

Synthesis, Characterization, and Thermal Properties of Phosphorus-Containing, Wholly Aromatic Thermotropic Copolyesters

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ABSTRACT: A series of phosphorus-containing, wholly aromatic thermotropic copolyesters from acetylated 2-(6-oxide-6H-dibenz(c,e)(1,2)oxa phosphorin-6-yl)-1,4-dihydroxy phenylene, *p*-acetoxybenzoic acid, terephthalic acid, and isophthalic acid were prepared by melting polycondensation. The structure and basic properties of the polymers, such as the glass-transition temperature (T_g), melting temperature (T_m), thermal stability, crystallinity, and liquid crystallinity, were investigated with Fourier transform infrared, elemental analysis, differential scanning calorimetry (DSC), thermogravimetric analysis, wide-angle X-ray diffraction, and hot-stage polarizing optical microscopy. The copolyesters had relatively high T_g values ranging from 183 to 192°C. The T_m values obtained from

DSC curves for samples P-20 and P-25 were 290 and 287°C, respectively (where the number in the sample name indicates the molar fraction of the phosphorus-containing monomer in the reactants). The initial flow temperatures of other samples observed with hot-stage polarizing microscopy were 271–290°C. The 5% degradation temperatures in nitrogen ranged from 431 to 462°C, and the char yields at 640°C were 41–52%. All the copolyesters, except P-40, were thermotropic and nematic. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1278–1284, 2002

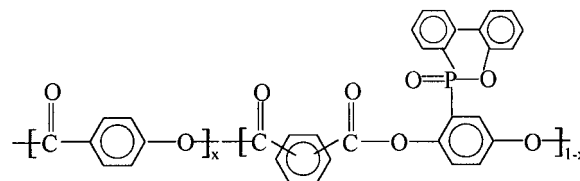
Key words: flame retardance; differential scanning calorimetry (DSC); glass transition; thermogravimetric analysis

INTRODUCTION

Wholly aromatic thermotropic polyesters are currently receiving considerable attention for their excellent mechanical properties, thermal stability, chemical resistance, and low melting viscosity. However, because of their high aromatic contents, this class of polymers generally has high melting temperatures (T_m 's), which prevent melt processing before thermal decomposition. Several methods of structural modification can be adopted to decrease the melting-transition temperatures of these polymers to a level that is lower than their decomposition temperatures so that they can be processed conveniently. One method is to introduce a bulky substituent onto the mesogenic group, the steric effect of which hinders regular chain packing and reduces crystal perfection.^{1–6} Another useful approach for reducing T_m is the random copolymerization of monomers with different mesogenic units, by which the symmetry of the primary structure of the polymer is lowered and the lateral packing is disrupted.^{7–10} A third way is to use monomers with nonlinear or kinked structures to lower the persistence length of the polymer chain and to reduce lateral

interactions in the solid state.^{11–14} In addition, the introduction of flexible spacers between rigid-rod mesogens also can be used to lower T_m by reducing the aspect ratio of the polymer chain.^{15–17}

In this study, a series of wholly aromatic thermotropic copolyesters with relatively low thermal transition temperatures were investigated. The copolyesters were based on terephthalic acid (TPA), isophthalic acid (IPA), *p*-hydroxybenzoic acid (*p*-HBA), and the phosphorus-containing monomer [2-(6-oxide-6H-dibenz(c,e)(1,2)oxa phosphorin-6-yl)-1,4-dihydroxy phenylene (DOPO-HQ)]. The formula of the copolyesters is



where x and $1 - x$ denote the overall composition, not the block length. The ratio of TPA to IPA was 1:1. Introducing a phosphorus-containing monomer into the main chain has two advantages: First, as previously noted, the bulky substituent is beneficial for lowering T_m values of the copolyesters. Second, it should offer excellent flame retardancy to the copolyesters.^{18–20} Test results showed that the limiting oxygen indices (LOIs) of these copolyesters were up to 70,

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TABLE I
Polymerization Conditions of Copolyesters

