Synthesis and Properties of Phosphorus Containing PET and PEN (I)

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ABSTRACT: 2-(6-Oxido-6H-dibenz $\langle c,e \rangle \langle 1,2 \rangle$ oxaphosphorin-6-yl) dimethyl itaconate (ODOP-DI) was prepared by the addition reaction between 9,10-dihydro-9-oxa-10phosphaphenanthrene-10-oxide (DOPO) and dimethyl itaconate while DOPO was synthesized through multistep reaction from *o*-phenylphenol and phosphorus trichloride. The compound (ODOP-DI) was used as a reactive flame retardant in polyethylene 1,4-terephthalate (PET) and polyethylene 2,6-naphthalate (PEN) for film, fiber, and electronic applications. The thermal properties of the resulted copolyesters were investigated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Owing to the incorporation of the rigid structure of DOPO and pendant P groups, the resulted phosphorus containing copolyesters exhibited better flame retardancy, higher char yield, and thermal stability than homopolymers of PET and PEN. UL 94-VO rating could be achieved with a phosphorus content of as low as 0.75% for PET, 0.5% for PEN, and no fume and toxic gas emission were observed. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1959–1964, 1998

Key words: 2-(6-oxido-6H-dibenz $\langle c,e\rangle\langle 1,2\rangle$ oxaphosphorin-6-yl)-dimethyl itaconate; flame retardancy

INTRODUCTION

Owing to extreme environmental and health restrictions, the flammability of commercial polymers has received considerable global attention during the last 2 decades. Among various desirable properties of flame-retardant polymers, the increased thermal stability has been emphasized.¹⁻⁶ Phosphorus compounds have been used as flame retardants in synthesizing various phosphorus-containing polymers, either alone or in conjunction with nitrogen and/or halogen.^{7,8} In a fire, halogens bromine and chlorine produce problems of smoke, toxicity, and corrosion. Organic phosphates do not cause any of these problems. Organophosphorus compounds have demonstrated good ability as flame retardants for polymeric materials by forming a carbonaceous char that acts as a physical barrier to heat transfer from the flame to the polymer and diffusion of combustible gases.^{9–11} Furthermore, the covalently incorporated flame retardant, i.e., using a reactive flame retardant, has led to high flame retardancy.^{11–14} Thus, organophosphorus compounds should be the most desirable class of flame-retardant additive.

The demand for polyethylene 1,4-terephthalate (PET), in film, bottle, and fiber form, is very large.¹⁵ Polyethylene 2,6-naphthalate (PEN) is

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well known as a high-performance engineering thermoplastic because of its good thermal stability, chemical resistance, and excellent mechanical properties. The versatility in formulations also enables wide use of these polyesters in electronic and electrical applications, printed circuits, and wiring applications etc.¹⁶⁻¹⁸ However, like other organic polymeric materials, the flammability of PET and PEN is a shortcoming in some applications. In this article, our attempt is to incorporate a flame-retardant phosphorus-containing group into PET and PEN to form flame-retardant copolyesters via the transesterification $process^{19-22}$ utilizing ODOP-DI. The monomer was characterized by EA, GC-MASS, and IR spectroscopy. The thermal stability and flammability of the copolyesters were evaluated by DSC, thermogravimetry, and UL-94 V-test, respectively.

EXPERIMENTAL

Raw Materials

9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10oxide (DOPO), was prepared in our laboratory.²³ Dimethyl itaconate, dimethyl terephthalate, and 2,6-dimethyl naphthalate (Amoco) were the commercial products and were used without further purification. Ethylene glycol (Ferak) was reagent grade and was also used without further purification. All catalysts were commercial products (guaranteed reagent grade) and were used without purification. The solvents, phenol (Ferak), and tetrachloroethane (Merk) were used for the determination of intrinsic viscosities of PET, PEN, and their copolyesters.

Instrumentation

Elemental analyses were performed using a Heraeus CHN-O-Rapid elemental analyzer. IR spectra were recorded with an infrared spectrophotometer (Nicolet 5DX-B). Mass spectra were recorded by a VG 70-520 GC/MS. Intrinsic viscosities were obtained by using an Ubbelohde capillary viscometer (Schott-AVS310). Melting points of ODOP-DI were determined in a polarizing microscope (Laboratory Devices MEL-TEMP II). DSC data were obtained from 8–10 mg samples in a nitrogen atmosphere at 20°C min⁻¹ heating rate using a Perkin-Elmer DSC 7 differential scanning calorimeter. TGA data were obtained from 8–10 mg samples in a nitrogen atmosphere in a nitrogen atmosphere site at a scanning calorimeter. at a 20°C min⁻¹ heating rate using a Perkin-Elmer TGA 7 thermogravimetric analyzer.

