.42	74.43	4.07	4.14	6.01	5.92

* DTA method.

Table 2. Preparation of homopolyesters

Polymer no.	Diacid chloride	Yield (%)	η_{red}* (dl/g)	PMT (°C)	P Calc.	% Found
1	Terephthaloyl	89	0.14	307–316	7.08	6.99
2	Isophthaloyl	63	0.08	309–314	7.08	6.78

* Measured at a concentration of 0.2 g/dl in chloroform at 30°.

Homo- and copolyesters

Dibenzophosphole-containing homo- and copolyesters were synthesized by interfacial polycondensation. The results for preparation of these polyesters are shown in Tables 2 and 3. All the polymers were obtained as white powders and solids. The preparation of dibenzophosphole-containing homopolyesters resulted in relatively low yields and reduced viscosities. Copolyesters were produced in yields of 68–95% and at reduced viscosities of 0.15–2.51 dl/g. The yields and the viscosities of copolymers decreased with increasing dibenzophosphole content. These results might be due to low basicity of (**II**) with electron-withdrawing phosphoryl group. The structure of the polyesters was confirmed by elemental analyses and i.r. spectra. The i.r. spectra showed absorption bands analogous to those of the model compound (**III**) and a characteristic ester band was observed at 1730 cm^{-1}. The elemental analyses of the homopolyesters agreed with calculated values.

Table 3. Preparation of copolyesters

Polymer no.	Molar ratio* (II)	Molar ratio* Bisphenol A	Yield (%)	η_{red}† (dl/g)	PMT (°C)
3	0.9	0.1	75	0.21	309–320
4	0.8	0.2	68	0.15	303–314
5	0.7	0.3	76	0.20	302–308
6	0.6	0.4	82	0.22	298–307
7	0.5	0.5	81	0.32	296–305
8	0.4	0.6	89	0.36	297–306
9	0.3	0.7	94	0.45	298–307
10	0.2	0.8	90	0.85	300–311
11	0.1	0.9	95	2.51	—

* Molar ratio to terephthaloyl chloride.

† Measured at a concentration of 0.2 g/dl in chloroform at 30°.

Solubility

Table 4 shows the results of qualitative solubility tests on these polymers. Dibenzophosphole-containing homopolyesters dissolved in good solvents for polyesters (such as phenol-sym-tetrachloroethane (60:40), *m*-cresol and chloroform) and also in DMA, DMF and DMSO. Copolymers were also soluble in good solvents for polyesters. With increasing bisphenol A content, however, the copolymers became insoluble in the polar aprotic solvents as described

Table 4. Solubility of polymers

Solvent	Polymer no. 1	2	3	4	5	6	7	8	9	10	11
DMF	+	+	+	+	+	+	+	+	+	±	–
DMA	+	+	+	+	+	+	+	+	+	±	–
DMSO	+	+	+	+	±	–	–	–	–	–	–
conc. H_2SO_4	+	+	+	+	+	+	+	+	+	+	+
Acetic acid	±	±	–	–	–	–	–	–	–	–	–
Phenol-sym-tetra chloroethane (60:40)	+	+	+	+	+	+	+	+	+	+	+
m-Cresol	+	+	+	+	+	+	+	+	+	+	+
Nitrobenzene	+	+	+	+	+	+	+	+	+	+	±
Chloroform	+	+	+	+	+	+	+	+	+	+	+
Benzene	–	–	–	–	–	–	–	–	–	–	–
Ethanol	–	–	–	–	–	–	–	–	–	–	–
Acetone	–	–	–	–	–	–	–	–	–	–	–