Sample	Reaction conditions					
	Temperature (°C)/pressure (Pa)/time (min)					
P-17	240/101 k/30	260/101 k/30	280/101 k/40	300/101 k/40	320/300/20	340/30/10
P-20	240/101 k/30	265/101 k/30	290/101 k/40	300/101 k/30	320/200/20	340/40/10
P-25	240/101 k/30	260/101 k/30	290/101 k/30	300/101 k/30	330/150/15	345/30/15
P-29	250/101 k/20	260/101 k/30	280/101 k/40	310/101 k/40	320/130/20	340/50/20
P-33	240/101 k/30	260/101 k/30	280/101 k/30	300/101 k/20	310/110/20	320/40/10
P-40	240/101 k/30	260/101 k/30	280/101 k/30	300/101 k/20	300/200/20	310/30/05

which is higher than that of general aromatic polyesters. In addition, phosphorus-containing copolyesters meet the requirements of low toxicity and low smoke during combustion for environmental and health considerations. At the same time, IPA with a nonlinear structure also serves to reduce T_m . The copolyesters were characterized with Fourier transform infrared (FTIR) and element analysis. Their thermal properties were evaluated with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Mesogenic phases were observed with hot-stage polarizing microscopy.

EXPERIMENTAL

Materials

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was kindly supplied by Weili Flame Retardant Chemicals Co., Chengdu, China. *p*-HBA, TPA, and IPA (Wulian Chemical Co., Wulian, China) were used after drying at 70°C for 24 h in vacuo. Reagent-grade 2-ethoxyethanol (Tiantai Chemical Plant, Tianjin, China) and acetic anhydride (Chengdu Chemical Reagent Plant, Chengdu, China) were used as received. *p*-Benzoquinone, used to prepare DOPO-HQ, was synthesized in our laboratory.

Monomer synthesis

According to a published procedure,¹⁸ DOPO-HQ was synthesized from DOPO and *p*-benzoquinone. 2-Ethoxyethanol was used as a reaction solvent. *p*-Acetoxybenzoic acid (ABA) was prepared as described in a previous publication.²¹ Acetylated DOPO-HQ (DOPO-AHQ) was prepared by the refluxing of DOPO-HQ with acetic anhydride for 13 h under a nitrogen atmosphere. The reaction mixture was poured into a large excess of distilled water. The precipitates that formed were filtered and washed with distilled water. The product DOPO-AHQ was recrystallized from aqueous ethanol and then dried in vacuo at 70°C for 24 h. The product yield of DOPO-AHQ was 91%, and the melting point was 102–104°C.

FTIR (KBr): 3065 (aromatic C—H), 2934 (aliphatic C—H), 1768 (C=O), 1171 (C—O), 1596 (P—Ar), 1198 (P=O), 916, 757 cm^{-1} (P—O—Ar; there was no hydroxyl group stretching peak). ELEM. ANAL. Calcd. for $\text{C}_{22}\text{H}_{17}\text{O}_6\text{P}$ (408): C, 64.70%; H, 2.45%. Found: C, 64.67%; H, 2.48%.

Polymer synthesis

The polymerization conditions used for the synthesis of the copolyesters are presented in Table I. The number in the sample name indicates the molar fraction of the phosphorus-containing monomer in the reactants. For example, P-17 indicates that the copolyester was synthesized by a reaction with 17 mol % DOPO-AHQ. All the copolyesters were prepared in a similar manner. Therefore, only the synthesis of the polymer labeled P-17 is described as a representative example. A mixture of DOPO-AHQ, ABA, TPA, and IPA in a molar ratio of 2:8:1:1 was charged into a 100-mL, three-neck flask that was equipped with a mechanical stirrer, a nitrogen inlet, and a distillation trap connected to a vacuum line. Before the reaction, the flask was evacuated and imbued with nitrogen. The flask was placed in a salt bath preheated to 240°C and was kept at this temperature for 30 min. The byproduct, acetic acid, was taken off by a nitrogen flow. The temperature was raised stepwise: 260°C for 30 min, 280°C for 40 min, and 300°C for 40 min. Then, a low vacuum was applied. The temperature was raised to 340°C over 40 min; meanwhile, a high vacuum was gradually achieved, up to 30 Pa. After the reaction, the flask was immersed in an ice–water bath. The resulting product was ground and dried at 80°C for 24 h.