Synthesis of ODOP-DI

The 2-(6-oxido-6H-dibenz $\langle c, e \rangle \langle 1, 2 \rangle$ oxaphosphorin-6-yl) dimethyl itaconate (ODOP-DI) was prepared from dimethyl itaconate and 9,10-dihydro-9-oxa-10phosphaphenanthrene 10-oxide (DOPO), which was prepared by our laboratory.²³ A typical procedure for the preparation of ODOP-DI is as follows: xylene (200 mL) and DOPO (100 g) were added to a flask and heated to 90°C with stirring under nitrogen atmosphere. To the stirring mixture, dimethyl itaconate (68.53 g) was added incrementally over 2 h. After the completion of dimethyl itaconate addition, the reaction mixture was refluxed for another 10 h, resulting in precipitation of product. The product was filtered and recrystallized from xylene. The yield of ODOP-DI was 96%; m.p. 104-105°C; EI mass spectrum intensity (%) 374 (60, M⁺).

Anal. calcd for $C_{19}H_{19}O_6P$: C, 60.96%; H, 5.12%; O, 25.64%; P, 8.27%. Found: C, 60.92%; H, 5.08%; O, 25.72%; P, 8.28%.

Synthesis of PET and PET-co-ODOPDI

To a three-necked 500-mL glass vessel equipped with a stirrer and a distillation column, 0.5 mol of dimethyl terephthalate (DMT) and ODOP-DI (the mol ratio of DMT : ODOP-DI = 0.5 : 0; 0.482 : 0.018;0.473 : 0.027; 0.463 : 0.037; and 0.451 : 0.049 to obtain various P% content), 1.0 mol ethylene glycol, and 3×10^{-4} mol zinc acetate were introduced. The reaction was carried out with stirring under a nitrogen atmosphere at 185°C. Methanol was continuously removed by distillation for a period of 5 h to complete the transesterification. After the addition of 3×10^{-4} mol antimony trioxide, the reaction mixture was heated to 250°C and maintained at that temperature for 15 min. The pressure of the reaction system was gradually reduced first to 180-200 mmHg over the course of 10 min and then the temperature was raised to 270°C. In the course of another 10 min, the pressure was further reduced to 1-3 mmHg, and the reaction temperature was raised to 285°C. The polymerization was conducted isothermally at $285 \pm 2^{\circ}$ C for the required period of time with simultaneous removal of ethylene glycol and other volatiles by distillation. Finally, the pressure was returned to normal atmospheric pressure using nitrogen to prevent degradation by oxidation, and the polymer was then extruded. The polyesters of PEN and PEN-co-ODOPDI were prepared by the same procedure.

Intrinsic Viscosity Determination

Intrinsic viscosity of the polymer was measured using an Ubbelohde viscometer. The advantage of using this viscometer is that the measurement is independent of the amount of solution in the viscometer, and viscosity can easily be calculated by the Ram Mohan Rao equation.²⁴ The polymer sample (0.06 g) was accurately weighed (0.001 g)and dissolved in 25 mL of symmetric tetrachloroethane/phenol (2:3 w/w). The solution was maintained at 120°C for 20-25 min to achieve a complete solution of the polymer in the solvent. The solution was then cooled to room temperature and filtered through a 0.45 μ m disposable membrane filter (cellulose acetate). Using the viscometer at 30°C, the intrinsic viscosity was calculated from the relative viscosity by means of the Ram Mohan Rao equation.

UL-94V Flame-Retardant Test

The UL-94V test was performed according to the testing procedure of FMVSS 302/ZSO 3975 with a test specimen bar of 127 mm in length, 12.7 mm in width, and about maximum up to 12.7 mm in



(ODOP-DI)





Figure 1 IR spectrum of ODOP-DI.



Scheme II Schematic diagram of Copolyesters

thickness. The UL-94V test determines the upward-burning characteristics of a solid. Five sample bars suspended vertically over surgical cotton were ignited by a Bunsen burner, two ignitions with 10-s burning time were applied to each sample bar. The samples of polyester with various P-content of PET, PET-co-ODOPDI, PEN, and PEN-co-ODOPDI were subjected to the UL-94V test.

RESULTS AND DISCUSSION

The ODOP-DI synthesis is shown in Scheme 1, and its IR spectrum is shown in Figure 1. The strong absorption around 1238 cm⁻¹ corresponds to vibration with P=O, which is characteristic of phosphoric compounds. The ODOP-DI also showed strong absorptions around 1148 and 904 cm⁻¹ corresponding to P=O=C (aromatic) stretching; the P=C stretching absorptions around 1400–1500 cm⁻¹, C=C absorption around 1600 cm⁻¹ and C=O absorption around 1750–1735 cm⁻¹, which support the ODOP-DI structure. The formation of PET-co-ODOP-DI and PEN-co-ODOP-DI is shown in Scheme II.

Thermal Properties of PET-co-ODOP-DI and PEN-co-ODOP-DI

The thermal properties and the resultant intrinsic viscosities of the phosphorus-containing copolyesters are listed in Table I. Essentially all polyesters synthesized had intrinsic viscosities greater than 0.5 dL/g (equivalent to the weightaverage molecular weight greater than 30,000). Because the molecular weights are rather high, the effect of molecular weight on the thermal stability can be consider to be less significant than that of the composition.