+ :soluble, ± : partially soluble, – : insoluble

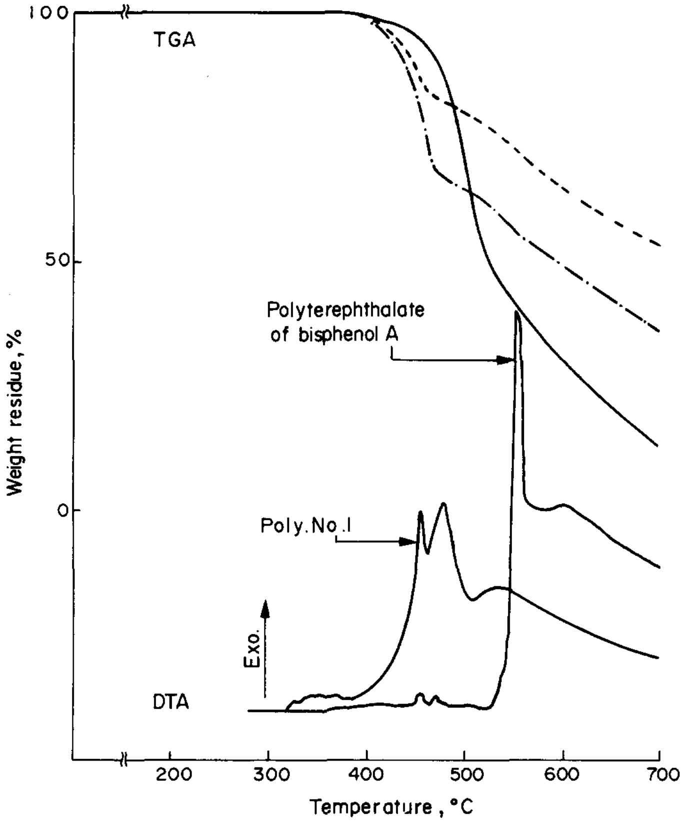


Fig. 1. DTA and TGA curves of Poly. nos 1 (----) and 7 (-·-), and polyterephthalate of bisphenol A (——) in air.

above. This might be due not only to the high viscosity of copolymers but also to the influence of the bisphenol A component in the polymer backbone. Thus it appears that incorporation of the dibenzophosphole ring into polymers enhances the solubility of polymers in polar aprotic solvents.

Thermal stability

Thermal stabilities of the polyesters were investigated by DTA and TGA at a heating rate of 10°/min. Typical TGA and DTA curves are illustrated in Figs. 1 and 2. All the data of thermal properties are listed in Table 5.

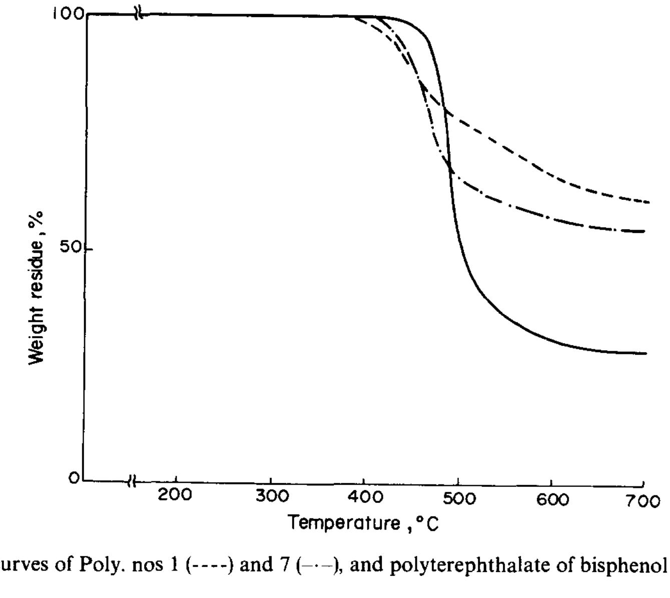


Fig. 2. TGA curves of Poly. nos 1 (----) and 7 (-·-), and polyterephthalate of bisphenol A (——) in N_2.

