Synthesis and Characterization of Copolyesters Containing the Phosphorus Linking Pendent Groups

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ABSTRACT: Poly(ethylene terephthalate)-*co*-poly(ethylene DDP)s [PET-*co*-poly(ethylene DDP)s], were synthesized by charging 9,10-dihydro-9-*oxa*-10-phosphaphenanthrene-10-oxide (DOP), itaconic acid, terephthalic acid, and ethylene glycol in one reactor to conduct the microaddition reaction (using H_2PtCl_6 as catalyst), esterification reaction, and polycondensation reaction. H_2PtCl_6 has demonstrated to be a highly efficient microaddition catalyst to improve the DDP conversion. The microaddition reaction of the phosphorus compound (DOP) with the itaconic acid can be proceeded at a significantly lower temperature (110°C) and results in higher conversion (> 98%). The use of the H_2PtCl_6 catalyst makes it possible to charge all the reactants in one reactor to produce high molecular weight phosphorus-containing copolyesters without requiring the presynthesis of the DDP. These resulting copolyesters are identified by Fourier transform infrared spectroscopy, ^{1}H-NMR, and differential scanning calorimetric analysis. Thermal characteristics, thermal stability, intrinsic viscosity, acid value, and rheological and mechanical properties of these copolyesters were also characterized. The presence of the bulky pendent phosphorus side groups in the copolyester tends to decrease the structural regularity and retards its crystallization. The formation of a protected char layer for the phosphorus-containing copolyester raises the decomposition temperature of the copolyester under an oxygen atmosphere higher than that of PET. The limiting oxygen index values of all phosphorus-containing copolyesters are all higher than 33. Higher phosphorus content results in decreasing crystallinity, lower melting temperature, lower decomposition temperature, as well as lower tensile strength, but increasing residual char after thermal degradation and higher limiting oxygen index value. The rheological behaviors of copolyesters remain similar to that of PET. The glass temperatures of copolyesters are all ∼ 77°C (76.8°–77.2°C). Incorporation of phosphorus moieties into its molecular chain has a significant effect on thermal and flame retardancy behavior. However, the crystal lattice of all copolyesters do not change with incorporation of the pendent phosphorus side group in the backbone of the copolyester. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 109–122, 1999

Key words: phosphorus-containing copolyester; synthesis; characterizations; flame retardant

INTRODUCTION

To impart flame retardancy of polyester, it can be achieved by blending, finishing, and copolymerization. The method of blending an additive-type flame retardant has the advantages of convenience and low manufacturing cost.[1] However, organic flame retardant in the blend may not be able to retain during melt processing because of volatility or decomposition at an elevated temperature. In addition, poor compatibility between polymers and flame retardant may cause migra-

Reaction Method A

Scheme 1   Synthesis of PET-*co*-PEDDP polymer by reaction method A.

tion of flame retardant to the surface of the fabricated products and results in reduced flame retardation.[2–5]

Polyesters are usually extruded into filaments at a temperature higher than 290°C that often makes the organic flame retardant degraded, and results in breaking of filaments. If polyesters are blended with an inorganic flame retardant, the spinnerets may be blocked when they are spun and affect the pack pressure in spinning. Additionally, inorganic flame retardants are usually detrimental to the physical properties of polyesters.

When polyesters are woven into fabrics or nonwoven fabrics, another approach is to coat or finish a layer of flame retardant on fabricated articles of polyester fabrics to render such fabrics flame retardant. This method had the advantages of easy treatment. However, its disadvantage is that only the surface of the fabricated articles is flame retarded and coated flame retardant will be gradually washed off.

Copolymerization is an alternative to improve the flame resistance of polyester. Incorporating a chemically reactive flame retardant into a polymer chain, it will not migrate to the surface of the polymer during processing. Both the flame-re-

tarding effect and physical properties of the polymer are not affected. They also display well washing fastness and permanent flame retardancy. The permanent attachment of a flame retardant through copolymerization leads to high efficiency in flame retardance.[6–11]

To improve heat resistance, compatibility, and migration problems of a conventional retardant, we have imported a phosphorus-containing comonomer into the main chain of the polyester. To avoid the generation of toxic, corrosive, or halogenated gases in combustion, nonhalogenated flame retardants are preferred. Consequently, phosphorus-containing compounds are often chosen for the flame retardation of organic polymers.[6,12–16] As the phosphorus-containing comonomer is chemically incorporated into the polyester backbone with low molar ratio, it can be considered as a flame-retardant poly(ethylene terephthalate) (PET). If the flame-retardant comonomer is chemically incorporated into the polyester backbone with high molar ratio, it serves as a compatible high molecular flame retardant. When this compatible high molecular flame retardant is blended with polyester, it will not migrate to the surface during melt processing, such as extruding, injection molding and spin-

Reaction Method B

Scheme 2 Synthesis of PET-*co*-PEDDP polymer by reaction method B.

ning. Therefore, the efficiency of flame retardancy will not be affected. The blended polyester can retain their physical properties and permanent flame retardancy.