Polymer characterization

The elemental analysis of C and H was performed with a Carlo Erba 1106 elemental analyzer (Rodano, Italy). P was measured with the Schoniger combustion flask method and was detected with a UV spectrophotometer. The FTIR spectra of the polymers were recorded with an FTIR170 SX spectrometer. The intrinsic viscosities of the

TABLE II
Elemental Analysis Data for Copolyesters

Sample	Ratio of monomers	Elemental analysis (wt %) ^a		
	DOPO-AHQ:ABA:TPA:IPA	Phosphorus	Carbon	Hydrogen
P-17	2:8:1:1	3.16 (3.32)	69.75 (69.38)	3.39 (3.32)
P-20	2:6:1:1	3.72 (3.81)	69.65 (69.29)	3.43 (3.32)
P-25	2:4:1:1	4.43 (4.47)	69.21 (69.16)	3.41 (3.31)
P-29	2:3:1:1	4.81 (4.89)	68.93 (69.09)	3.37 (3.31)
P-33	2:2:1:1	5.31 (5.40)	68.44 (68.99)	3.38 (3.31)
P-40	2:1:1:1	5.94 (6.03)	68.73 (68.87)	3.35 (3.31)

^a Values in parentheses represent calculated values where it was assumed that actual compositions were the same as those in feed.

copolyesters were measured in a mixture solution of phenol-1,1,2,2-tetrachloroethane (60:40 w/w) at 30°C at a concentration of 0.5 g/dL with an Ubbelohde capillary viscometer. DSC was conducted on a PerkinElmer DSC7 instrument under a nitrogen atmosphere at a heating rate of 20°C min⁻¹. Approximately 10-mg samples were used for the DSC analysis. The temperature at which an initial baseline shift was observed on the DSC curves was taken as the glass-transition temperature (T_g). The T_m values of the polymers were taken from the first endothermic peaks. Indium was used as a reference for temperature calibration. Wide-angle X-ray diffraction (WAXD) was performed at room temperature on a Rigaku Geiger Flex D-max-III_a X-ray diffractometer (Woodlands, TX) with Ni-filtered Cu K α radiation. The rotated velocity of the goniometry was 4°/min. All the samples were an-

nealed at 220°C for 2 h. TGA of the copolyesters was performed with a PerkinElmer TGA7 instrument at a heating rate of 10°C min⁻¹ from ambient temperature to 640°C in a nitrogen atmosphere. Polymer samples weighing 3–4 mg were used. Values for the decomposition temperature when a 5% weight loss occurred ($T_{d 5\%}$) were determined. The mesophases of the copolyesters were identified with a Leitz Orthouz II Pol-Bk hot-stage polarizing microscope (Stuttgart, Germany).

RESULTS AND DISCUSSION

Polymerization and structure

Copolyesters with different monomer ratios were prepared by the transesterification of diacids and acetic diols in the melting phase. The byproduct, acetic acid,