Table 5. Data for thermal behaviour of dibenzophosphole-containing homo- and copolyesters

Polymer no.	Decomp. temp.* (°C)		Weight residue at 700° (%)	
	In air	In N_2	In air	In N_2
1	449	445	53	62
2	453	469	42	69
3	444	453	43	61
4	432	452	39	64
5	428	463	37	59
6	431	448	40	59
7	438	446	37	55
8	439	447	33	49
9	446	447	28	47
10	447	452	27	39
11	454	459	15	33

* A 10% weight-loss temperature observed in TGA.

Dibenzophosphole-containing homopolyesters started to decompose over 360°, but the weight loss up to 400° was small. Rapid weight loss was observed beyond 400°. The subsequent degradation proceeded over 500°. In N_2, the polymers exhibited initial degradation analogous to that in air and gradually decomposed over 550°. Ultimate amounts of residue at 700° were higher in N_2 than in air. The polyterephthalate of bisphenol A showed an initial decomposition at 390°, and the rate of weight loss was smaller than that of dibenzophosphole-containing homopolyesters until a temperature of 450° was reached. However, very rapid weight loss was observed beyond this temperature and the amount of residue at 700° was small. The phosphorus-free polyester decomposed most rapidly at 450–600° in N_2 and hardly lost any weight beyond 600°. Dibenzophosphole-containing homopolyesters left smaller residues up to 500° than the phosphorus-free polyarylate. Above this temperature, the dibenzophosphole-containing homopolymers maintained larger amounts of residue than polyterephthalate of bisphenol A. It is clear that the behaviour is independent of atmosphere. Copolyesters exhibited thermal stability lying between dibenzophosphole-containing homopolymer (Poly. no. 1) and the polyterephthalate of bisphenol A both in air and in N_2. In addition, it is found that increasing dibenzophosphole content tends to increase the weight of residual polymer after heat treatment to 700°.

DTA curves of dibenzophosphole-containing homopolyesters were complex and the following peaks were shown in air; at 450–460° (sharp peak), at 470–480° (slightly broad) and at around 540° (broad). Polyterephthalate of bisphenol A presented two exothermic peaks at 522° (sharp) and 600° (broad) in DTA curve in air. Most DTA curves of copolymers displayed a few sharp exothermic peaks which might be due to thermal decomposition of dibenzophosphole-moiety and 2,2-diphenylpropane-moiety. These exothermic peaks correspond to weight losses and might be attributed to thermooxidative degradation. In N_2, most DTA curves were too complex and broad to be distinguished between endotherms and exotherms.

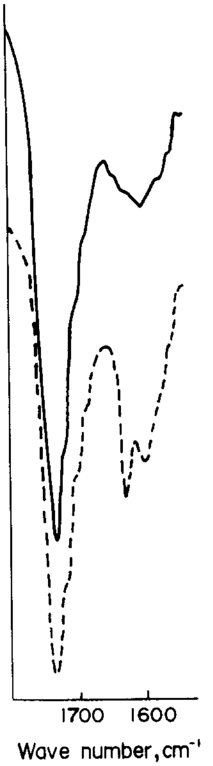


Fig. 3. Change of i.r. spectra of Poly. no. 11 before (——) and after (----) irradiation.

These facts suggest that thermal stabilities of dibenzophosphole-containing polyesters are comparable to that of phenoxaphosphine-containing polyesters and that the initial decomposition temperatures are similar to those of phosphorus-free polyarylates.

Qualitative tests of flame resistance were performed. Except for Poly. no. 11 which has the mini-