This article reports syntheses of a series of high molecular weight phosphorus-containing copolyesters, PET-*co*-poly(ethylene DDP) (PET-*co*-PEDDP)], with phosphorus contents ranging from 0.7 to 3.0 wt % by melt polycondensation. These copolyesters are based on terephthalic acid (TPA), ethylene glycol (EG), and 9,10-dihydro-10[2,3-di-(hydroxy carbonyl)propyl]-10-phosphaphenanthrene-10-oxide (hereinafter referred to as DDP).

These phosphorus-containing copolyesters were identified by infrared (IR) spectroscopy and ^{1}H-NMR spectroscopy. Thermal, rheological, and mechanical properties of these phosphorus-containing copolyesters were also characterized. Furthermore, the widely used indexes of flame resistance and the limiting oxygen index (LOI) were also examined.

EXPERIMENTAL

Reagents

TPA and EG were obtained from Tuntex Distinct Corp. of Taiwan. 9,10-Dihydro-9-*oxa*-10-phospha-

phenanthrene-10-oxide (DOP) and itaconic acid (ITA) were purchased from Sanko Ltd. of Japan. Tetrabutyl orthotitanate was purchased from Merck Schichardt Ltd. 1,1′,2,2′-tetrachloroethane, phenol, and trifluoroacetic acid were also purchased from Merck Schichardt Ltd. Dihydrogen hexachloroplatinate was bought from United Chemical Technologies, Inc.

Synthesis of Phosphorus-Containing Copolyesters

To synthesize phosphorus-containing copolyesters, the reactive phosphorus-containing comonomer (DDP) is not commercially available and has to be presynthesized.[17] This necessitates additional equipment for synthesis of this reactive comonomer (DDP), separation, and purification of the resulting phosphorus-containing comonomer. We discovered a metal complex catalyst, that high molecular weight phosphorus-containing copolyesters can be manufactured by charging DOP, ITA, TPA, and EG in a single reactor.

There are three methods (A, B, and C) to synthesize these phosphorus-containing copolyesters. Method A is conducted by charging all reactants (TPA, ITA, DOP, and EG) in one reactor using H_2PtCl_6 as the microaddition reaction catalyst through microaddition, esterification, as well as polycondensation (as shown in Scheme 1).

Reaction Method C (reactor I)

Scheme 3-I   Preperation of PET-*co*-PEDDP polymer by reaction method C (reactor I).

Method B has the same procedures and conditions as method A, except that no catalyst for microaddition reaction is involved, and the microaddition temperature is higher than that of method A (160° *vs.* 110°C) (as shown in Scheme 2). Method C uses two reactors for two batches (as shown in Schemes 3-I and 3-II). The first reactor is used to synthesize phosphorus-containing diacid (DDP) through microaddition reaction of DOP with ITA (as shown in Scheme 3-I). The second reactor is used to synthesize copolyesters by charging DDP, TPA, and EG through esterification and polycondensation (as shown in Scheme 3-II). The three synthesis methods are further described.

Method A (Scheme 1)

A typical example for preparation of copolyesters by method A is described as follows: 74.78 g of DOP, 44.98 g of ITA, 163 g of TPA, 249.4 g of EG, and 0.0078 g of H_2PtCl_6 as microaddition catalyst are added to a 1500-mL stainless reactor equipped with a fractionating column, stirrer, and nitrogen gas inlet. The reactor is heated to 110°C and maintained for 4 h while stirring and purging with nitrogen gas at flow rate of 30 mL min^{-1}. After completion of the microaddition reaction, the temperature is then raised to 230°C throughout the esterification. When the conversion reaches 96%, 0.3087 g of tetrabutyl orthotitanate catalyst is added. The reaction temperature is further raised to 250°–270°C, and the pressure is gradually reduced to < 1 mmHg within 45 min and maintained for 2 h to yield a high molecular flame-retardant polyester.

Method B (Scheme 2)

The same procedures and reaction conditions are used as the reaction method A, except that no catalyst for microaddition reaction was involved, and the temperature of microaddition reaction is 160°C.