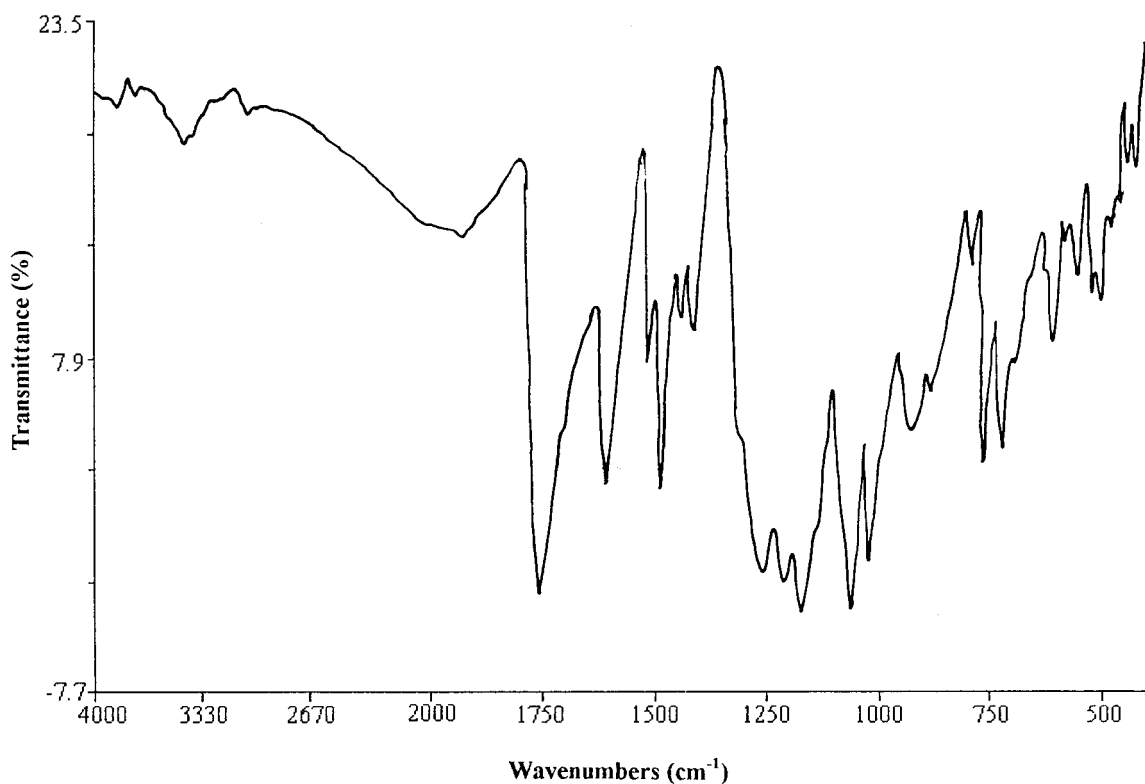


Figure 1 FTIR spectrum of copolyester P-29.

TABLE III
General Properties of Copolyesters

Sample	η_{int} (dL/g)	T_g (°C)	T_m (°C)	T_d (°C)	Char yield (%)
P-17	2.18	184	290 ^a	431	49.6
P-20	1.53	183	290	440	41.1
P-25	1.34	185	287	448	51.6
P-29	0.92	188	284 ^a	450	46.5
P-33	0.69	192	279 ^a	462	48.6
P-40	0.54	192	271 ^a	451	49.1

^a The temperatures were obtained from a hot-stage polarizing microscope.

was removed from the reaction mixture through a nitrogen flow at an earlier stage and through distillation in vacuo at a later stage. An obvious rod-climbing phenomenon and stir opalescence (except P-40) were observed during polymerization.

Table II shows the results of the elemental analysis of the polymers, which indicated that the actual

compositions were very close to those of the feed. The structures of the resulting polymers were also characterized with FTIR. For example, the spectrum of P-29 is shown in Figure 1. The characteristic peaks are at 1739 (C=O), 1178 (P—O—Ar), and 1475 cm^{-1} (P—Ar). The results of elemental analysis and characteristic bands in FTIR spectra correlate sufficiently well with the proposed structures of the copolyesters.

The polymers were not soluble in common organic solvents such as CHCl_3 , tetrahydrofuran, dimethylformamide, dimethylacetamide, and *N*-methylpyrrolidone, but they were soluble in *p*-chlorophenol and a mixture solution of phenol-1,1,2,2-tetrachloroethane. Therefore, their solution viscosities were measured in mixed solvents, and the intrinsic viscosity (η_{int}) values of the copolyesters are given in Table III. The values range from 0.54 to 2.18; this indicates that the molecular weights of the prepared polymers were reasonably high.