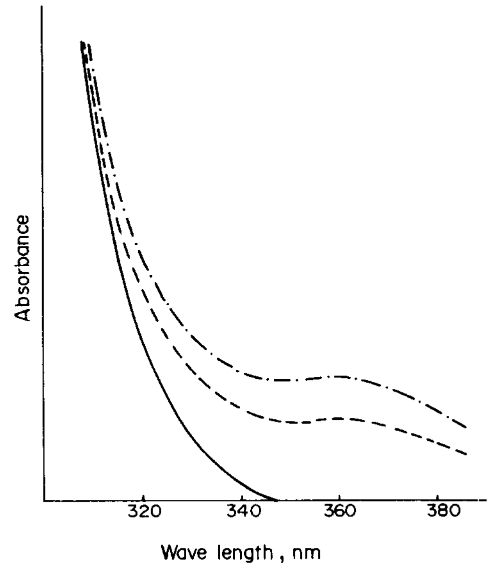


Fig. 4. Change of u.v. spectra of Poly. no. 7 with the elapse of irradiation time; before (——), and after 2 hr- (----) and 4 hr-irradiation (—·—).

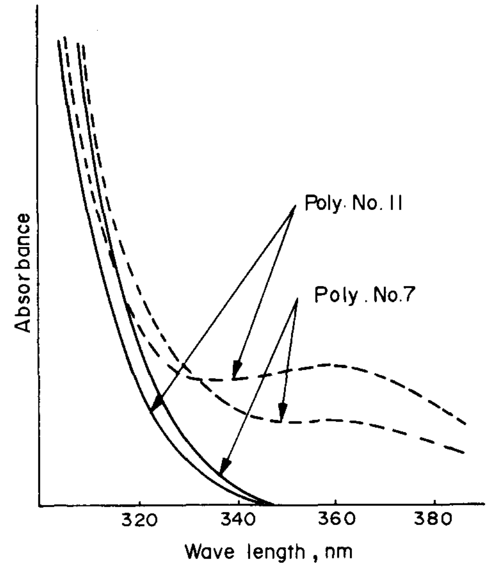


Fig. 5. Change of u.v. spectra of copolyesters before (——) and after 2 hr-irradiation (----).

mum dibenzophosphole content, the dibenzophosphole-containing homo- and copolyesters self-extinguished much more quickly than the polyterephthalate of bisphenol A after a flame was removed. This fact indicates that incorporation of dibenzophosphole ring into polymer backbone enhances the flame resistance of the polymers.

Photostability

The Fries rearrangement is known to occur when polyarylates are irradiated with u.v. [9–11]. Korshak *et al.* reported that incorporation of phosphorus or sulphur into the polymer backbone improved the photochemical resistance of polymers to u.v. [11]. Therefore, we examined photostability of dibenzophosphole-containing polyesters in chloroform solution to external irradiation. After the solution of polymer was exposed to u.v., a part of the solution was diluted and the u.v. spectrum was obtained. As shown in Figs 3 and 4, the product after exposure to u.v. had an i.r. absorption at $1630\,cm^{-1}$ and a u.v. absorption at 360 nm, due to ketone carbonyl groups formed by the Fries rearrangement. The absorptions were not observed in the spectra of the polyesters before irradiation. Figure 4 shows the change of u.v. spectrum with irradiation time. The intensity of the absorption at 360 nm increased in the u.v. spectra of Poly. no. 7 after 4 hr-irradiation. It appears that these dibenzophosphole-containing polyesters also undergo the Fries rearrangement. The longer the irradiation time, the more rearrangement occurred. Figure 5 presents the u.v. spectra of copolyesters before and after 2 hr-irradiation. This Figure shows that the polyesters become more photostable with increase of dibenzophosphole content. From these facts it is found that dibenzophosphole-containing polyesters also undergo photoinitiated rearrangement, but they have better stability for the photorearrangement than phosphorus-free polyarylate.

Dibenzophosphole-containing homopolyester gave a precipitate within 1 hr-irradiation and copolyesters also precipitated after longer exposure to u.v. With respect to this point, it was reported that exposure of polyarylate to u.v. of short wave length ($\lambda < 300$ nm) resulted in cross-linking and photodegradation simultaneously [12, 13]. Analogous cross-linking might occur in this study, because a quartz cell and polychromatic light were used: the polymers were also exposed to u.v. of short wave length in these conditions. Photostabilities of phosphorus-containing polymers have received little attention and require further investigation.

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