Reation Method C (Reaction II)

TPA   EG

DDP

Ti(OBu)₄

esterification at 230°C   polycondensation at 270 °C

PET-co-PEDDP

Scheme 3-II   Synthesis of PET-*co*-PEDDP polymer by reaction method C (reactor II).

Method C (Schemes 3-I and 3-II)

A typical example for preparation of the copolyesters by reaction method C is described as follows.

Reactor I: Synthesis of Phosphorus-Containing Diacid (DDP) (Scheme 3-I)

DOP (216 g) and 130 g of ITA were added to a 1500-mL stainless reactor equipped with a frac-

Table I   Processing Condition for the Injection Molding of Phosphorus-Containing Copolyester and PET

Sample[a]	P[b] (wt %)	Barrel Temperature (°C)				Mold Temperature (°C)
		Stage 1	Stage 2	Stage 3	Nozzle	
PET	0.0	245	250	245	245	50
P$_A$07	0.7	235	245	240	245	50
P$_A$12	1.2	215	235	230	225	50
P$_A$20	2.0	210	210	205	205	50
P$_A$30	3.0	200	180	180	150	50

[a] P$_A$07, P$_A$12, P$_A$20, and P$_A$30 copolyesters are synthesized by reaction method A with 0.7%, 1.2%, 2.0%, and 3.0% (by wt) phosphorus content, respectively.
[b] Wt % of phosphorus content base on total polymer.

Table II   Phosphorus-Containing Copolyesters Synthesized Condition of Each Method and Their Resulting

Sample[a]	Reaction[b] Method	Phosphorus[c] Content (wt %)	DOP[d] (mol %)	Microaddition Catalyst	Microaddition Temperature (°C)	Separation & Purification	DDP[e] Conversion (%)	IV (dL g^{-1})	AN (mEq kg^{-1})
PET	—	0	0	—	—	—	—	0.635	23.2
P$_A$07	A	0.7	4.5	H$_2$PtCl$_6$	110	No	99.0	0.633	19.5
P$_A$12	A	1.2	7.9	H$_2$PtCl$_6$	110	No	98.5	0.624	18.3
P$_A$20	A	2.0	15.0	H$_2$PtCl$_6$	110	No	98.3	0.640	19.5
P$_A$30	A	3.0	22.6	H$_2$PtCl$_6$	110	No	98.1	0.638	22.5
P$_B$20	B	2.0	15.0	Non	160	No	81.0	0.491	34.2
P$_B$30	B	3.0	22.6	Non	160	No	79.0	0.500	36.5
P$_C$30	C	3.0	22.6	Non	160	Yes	83.3	0.640	21.3

[a] P$_A$07, P$_A$12, P$_A$20, and P$_A$30 copolyesters are synthesized by reaction method A, with 0.7, 1.2, 2.0, and 3.0 wt % phosphorus content, respectively, & P$_B$20 and P$_B$30 copolyesters are synthesized by reaction method B, with 2.0 and 3.0 wt % phosphorus content, respectively, P$_C$30 copolyester is synthesized by reaction method C, with 3.0 wt % phosphorus content.

[b] Reaction method A is a one reactor-one batch method, with H$_2$PtCl$_6$ as a microaddition catalyst; reaction method B is a one reactor-one batch method, without microaddition catalyst. Reaction method C is a two reactors-two batches method with separation and purification.

[c] Desized phosphorus content of phosphorus-containing copolyesters.

[d] Desized molar fraction of the phosphorus compound (DOP) of the phosphorus-containing copolyester.

[e] DDP conversion is calculated from ^{31}P-NMR results as shown Figure 1, % DDP conversion = $I_{DDP}/(I_{DOP} + I_{DDP}) \times 100\%$.

tionating column, stirrer, and nitrogen gas inlet. The reactor was heated to 160°C and maintained for 1.5 h with continuous stirring and nitrogen purging to produce a crude phosphorus-containing diacid (DDP). The crude DDP was purified by adding the crude DDP to 500 mL of acetone and refluxing at 60°C for 2 h. Alternatively, the crude DDP can be purified by crystallizing from acetone. The melting point of the purified product is 195°C, and the conversion is 83.3%.

