

Synthesis and Properties of Novel Flame Retardant Poly(butylene terephthalate)

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Abstract: The phosphorus comonomer [(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)methyl]-methyl butanedioate (DOP-MBDA) was synthesized through the addition reaction of dimethyl itaconate (DMI) with 9,10-dihydro-9-oxa-10-phosphaphenan threne-10-oxide (DOP). A series of novel flame retardant poly(butylene terephthalate)s (PBTs) containing different amounts of phosphorus were prepared using DOP-MBDA as a comonomer. These novel polymers were characterized by ¹H-NMR, IR, and differential scanning calorimetry (DSC). The novel phosphorus-containing poly(butylene terephthalate)s, referred to as FR-PBTs, exhibited interesting thermal and mechanical behavior, as well as superior flame retardancy. These properties are attributed to the effect of incorporating the rigid structure of DOP-MBDA and the pendant phosphorus group into the poly(butylene terephthalate) (PBT) homopolymer. The UL 94-V2 rating could be achieved with this novel flame retardant PBT, which has a phosphorus content as low as 0.5 wt%, and the FR-PBTs emitted less fumes and toxic gases than the PBT homopolymer.

Keywords: copolymerization, flame retardance, polyesters, phosphorus monomers.

Introduction

Environmental and health concerns have prompted extensive research into the incorporation of flame retardant compounds into common organic polymers so as to control their inherent flammability. Traditionally, halogen-containing moieties have been incorporated into polymers to increase flame retardancy. However, the combustion of compounds containing halogens such as bromine and chlorine can produce toxic and corrosive products, not to mention thick smoke.¹⁻³

As the requirements for environmental and health consideration have been getting serious in the world, the prohibition of using halogen into polymeric materials as a flame retardant has been recommended strongly by Blue Angel and TOC 99 in Europe. Other organizations are also considering the adoption of similar regulations.

One group of compounds that have shown promise as non-halogen flame retardants are organic phosphates, which are known to be environmentally friendly materials and do not cause any of the problems associated with halogen compounds.^{4,5} Moreover, organophosphorus compounds have shown promise as flame retardants for polymeric materials

because on combustion they form a carbonaceous char which acts as a physical barrier to heat transfer from the flame to the polymer and to the diffusion of combustible gases.^{6,7}

In the commercial flame retardant poly(ethylene terephthalate) (PET) fiber containing a phosphonate group by Hoechst^{1,2} (trade name Trevira), the phosphorus moieties are chemically linked onto the polymer main chain and impart flame resistance to the PET fibers.⁸

In contrast with PET, it is difficult to find flame retardant poly(butylene terephthalate) (PBT) that is covalently incorporated with phosphorus moieties, even though PBT is rapidly increasing in popularity as an engineering thermoplastic polymer and has been widely used in electrical, electronic and automotive industrial applications over the last two decades.

In order to prepare the flame retardant PET incorporated with phosphorus moieties, the phosphorus groups with acidic end groups have been used. In the preparation of flame retardant PBT, however, the acidic end groups act as a catalyst for the conversion reaction of butanediol to tetrahydrofuran and also react with butanediol. Consequently, water as well as tetrahydrofuran is produced. If water exists during polymerization reaction in PBT, the titanated catalyst, which is not generally used in the preparation of PET, loses its activity. This is the reason for the difficulties of incorporat-

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ing phosphorus groups into PBT.

To date, most commercial flame retardant PBTs have been halogenated PBTs. Although many attempts have been made to modify PBT with organophosphorus compounds to create flame retardant PBTs, only a few blended types (not incorporated types) are available.

Among these PBT blends, the blend of PBT with red phosphine has attracted particular interest. Unfortunately, the use of blended flame retardant PBTs with red phosphine is hampered by the production of phosphine gas, which is very toxic, during processing. Besides red phosphine, several organophosphorus compounds including phosphorus-nitrogen compounds, phosphorus oxynitride, and phosphazenes, have been used as flame retardant additives for the blended flame retardant PBTs.^{9,10} Because phosphorus-nitrogen containing compounds are very stable thermally, they only begin to decompose above 450 °C and leave large amounts of solid residue. In spite of their high thermal stability, the blended flame retardant PBTs with phosphorus-nitrogen compounds cannot meet the requirements of the UL-94 test because phosphorus-nitrogen compounds cannot be dispersed uniformly along the polymer backbone, even though the blended loading of phosphorus-nitrogen compounds was as high as 30 wt%.⁸

For the development of flame-retardant PBT incorporated with non-halogen compound, in this study, we synthesized a phosphorus comonomer [(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)methyl]-methyl butanedioate (DOP-MBDA) which does not produce water during the polymerization reaction and prepared a series of novel flame retardant PBTs (FR-PBTs) using this comonomer. The flame retardancy and thermal and mechanical properties of this novel flame retardant PBT were also investigated in this work.