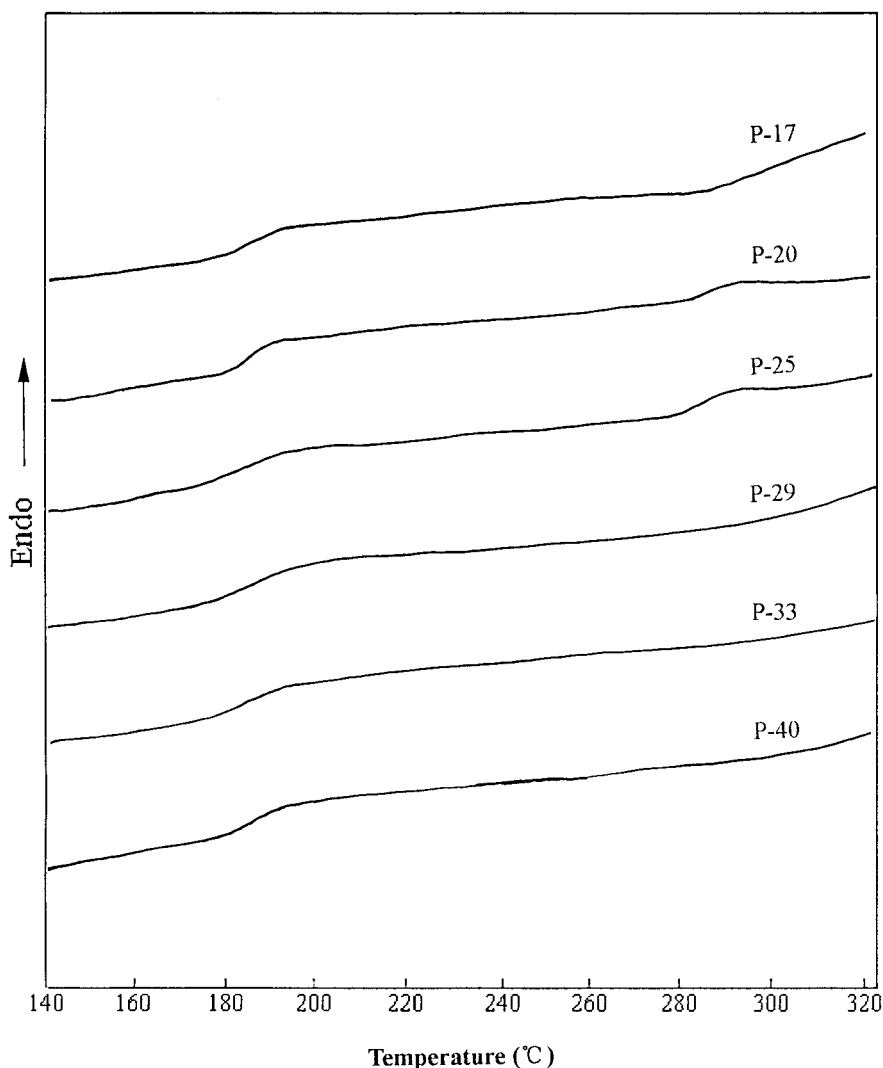


Figure 2 DSC thermograms of copolyesters in N_2 at a heating rate of $20^\circ\text{C}/\text{min}$.

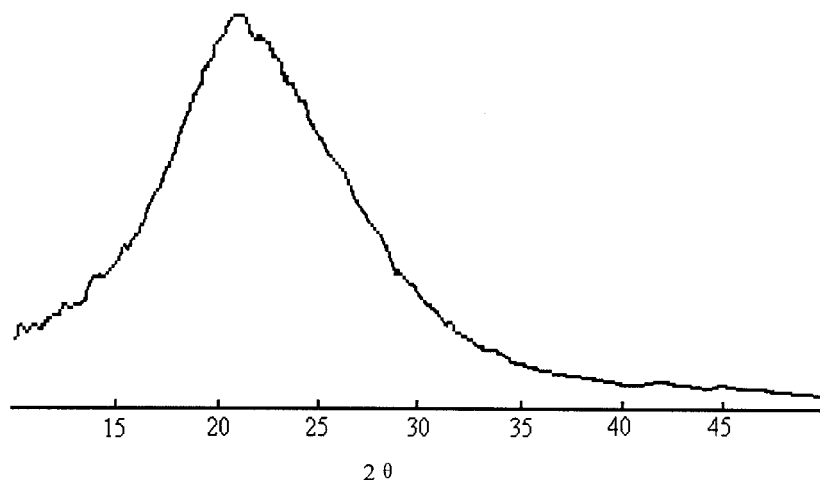


Figure 3 WAXD diffractogram of copolyester P-20 after annealing at 220°C for 2 h.

Thermal transition behavior

Thermal behaviors of the copolyesters were measured with DSC, hot-stage polarizing optical microscopy, and TGA. Experimental data obtained from DSC are presented in Table III. Figure 2 shows the DSC curves of the polymers. The T_g values of the polymers ranged from 183 to 192°C and were insensitive to the compo-

sitions of the copolyesters. The relatively high values of T_g may be attributed to the rigidity of the backbones. In addition, the bulky substituent hindered the rotation of the main chain, which was expected to result in harder segmental motions.

The DSC thermograms of the copolyesters labeled P-20 and P-25 showed small endothermic peaks at 290