Reactor II: Synthesis of Phosphorus-Containing Copolyester (Scheme 3-II)

Purified DDP (124.25 g), 163 g of TPA, and 249.4 g of EG were added into a 1500-mL stainless reactor equipped with a fractionating column, stirrer, and nitrogen gas inlet. The reaction mixture was heated to 230°C and maintained at this temperature while purging with nitrogen gas until the conversion of this esterification is at 96%. Tetrabutyl orthotitanate catalyst (0.3087 g) is then added to the reaction system. The reaction temperature was further raised to 270°C, and the pressure was gradually reduced within 45 min to < 1 mmHg and maintained for 2 h to give the phosphorus-containing copolyester.

Characterizations

The intrinsic viscosities of copolyesters were determined by an Ubbelohde viscometer at 30°C in the phenol/1,1′,2,2′-tetrachloroethane (60/40 wt%) solution. Acid values are obtained by dissolving samples
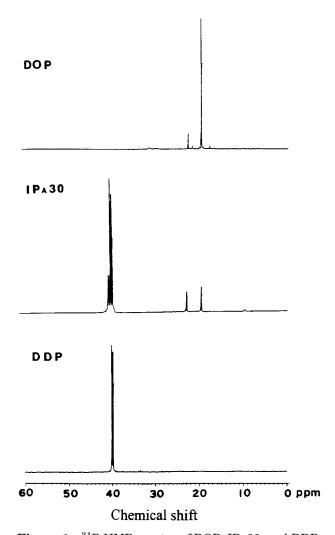

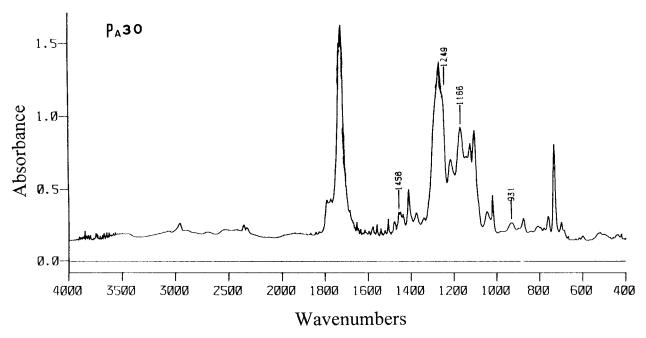**Figure 1** ^{31}P-NMR spectra of DOP, IP$_A$30, and DDP.

Figure 2 Fourier transform IR spectrum of P_A30.

in a 3 : 2 solvent mixture of phenol and chloroform, and titrated with $0.1N$ KOH/phenyl alcohol solution using phenol red as an indicator. The ^{31}P-NMR spectra of DDP are conducted with a Bruke Am NMR by using trifluoroacetic acid as a solvent and phosphorus acid as an internal standard. The DDP conversion (the conversion of DOP reacted with ITA to convent to DDP) is calculated from the result of ^{31}P-NMR. Metertek SP-830 UV spectrophotometer is used to determine the phosphorus content of the copolyester.[18] IR spectra are recorded by a Bio-RAD FTS-40 FTIR Spectrophotometer, and ^{1}H-NMR spectra of the copolyesters in d-trifluoroacetic acid are determined with a Bruke Am 400 NMR.

Melting point (T_m), heating crystallization temperature (T_{hc}), and glass transition temperatures (T_g) of the phosphorus-containing copolyesters were determined by a DuPont 910 differential scanning calorimetry (DSC) at heating rate of $10°C$ min^{-1} under a nitrogen atmosphere. The cooling crystallization temperature (T_{cc}) was obtained by cooling the sample from $300°C$ at a cooling rate of $10°C$ min^{-1}. Thermogravimetric analysis was conducted by using a DuPont Model 951 TGA using a heating rate of $20°C$ min^{-1} under oxygen and nitrogen atmospheres, respectively. Rheological properties were performed using a Gottfert 2001 Capillary Rheometer at $270°C$. The flammability test is based on LOI measurement according to the ASTM D2863-67

method. Crystallinity was determined by a Rigaku D/MAX-RC X-ray diffractometer using the Ni-filtered CuK_α radiation at 100 mA and 40 kV.
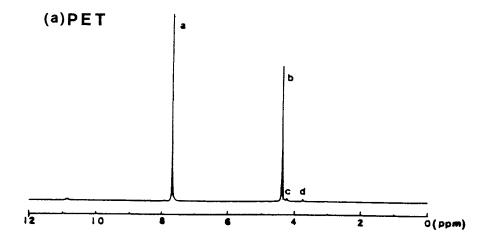
Dynamic mechanical analysis (DMA) was conducted by using a DuPont DMA Model 983 at temperature range from -150 to $150°C$ under a nitrogen atmosphere. The dimension of DMA specimen is 50 mm $\times$ 12.7 mm $\times$ 3.2 mm.