Experimental

Chemicals. 9,10-Dihydroxy-9-oxa-10-phosphaphenanthrene-10-oxide (DOP) was prepared according to the method described in the literature.¹¹ Itaconic acid, dimethyl itaconate, dimethyl terephthalate (DMT) and butanediol (BD) were obtained from commercial sources and were used without further purification. All catalysts were obtained from commercial sources and were used without further purification. Phenol (Aldrich), 1,1,2,2-tetrachloroethane (Aldrich) and trifluoroacetic acid (Aldrich) were used without further purification.

Characterization. ¹H-NMR spectra were measured on a JEOL 400 MHz ¹H-NMR spectrophotometer and IR spectra were recorded with a Nicolet 800 infrared spectrophotometer. Inherent viscosities of the polymers were obtained using an Ubbelohde capillary viscometer.

The accurately weighed polymer sample was dissolved in 25 mL of mixed solvent of 1,1,2,2-tetrachloroethane/phenol = 6/4 (w/w). The solution was maintained at 80 °C for 2 hrs to achieve complete dissolution of the polymer. The solution was then cooled to room temperature and filtered. Using the viscometer at 30 °C, the inherent viscosity was calculated from the relative viscosity.

The melting point of DOP was determined using a polarizing microscope. Differential scanning calorimetry (DSC) data were obtained from 8~15 mg samples in a nitrogen atmosphere at a heating rate of 20 °C/min using a Perkin Elmer 7-Series differential scanning calorimeter. The tensile properties of the polymers were measured according to the ASTM D 638 using a Model 4303 Instron from Instron Company. The flexural strength and modulus of the polymers were measured according to the ASTM D 790 and the impact strength of the polymers was measured following the ASTM D 256 method with ASTM standard samples of the polymers.

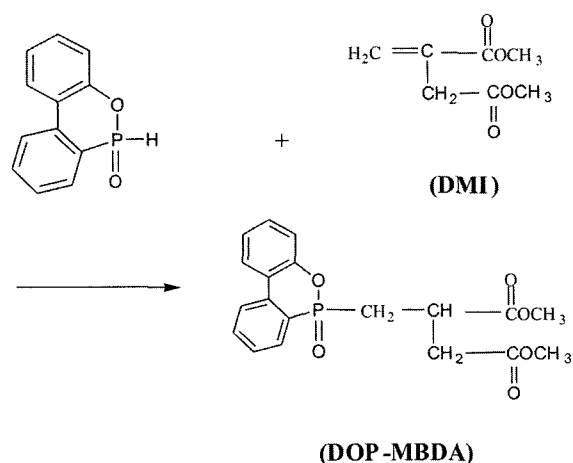
Synthesis of DOP-MBDA. DOP-MBDA was prepared from dimethyl itaconate and DOP. A typical example of the synthetic procedure used to prepare DOP-MBDA is as follows: 83.24 g (0.4 mol) of DOP was added to a round bottom flask and heated to 150 °C with stirring under nitrogen atmosphere. To the DOP solution, a slight excess of dimethyl itaconate (DMI) (68.6 g, 0.44 mol) was added dropwise over 1 hr with stirring. After the completion of DMI addition, the reaction mixture was refluxed for 12 hrs. Then, unreacted dimethyl itaconate was distilled at 150 °C under a reduced pressure (less than 10 mmHg) for 2 hrs. The crude product was cooled to 40 °C and 150 mL of methylene chloride was added to the crude DOP-MBDA solution. The mixture of methylene chloride and crude DOP-MBDA was stirred for 1 hr and separated by separating funnel. The organic layer was washed with 10 wt% NaHCO₃ solution and then with 150 mL of distilled water. The resulting organic layer was dried by exposure to 10 g of MgSO₄ for 30 min. After drying, the solution was filtered to remove the MgSO₄. Finally, the filtrate was distilled at room temperature under a reduced pressure (less than 10 mmHg) for 2 hrs to give a colorless transparent semi-solid. This semi-solid was recrystallized from ethylene glycol to obtain the final DOP-MBDA product.