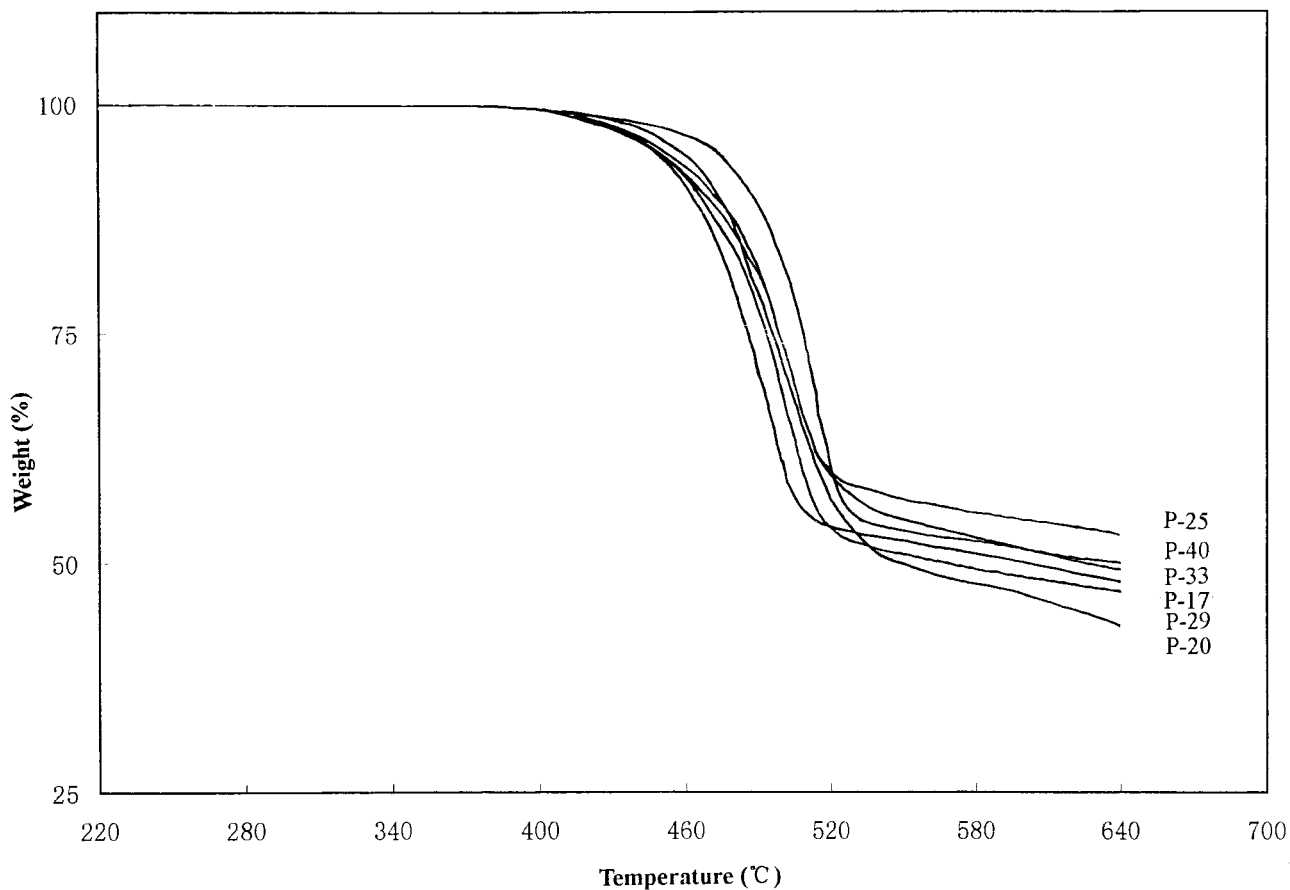
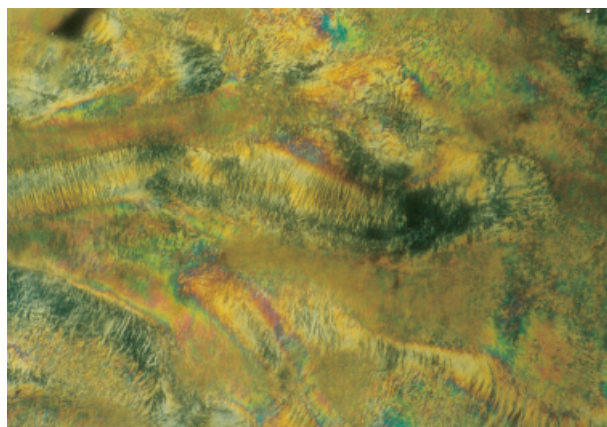
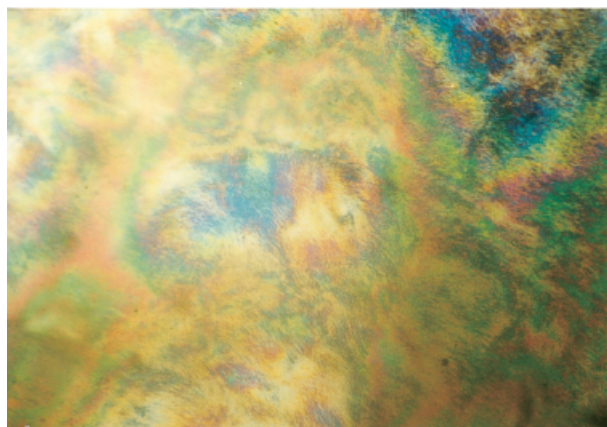


Figure 4 TGA thermograms of copolyesters in N_2 at a heating rate of 10°C/min.