Tensile properties were performed by using an Instron universal testing machine Model 4201 according to the ASTM D368 with a crosshead speed of 5 mm min^{-1}. Impact properties are performed by using a Test Machine Inc. impact tester according to the ASTM D256 method. The testing specimens were prepared by an injection-molding machine of Toshiba 55EPN. Detailed processing conditions for injection molding are listed in Table I.

RESULTS AND DISCUSSION

Syntheses and Characterization

The phosphorus-containing copolyesters of P_A07, P_A12, P_A20, and P_A30 were obtained by method A, as shown in Scheme 1 (copolyesters by method A with a phosphorus content of 0.7 wt % is denoted as P_A07, 1.2 wt % is denoted as P_A12, and so on).
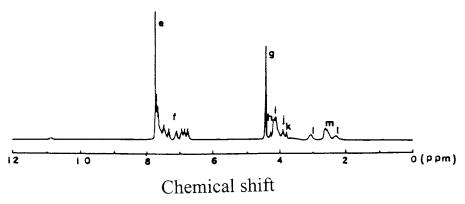
(a)PET

(b)P$_A$30

Chemical shift

Figure 3 ^{1}H-NMR spectra of PET and P$_A$30.

The phosphorus-containing copolyesters of P$_B$12 and P$_B$30 were synthesized by method B, with a phosphorus content of 1.2 wt % and 3.0 wt %, respectively, as shown in Scheme 2. P$_C$30 was synthesized by method C, with a phosphorus content of 3.0 wt % as shown in Scheme 3. Table II lists various copolyesters, synthesized method, conversion, intrinsic viscosities (IVs), and acid values (ANs). The DDP conversion is indicative of the efficiency of DOP converting into DDP during synthesis. Typical DDP conversion is calculated from ^{31}P-NMR results (as shown Fig. 1). The DDP conversion of IP$_A$30, an intermediate of P$_A$30 prior to esterification reaction, is calculated as follow:

$$\% \text{ DDP conversion} = \frac{I_{DDP}}{I_{DOP} + I_{DDP}} \times 100\%$$

where I_{DDP} is the intensity of ^{31}P-NMR at 40 ppm chemical shift, and I_{DOP} is the intensity of ^{31}P-NMR at 20 ppm chemical shift. Table II reveals that copolyesters with higher IV and lower AN were obtained by methods A and C than that of method B. Relative to method A, the procedures of method C are tedious and require additional equipments for synthesis, separation, and purification. By comparison, results from method A is better than method B, based on higher IV and lower AN of the resultant copolyesters. It reveals that the metal complex H$_2$PtCl$_6$ is a highly efficient catalyst. Therefore, the microaddition reaction of the DOP with ITA in method A can be proceeded at a substantially lower temperature (110°C *vs.* 160°C) and results in higher conversion (>98% *vs.* 79%, 81%). The use of this catalyst makes it possible to charge all the reactants in

PET

a

b   c   d

PET-CO-PEDDP

e   e   h   k

m

Scheme 4 Chemical structures of PET and PET-*co*-PEDDP polymer.

one reactor and produces high molecular weight, phosphorus-containing copolyesters. We will concentrate our discussion on syntheses of these phosphorus-containing copolyesters (P_A07, P_A12, P_A20, and P_A30) by method A. The high phosphorus conversion by method A shown in Table II reveals that the phosphorus content of the resulting copolyesters can be effectively controlled *via* changing the reactant feed ratios. Additionally, copolyesters with high intrinsic viscosity (> 0.620 dL g^{-1}) and low acid value (< 23 mEq kg^{-1}) can be achieved. Table II shows that method B gives copolyesters with relatively lower intrinsic viscosities (≤ 0.500 dL g^{-1}) and higher acid values (> 34 mEq kg^{-1}) due to lower DDP conversion relative to method A. It is well known that higher impurity in reactants in any polycondensation reaction would result in lower molecular weight of the product. The result of P_C30 indeed demonstrates this point that method C is able to produce product with high intrinsic viscosity (0.640 dL g^{-1}) and low acid value (21.3 mEq kg^{-1}), because DDP is separated and purified before copolycondensation.

The IR spectrum of the P_A30 copolyester is shown in Figure 2. Absorptions of $\nu_{p=0}$ at 1249 cm^{-1}, ν_{p-o-c}(aromatic) at 1166 cm^{-1}, 931 cm^{-1}, and ν_{p-ph} at 1456 cm^{-1}, respectively, are the characteristic absorptions of the copolyesters.[6,7,19–22] Proton NMR spectra of both PET and P_A30 copolyester are illustrated in Figure 3(a,b). The chemical structure and resonance peak assignments are shown in Schemes 4 and 5 and in Table III.