Synthesis of PBT and FR-PBTs. For the preparation of FR-PBTs, first, DMT, BD, and DOP-MBDA were added into a stainless steel reactor equipped with a condenser column and mechanical stirrer. Lithium acetate (LiOAc) and tetrabutyltitanate (TBT) were added to the reaction mixture as catalysts. The reaction mixture was mixed until homogeneous at 130 °C and then heated to 180 °C at a heating rate of 0.33 °C/min over 2.5 hrs. Methanol formed from the reaction of diester and diol started to come out from 150 °C. The reaction mixture was further heated to 200 °C, followed by gradual heating up to 255 °C at a heating rate of 0.61 °C/min. During heating from 200 to 255 °C, the pressure of the reactor was gradually reduced at a rate of 9.5 torr/min to a final

pressure of less than 1 torr. The reaction mixture was maintained at this condition for 2 hrs to obtain FR-PBTs. The contents of DOP-MBDA in FR-PBTs prepared were 5.5, 8, 10, and 15 wt%. The synthetic route used to prepare the DOP-MBDA comonomer and the typical preparation conditions of FR-PBT are shown in Scheme I and Table I, respectively. For comparison purposes, PBT was also prepared by the procedures described above without addition of DOP-MBDA.

Oxygen Index Flammability Measurement. Limited oxygen index (LOI) measurements were performed on the CS-108B instrument from CSI Company. The polymer samples were molded to a size of 100 mm in length, 6.5 mm in width, and 3 mm in thickness. The LOI measurement was performed according to ASTM D2863-1991.

UL-94 V Flame Retardancy Test. The UL-94 V test was performed according to the UL-94 V standard method with



Scheme I. Synthesis of DOP-MBDA comonomer.

Table I. Preparation Condition of FR-PBT

Reaction Step	Composition ^a		Reaction Condition
Ester Interchange	DMT	80 g	1) mixing ; 130 °C × 30 min
	BD	53 g	2) heating ; 180 °C × 150 min
	DOP-MBDA	5.4 g	- heating rate = 0.33 °C/min
	TBT	0.01 g	
	Li(OAc)	0.003 g	
Polycondensation	Prepolymer	138.4 g	3) heating ; 200 °C
			- heating rate = 5 °C/min
	TBT	0.01 g	4) heating and reducing pressure ; 255 °C × 1 torr
	Li(OAc)	0.004 g	- heating rate = 0.61 °C/min
			- reducing rate of pressure = 9.5 torr/min
		5) holding condition ;	
		255 °C × 1 torr × 120 min	

^aTBT = Tetrabutyl titanate, Li(OAc) = Lithium acetate.

a test specimen of 125 mm in length, 13 mm in width, and 1.6 or 3.2 mm in thickness. Five sample bars suspended vertically over surgical cotton were ignited by a Bunsen burner; two ignitions with burning times of 10 sec each were applied to each sample bar.

Results and Discussion

The IR-spectrum of synthesized DOP-MBDA is shown in Figure 1. The colorless transparent semi-solid intermediate obtained in the synthesis of DOP-MBDA had a boiling point of 235~237°C/1 mmHg. The final DOP-MBDA product had a melting point of 89°C, indicating that the monomer was successfully synthesized. The yield of the DOP-MBDA product was 90.2 wt% (12.32 g).

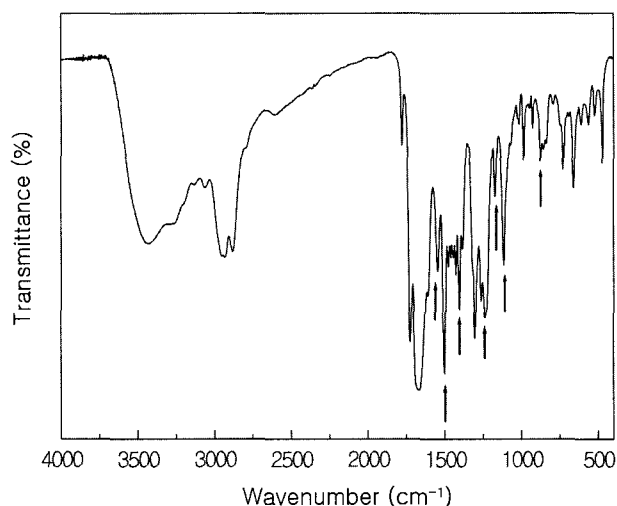


Figure 1. IR Spectrum of DOP-MBDA.