(a)



(b)

Figure 5 Photomicrographs of copolyesters (original magnification, 250 \times): (a) P-20 and (b) P-25.

and 287 $^{\circ}\text{C}$, which suggested a correspondence to T_m . The enthalpy of melting (ΔH_m) values of P-20 and P-25 were 1.2 and 0.8 J/g, respectively. Both values were very small and suggested that the degrees of crystallinity were very low. Other polymers only showed glass transitions and no significant endothermic peaks. The results revealed that these polymers were amorphous. These results were also confirmed with WAXD measurements. Figure 3 presents the WAXD diffractogram of P-20. Although there existed a melting transition peak in the DSC curve of P-20, no significant diffraction peak appeared in the X-ray diffraction pattern because of its low degree of crystallinity. Other samples showed similar broad and diffuse peaks on their WAXD curves. Perhaps the bulky substituent and nonlinear structure derived from IPA disturbed the regularity and symmetry of the molecular chain so that the potential crystallizability was greatly reduced. Additional work is required to characterize the structure more accurately.

Thermal stability

TGA traces of these copolyesters provided information regarding their thermal stability and thermal degradation behaviors. Figure 4 shows their thermal degradation curves under a nitrogen atmosphere. Thermal degradation revealed one decomposition step. The T_d 5% values of this series of copolyester ranged from 431 to 462 $^{\circ}\text{C}$. The results indicated that these polymers had good thermal stability. The char yields at 640 $^{\circ}\text{C}$ were 41–52%. The amount of char formed in the thermal decomposition was linearly proportionate to the LOI of halogen-free polymers.²² The char formation could limit the production of combustible gases, decrease the exothermicity of the pyrolysis reaction, and lower the thermal conductivity of the burning materials, consequently reducing the flammability of the polymers. The LOIs of the copolyesters were about 70, which was higher than that of general aromatic polyesters. The results indicated that the incorporation of phosphorus into the side groups increased the fire resistance of the polymers without drastically reducing their thermal stability.

Mesophase identification

For the characterization of the melt morphology of the copolyesters, the copolyesters were evaluated by visual observation on a hot-stage polarizing microscope. Samples were heated to 300 $^{\circ}\text{C}$ and pressed into thin films between two cover glasses, and shear force was applied by the upper cover slide being shifted. They were then quenched in an ice–water bath. The morphology of the polymers at elevated temperatures should have been frozen. All the copolyesters (except P-40) formed nematic melts according to observations of their optical texture on a cross-polarizing microscope. Two representative photomicrographs are given in Figure 5. Both photomicrographs display banded textures perpendicular to the direction of shear. The formation of a banded texture on shearing is a typical phenomenon for rigid-main-chain, thermotropic, liquid-crystal polymers.²³ However, copolyester P-40 did not reveal any mesophase under the observation conditions. It is possible that the relatively high density of the bulky substituent in the polymer chain destroyed the ability to form a liquid-crystal phase.

CONCLUSIONS

A series of phosphorus-containing, wholly aromatic thermotropic copolyesters were synthesized. Because of the rigidity of the main chain and the presence of the bulky substituent on the hydroquinone unit, the T_g 's of the polymers were rather high, ranging from 183 to 192 $^{\circ}\text{C}$. Except for P-20 and P-25, the copolyes-

ters showed no significant melting peaks on the DSC traces. The results of WAXD indicated that the polymers were almost amorphous. T_m of P-20 was 290°C, and T_m of P-25 was 287°C. The initial flow temperatures of other copolyesters observed on a hot-stage polarizing microscope were 271–290°C. TGA showed that all the polymers exhibited excellent thermal stability up to 430°C and had high char residues at 640°C. It was confirmed that the incorporation of phosphorus into the side groups led to good flame retardancy. All the polymers, except P-40, showed banded textures at elevated temperatures. Perhaps the relatively high density of the bulky substituent in the main chain of P-40 destroyed the ability to form a liquid-crystal phase.

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