Thermal, Rheological, and Physical Properties

The charged monomer molar fractions of the phosphorus-containing compound (DOP), melting temperatures (T_m), glass transition temperatures (T_g), cooling crystallization temperatures (T_{cc}), and heating crystallization temperatures (T_{hc}) of the synthesized phosphorus-containing copolyesters P_A07, P_A12, P_A20, and P_A30 are summarized in Table IV. All the intrinsic viscosities of these phosphorus-containing copolyesters are ~ 0.633 to 0.640 (as shown in Table II). These intrinsic viscosities indicate that the molecular weights of these phosphorus-containing copolyesters are high and fairly close. Therefore, the effect of molecular weight on polymer properties can be neglected. DSC thermograms of PET and copolyesters P_A07, P_A12, and P_A30 are shown in Figure 4. P_A07 and P_A12 copolyesters exhibit similar thermal behavior to that of PET, but have lower T_m (236°C and 228°C *vs.* 257°C) and higher T_{hc} (165°C and 174°C *vs.* 158°C). This is an indication of slower rate of crystallization of the copolyesters than PET. As can be seen from Figure 4, P_A30 copolyester only exhibits one glass transition, whereas crystallization does not occur. The pres-

T-E-T

P-E-T(T-E-P)

P-E-P

T-E-OH

Scheme 5   Sequences of PET-*co*-PEDDP polymer.

ence of the bulky pendent phosphorus side groups in the copolyester tends to decrease the structural regularity and retards its crystallization. The X-ray diffraction patterns of PET and copolyesters (P_A07, P_A12, and P_A30) are shown in Figure 5. The intensity of scattering is plotted as a function of 2θ. These relatively sharper peaks are from the crystalline region, and the broad region is from the noncrystalline region. Figure 5 clearly shows that the crystalline region of copolyester decreases qualitatively with the increase of the phosphorus content. As the phosphorus content of copolyester reaches 3% (i.e., the DDP comonomer molar fraction of copolyester is 22.6%), the result of wide-angle X-ray diffraction shows that the

relatively sharp peaks are almost vague of P_A30. High content of bulky pendent phosphorus side group (P_A30) in copolyester totally retards its crystallization. However, all copolyesters exhibit a similar diffraction pattern, implying the similar crystal lattices of all copolyesters, regardless of incorporating the phosphorus-containing comonomer in the backbone of the polyester.

The thermogravimetric analysis results of PET and the phosphorus-containing copolyesters under nitrogen atmosphere are summarized in Table V. It is clearly shown that an increase in the phosphorus content results in lower decomposition temperature, but higher residual char. The LOI value is used as an indicator to evaluate polymer flame retardancy. The flame retardancy of a phosphorus-containing polymer, the correlation with its phosphorus content, and residual char have been previously studied.[23–25] Table V summarizes LOI value, the corresponding residual char, and the decomposition temperatures of PET and phosphorus-containing copolyesters. Both LOI value and residual char increase as the phosphorus content is increased. Table V reveals that PET has the highest thermal decomposition temperature (T_d = 442°C) under a nitrogen atmosphere, followed by P_A07 copolyester (T_d = 442°C), P_A12 copolyester (T_d = 426°C), P_A20 copolyester (T_d = 419°C), as well as P_A30 copolyester (T_d = 413°C). Reduced thermal stability with higher phosphorus content is due to more P—O bond cleavage of those phosphorus-containing copolyesters. However, under oxygen atmo-

Table III   Assignments of Resonance Peaks of PET and Copolyester P_A30

Quence	Proton	Chemical Shift (ppm)
PET	a	7.79
	b	4.48
	c	4.34
	d	3.86
P_A30^a	e	7.79
	f	7.53–6.81
	g	4.48
	h	4.34
	i	4.25–4.17
	j	3.97
	k	3.86
	$l(l_1, l_2)$	3.12,2.34
	m	2.63–2.71

[a] P_A30 is the copolyester with phosphorus content of 3.0 wt % synthesized by reaction method A.