The IR spectrum of the DOP-MBDA monomer had absorption maxima at 3050, 3000, 2950, 1740, 1470, 1375, 1280, 1240, 1170, 1120, 914, and 760 cm^{-1} . The strong absorption at around 1240 cm^{-1} is characteristic of the P=O vibration in phosphoric compounds. The strong absorptions observed at around 1150 and 900 cm^{-1} correspond to aromatic P-O-C stretching. The P-C stretching absorption around 1400~1500 cm^{-1} , C=O absorption around 1700~1800 cm^{-1} , and C-O stretching absorption around 1100 cm^{-1} coincide well with the DOP-MBDA structure.

The IR spectrum of the DOP-MBDA product did not show an absorption at 1600 cm^{-1} , characteristic of the C=C bond of dimethyl itaconate. This indicates that the reaction went to completion. Elemental analysis yielded values of P = 8.29%, C = 61.03%, and H = 5.14%, which coincide well with the theoretical values of P = 8.27%, C = 60.98%, and H = 5.12%. The $^1\text{H-NMR}$ spectrum of the DOP-MBDA product dissolved in CDCl_3 showed peaks at 2.0~3.0, 6.3~6.5, and 7.0~8.0 ppm. The peak positions and integrals coincide well with theoretical predictions for the DOP-MBDA spectrum.

The synthetic scheme used to prepare the FR-PBTs is shown in Scheme II, and the IR spectra of PBT and the FR-PBT containing 8 wt% of the phosphorus compound (FR-PBT-8) are shown in Figure 2. The IR absorption peaks of FR-PBT-8 are very similar to those of PBT. This similarity may be due to the fact that the absorption intensities of the peaks at around 1300~1700 cm^{-1} from the DOP-MBDA moiety are too weak to make the FR-PBT spectrum significantly different from the PBT spectrum.

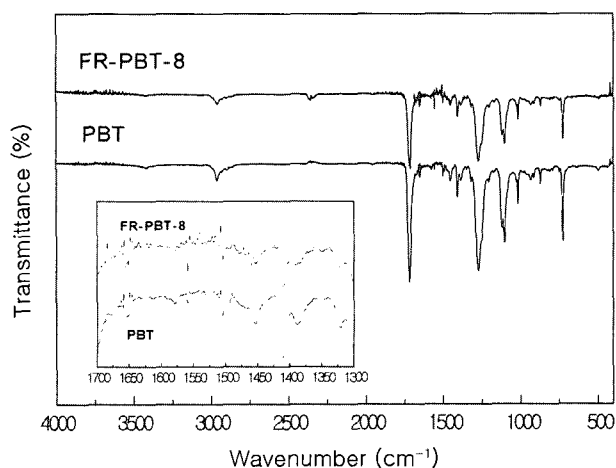
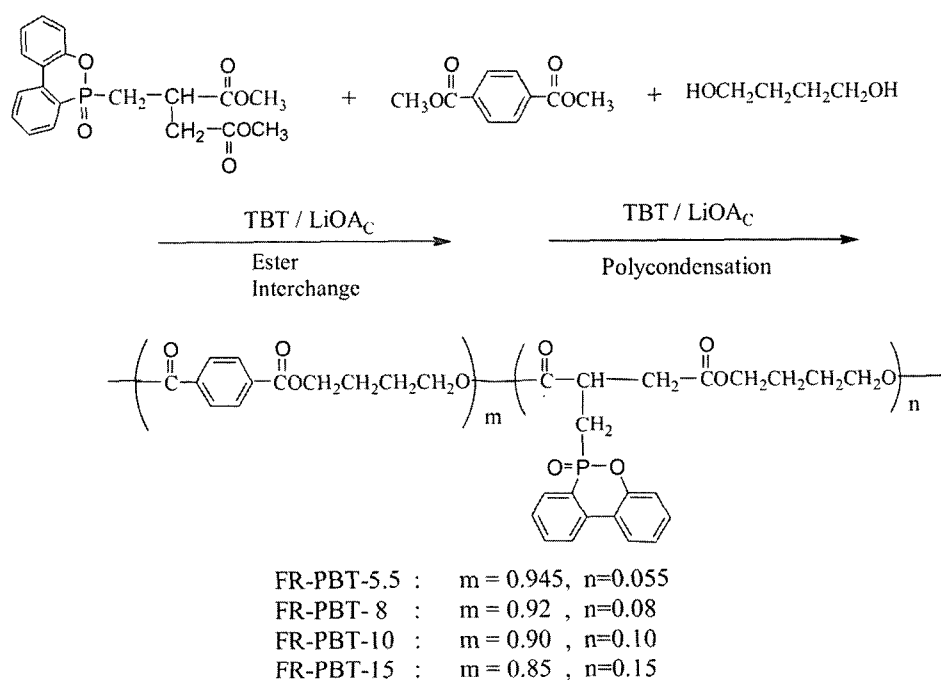


Figure 2. IR Spectra of PBT and FR-PBT-8.