Table I indicated that the melting points (T_m) and the glass transition temperatures (T_g) of both types of copolyesters (PET-co-ODOPDI and PENco-ODOPDI) were lower than that of homopolymers of PET and PEN with a trend toward lower T_m and T_g as the phosphorus content increased.

Thermogravimetric analysis (TGA) is the most favored technique for rapid evaluation in comparing and ranking the thermal stability of various polymers. Thermogravimetric analyses of the various P-containing copolyesters in nitrogen are shown in Table II. The results indicated that both PET-co-ODOP-DI and PEN-co-ODOP-DI with various P-contents had higher char yield than those of PET and PEN homopolymers (Fig. 2). Although the weight loss temperatures of 1, 5, and 10% for PET and PEN were slightly higher than those of P-containing copolyesters, their rapid weight loss occurred at lower temperatures than their corresponding P-containing copolyesters (Table II). This phenomenon played an important role in improving the flame retardancy of P-containing copolyesters. While on fire, the phos-

Table I	Thermal Properties and Intrinsic
Viscositi	es (I.V.) of Phosphorus-Containing
Copolye	sters

Sample	P-Content (0%)	T_{g}	T_m	1.V. (dL/g)
PFT Control	0.00	78	959	0.543
PET-A	0.00	78 72	$\frac{252}{242}$	0.545
PET-B	0.75	69	238	0.607
PET-C	1.00	69	235	0.576
PET-D	1.25	65	216	0.626
PEN-Control	0.00	118	260	0.564
PEN-A	0.50	109	248	0.635
PEN-B	0.75	105	241	0.511
PEN-C	1.00	104	No	0.572
PEN-D	1.25	102	No	0.566

		Temperature of Weight Loss				Char Yield
Sample	P-Content (%)	1%	5%	10%	Rapid	at 700°C
PET-Control	0.00	405	431	443	479	12
PET-A	0.50	397	423	433	480	14
PET-B	0.75	393	421	433	481	14
PET-C	1.00	397	421	433	482	16
PET-D	1.25	393	417	429	483	17
PEN-Control	0.00	417	441	451	475	21
PEN-A	0.50	417	437	451	482	23
PEN-B	0.75	407	435	447	485	25
PEN-C	1.00	405	429	443	485	27
PEN-D	1.25	401	429	443	489	27

Table II Thermogravimetric Properties of P-Containing Copolyesters

phorus-containing group first decomposed at a lower temperature, and then formed a phosphorus-rich residue that prevented further decomposition of the copolyester, by raising their rapid decomposition temperature to higher level and resulted in a higher char yield. The char yields at 700°C for PET, PET-D, PEN, and PEN-D were 12, 17, 21, and 27%, respectively.

UL-94V Test for Copolyesters of PET and PEN

The UL-94V test determines the upward-burning characteristics of a solid. Five sample bars of each



Figure 2 TGA thermograms of polyesters (A) PET-control, (B) PET-D, (C) PEN-control, PEN-D.

Sample	P-Content (%)	Burning Time (s)	Drip	Cotton	Classification
PET-CON	0.00	23	heavy	fire	V-2
PET-A	0.50	11	middle	no	V-1
PET-B	0.75	<1	scarcely	no	V-0
PET-C	1.00	0	no	no	V-0
PET-D	1.25	0	no	no	V-0
PEN-CON	0.00	12	middle	no	V-1
PEN-A	0.50	2	no	no	V-0
PEN-B	0.75	0	no	no	V-0
PEN-C	1.00	0	no	no	V-0
PEN-D	1.25	0	no	no	V-0

Table III UL-94 Test for P-Containing Copolyesters of PET and PEN

PET-co-ODOP-DI and PEN-co-ODOP-DI suspended vertically over surgical cotton were ignited by a Bunsen burner; two ignitions of 10 s each were applied to the sample. It is clear from the result of Table III that the flame retardancy of P-containing copolyesters increased with phosphorus content in the copolyesters. Besides P-containing PET being much more flame retardant than PET, it also generated less fume and drip than PET. The same phenomena were also observed in PEN and PEN-co-ODOPDI. It should be noted that less amount of ODOPDI was required to achieve UL-94 test V-0 rating for PEN than PET.

CONCLUSION

A reactive phosphorus-containing flame-retardant, 2-(6-oxido-6H-dibenz $\langle c, e \rangle \langle 1, 2 \rangle$ oxaphosphorin-6-yl) dimethyl itaconate (ODOPDI) was successfully synthesized. The compound was used as a starting material to incorporate the P-containing group into PET and PEN. The resulted Pcontaining copolyesters exhibited an excellent flame-retardant effect with a phosphorus content of as low as 0.75 and 0.5%, respectively, for PET and PEN.

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