Table IV   Phosphorus Content, Phosphorus Comonomer Molar Fraction, and Thermal Properties of Various Phosphorus-Containing Polyesters

Sample[a]	P[b] (wt %)	DOP[c] (mol %)	T_{cc}[d] (°C)	T_{hc}[e] (°C)	T_m[f] (°C)	T_g (DSC) (°C)
PET	0	0	188	158	257	81.7
P_A07	0.7	4.5	176	165	236	77.2
P_A12	1.2	7.9	161	174	228	77.2
P_A20	2.0	15.0	148	—	188	77.0
P_A30	3.0	22.6	—	—	—	76.8

[a] P_A07, P_A12, P_A20, and P_A30 are copolyesters with 0.7 wt %, 1.2 wt %, 2.0 wt %, and 3.0 wt % of phosphorus content, respectively.
[b] Wt % of phosphorus content base on total polymer.
[c] DOP is the phosphorus-containing compound.
[d] T_{cc} is the cooling crystallization temperature.
[e] T_{cc} is the heating crystallization temperature.
[f] T_m is melting temperature.
[g] T_g is the glass transition temperature.

sphere, the trend of thermal decomposition temperature has been reversed, as given in Table IV. The formation of a protected char layer[26,27] for the phosphorus-containing copolyester raises the decomposition temperature of the copolyester under oxygen atmosphere higher than that of PET. As illustrated in Table V, the LOI values of all phosphorus-containing copolyesters are higher than 33. These results indicate that these copolyesters have excellent flame retardancy.

The melt viscosity as a function of shear rate for PET and copolyesters at 270°C are delineated in Figure 6. All copolyesters exhibit similar shear thinning behavior as PET. The melt viscosity decreases slightly with the increase of the phospho-
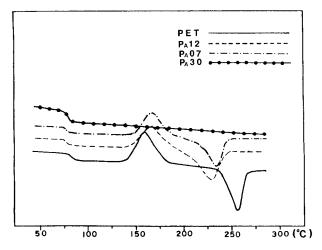
rus content due to the lower melting temperature of phosphorus-containing copolyesters. According to Figure 6, phosphorus-containing copolyester P_A07, P_A12, P_A30, and PET have similar rheological characteristic within the shear rate range of 10^2–10^4 L s^{-1}.

Curves of loss module (E'') vs. temperature from the DMAs of PET (P_A07, P_A12, and P_A30, respectively) are illustrated in Figure 7. All sam-
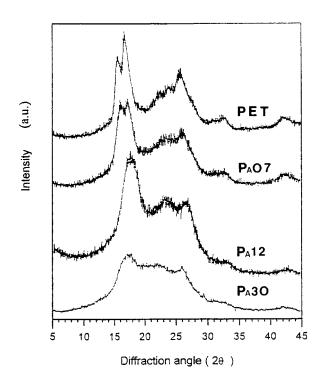

Figure 4   DSC heating scan thermograms of various phosphorus-containing copolyesters P_A07, P_A12, P_A30, and PET.

Figure 5   X-ray diffraction patterns of P_A07, P_A12, P_A30, and PET.

Table V   Decomposition Temperature, Residual Char, and LOI Values of PET, P_A07, P_A12, P_A20, and P_A30

Sample[a]	P (wt %)	T_d[b] (°C) Under Nitrogen	T_d[c] (°C) Under Oxygen	Residual Char[d] (wt %)	LOI
PET	0	442	382	4.2	23.7
P_A07	0.7	431	386	10.0	33.3
P_A12	1.2	426	389	11.8	34.1
P_A20	2.0	419	394	12.4	35.0
P_A30	3.0	413	397	12.5	35.2

[a] P_A07, P_A12, P_A20, and P_A30 are copolyesters with 0.7 wt %, 1.2 wt %, 2.0 wt % and 3.0 wt % of phosphorus content, respectively.
[b] Onset decomposition temperature under nitrogen.
[c] Onset decomposition temperature under oxygen.
[d] Wt % of residual char at 850°C under nitrogen.