In contrast to the IR spectra, the $^1\text{H-NMR}$ spectra of PBT and FR-PBT-8 (Figure 3) show clear differences. As shown in the inserts of Figure 3(B), FR-PBT-8 showed peaks at 2.0 ~ 4.0(m) and 7.28~8.14(m) ppm in addition to the peaks at 2.6(m), 4.60(m), and 8.41(m) ppm that it shares with the PBT homopolymer. These additional peaks are from the EG-DOP-MBDA unit in the copolymer main chain. The peak positions and integrals of the additional peaks coincide well with theoretical predictions. Furthermore, the integration ratio of the copolymer units varied with varying DOP-MBDA content in the polymer chain.

The inherent viscosities, thermal properties, and crystalli-



Scheme II. Synthesis of FR-PBTs.

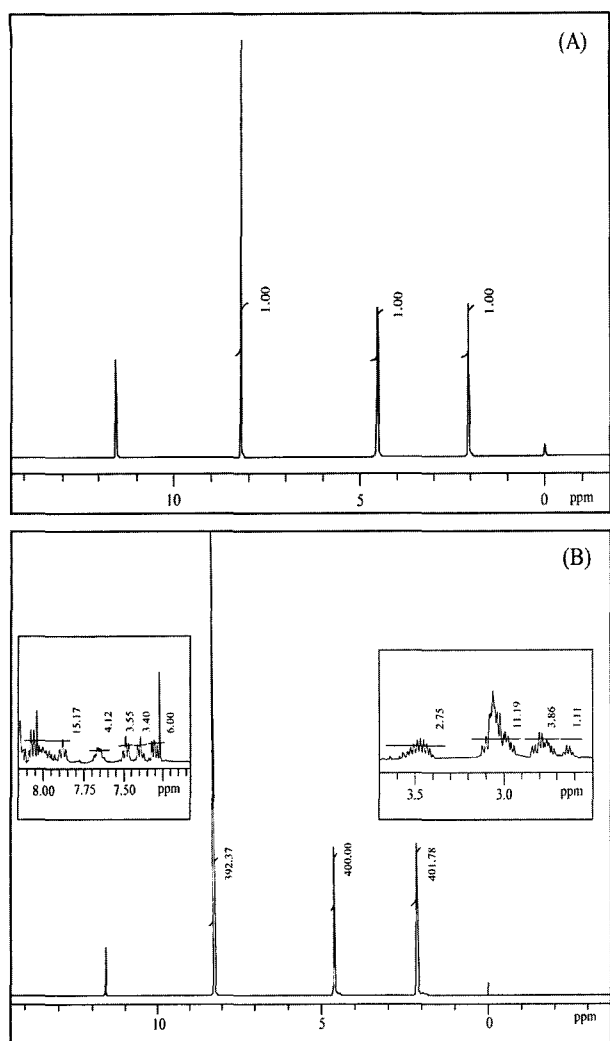


Figure 3. $^1\text{H-NMR}$ Spectra of (A) PBT and (B) FR-PBT-8.

zation half time of the FR-PBTs and PBT are summarized in Table II. All of the polymers prepared in this study had inherent viscosities above 0.8 g/dL, with the exception of the FR-PBT containing 15 wt% of the phosphorus com-

pound (FR-PBT-15), which had the inherent viscosity of 0.68 g/dL. Because the molecular weights of the polymers are relatively high, the effect of molecular weight on the polymer properties is considered to be less significant than the effect of composition.