ples give two transition temperatures. The lower temperature (around −50°C) correspond to the secondary transition[28,29] due to the rotation of ester (—COO—) and methylene (—CH$_2$—), whereas the higher one (∼ 100°C) corresponds to the glass transition of the main chain motion of the amorphous region. P_A07, P_A12, and P_A30 copolyesters demonstrate a similar dynamic mechanical behavior to that of the PET, but slightly lower T_g at ∼ 97°–102°C (E'' is usually higher than tan δ). In terms of microscale, PET is a homopolymer with homogenous sequence. On the other hand, the phosphorus-containing copolyesters are random copolyesters with heterogeneous sequential lengths ($\overline{L_{np}}$ = 1.158 for P_A30 copoly-
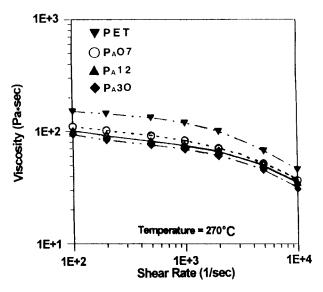
ester and $\overline{L_{np}}$ = 1.012 for P_A07 copolyester, respectively).[30] The width of transition peak has the trend of P_A30 copolyester > P_A12 copolyester > P_A07 copolyester > PET due to longer $\overline{L_{np}}$ of P30. The amorphous region of the copolyester increases with increased of $\overline{L_{np}}$. Furthermore, the sequence of transition temperature is: PET > P_A07 copolyester > P_A12 copolyester > P_A30 copolyester. This observed DMA results again emphasized that amorphous region of copolyester increases qualitatively with the increase of the phosphorus content.

Table VI delineates the tensile strength and Izod impact of the injection-molded specimens for phosphorus-containing copolyesters (P_A07, P_A12, P_A20, and P_A30) and PET. The general trend shows that lower tensile strength for the copolyester with higher phosphorus content. However, the Izod impact increases with the increase of the phosphorus content. The presence of higher phosphorus content of copolyester tends to reduce crystallinity and results in lower tensile strength but higher impact toughness.

CONCLUSIONS

A series of phosphorus-containing copolyesters can be synthesized by charging DOP, ITA, TPA, and EG in one reactor to proceed microaddition, esterification, as well as polycondensation reactions. H$_2$PtCl$_6$ has been demonstrated to be a highly efficient microaddition catalyst to improve DDP conversion. The microaddition reaction of the phosphorus compound (DOP) with ITA can proceed at a significantly lower temperature (110°C), but results in higher conversion (> 98%).

Figure 6   Melt viscosity as function of shear rate for phosphorus-containing copolyesters P_A07, P_A12, P_A30, and PET.
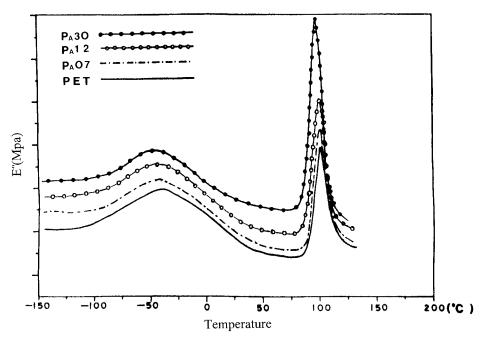
Figure 7 Loss modules (E'') *vs.* temperature from DMA spectra of P_A07, P_A12, P_A30, and PET.

The use of this H_2PtCl_6 catalyst makes it possible to charge all the reactants in one reactor to produce high molecular weight, phosphorus-containing copolyesters without requiring presynthesis of the DDP. Chemical structures of copolyesters were confirmed by Fourier transform infrared spectroscopy, ^{1}H-NMR, and DSC analyses.

For a phosphorus-containing copolyester, the incorporation of phosphorus moieties into a molecular chain has significant effect on its thermal and flame retardancy behavior. The presence of the bulky pendent phosphorus side groups in the copolyester main chain tends to decrease the

structural regularity and retards its ability to crystallize. The formation of a protected char layer for the phosphorus-containing copolyester raises the decomposition temperature of the copolyester under an oxygen atmosphere higher than that of PET. The LOI values of all phosphorus-containing copolyesters are all > 33. A higher phosphorus content results in lower crystallinity, lower melting temperature, lower decomposition temperature, and lower tensile strength, but greater LOI value and higher residual char after thermal degradation. The rheological behavior of these phosphorus-containing copolyesters is similar to that of PET. The glass temperatures of copolyesters are all ~ 77°C (76.8°C–77.2°C). Furthermore, the crystal lattice of all copolyesters does not change with incorporating the pendent phosphorus side group in the backbone of the copolyester.

Table VI   Tensile Strength and Izod Impact of PET, P_A07, P_A12, P_A20, and P_A30

Sample[a]	P (wt %)	Tensile Strength (MPa)	Impact Strength (J M^{-1})
PET	0	60.0	20.9
P_A07	0.7	41.0	24.3
P_A12	1.2	38.0	25.1
P_A20	2.0	33.5	26.4
P_A30	3.0	30.0	27.6

[a] P_A07, P_A12, P_A20, and P_A30 are copolyesters with 0.7 wt %, 1.2 wt %, 2.0 wt %, and 3.0 wt % of phosphorus content, respectively.

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