As shown in Table II, the glass transition temperatures (T_g) of the FR-PBTs are higher than that of the PBT homopolymer and show a trend toward higher T_g with increasing DOP-MBDA content. This may be due to the restriction of the rotational freedom of the polymer backbone by the bulky side group of DOP-MBDA. On the other hand, the cold crystallization temperatures (T_{mc}) of the FR-PBTs were lower than that of the PBT homopolymer and T_{mc} tended to decrease with increasing DOP-MBDA content. The melting points (T_m) of the FR-PBTs were also lower than that of the PBT homopolymer. The T_m of the FR-PBTs decreased with increasing DOP-MBDA content up to a content of 10 wt%, and then increased on going to 15 wt% DOP-MBDA. The trends observed in T_{mc} and T_m can mostly be explained in terms of the increasing suppression of effective molecular packing as more bulky side groups are included in the polymer chain. This effect would lead to a lower degree of crystallinity and a slower crystallization rate.^{8,12} When the amount of DOP-MBDA was increased from 10 to 15 wt%, however, the melting temperature increased. This result is not fully understood at present, but is being actively investigated as part of our ongoing work on FR-PBTs. Comparing the crystallization half times of FR-PBTs containing upto 10 wt% DOP-MBDA (16.85–29.67 min) and that of PET (42.23 min) in Table II, FR-PBTs are highly suitable for commercial applications involving injection molding.

The mechanical properties of the FR-PBTs and PBT are summarized in Table III. The tensile strength of the polymers increased slightly with increasing phosphorus content up to a content of 10 wt%, but further increase of the phosphorus content to 15 wt% caused the tensile strength to drop to a value much lower than that of the PBT homopolymer. This fall-off in strength may be due to a loss of the ductility of PBT on inclusion of too great an amount of the brittle

Table II. Viscosity, Thermal Properties, and Crystallization Half-Time of the Polymers

Polymer	η_{inh}^a (dL/g)	T_g^b ($^{\circ}\text{C}$)	T_m^c ($^{\circ}\text{C}$)	T_{mc}^d ($^{\circ}\text{C}$)	$T_{1/2}^e$ (min)
PET	-	-	-	-	42.23
PBT	0.97	38	225	188	5.65
FR-PBT-5.5	1.14	42	220	182	16.85
FR-PBT-8	0.98	43	218	183	27.54
FR-PBT-10	0.88	48	217	182	29.67
FR-PBT-15	0.68	51	220	180	238.65

^a η_{inh} = Inherent viscosity. ^b T_g = Glass transition temperature. ^c T_m = Melting temperature.

^d T_{mc} = Cold crystallization temperature. ^e $T_{1/2}$ = Crystallization half time at 10 $^{\circ}\text{C}$ above the T_{mc} of each polymer.

Table III. Mechanical Properties of PBT and FR-PBTs

	PBT	FR-PBT-5.5	FR-PBT-8	FR-PBT-10	FR-PBT-15
Tensile Strength (Kg/Cm ²), ASTM D638	540	540	560	580	300
Tensile Modulus (Kg/Cm ²), ASTM D638	8,700	9,000	9,300	9,400	9,500
Elongation (%), ASTM D638	200	100	50	14	3
Flexural Strength (Kg/Cm ²), ASTM D790	900	870	900	950	930
Flexural Modulus (Kg/Cm ²), ASTM D790	25,000	26,000	27,000	28,000	29,000
Izod Impact Strength (Kg · Cm/Cm), ASTM D256	4.9	4.4	3.3	2.9	2.2

Table IV. LOI and UL-94 V Flame Retardant Test for the Polymers

Polymer	LOI ^a	P ^b (%)	Ave. B. T ^c (sec)	Drip	Cotton	Classification
PBT	23	0	23	Heavy	Fire	HB
FR-PBT-5.5	23	0.28	13	Middle	Fire	V-2
FR-PBT-8	26	0.4	5	Scarcely	Fire	V-2
FR-PBT-10	27	0.5	3	Scarcely	No	V-1
FR-PBT-15	31	0.75	0	Scarcely	No	V-1

^aLOI = Limited oxygen index. ^bP = Phosphorus content. ^cAve. B. T. = Average burning time for first and second ignition.

DOP-MBDA moiety. The elongation at break decreased dramatically with increasing phosphorus content (see Table III), which represents direct evidence of the brittleness of the DOP-MBDA moiety. However, a previous study of blended flame retardant PBTs reported an elongation at break in the range of 10~30% at 6 wt% loading of flame retardant,¹¹ which is very low compared to the present results for FR-PBTs. The disparity between the previous results for the blended flame retardant PBT and those for the novel FR-PBT at the same loading of flame retardant may be due to less uniform dispersion of the flame retardant along the polymer backbone in the blended flame retardant PBT.

The flexural strength and the tensile and flexural moduli of the FR-PBTs increased slightly with increasing content of flame retardant (Table III). In contrast, the notched Izod impact strength of the FR-PBTs decreased from 4.9 (PBT) to 2.2 kg·cm/cm (FR-PBT-15) with increasing content of flame retardant (Table III).

Table IV presents the oxygen index values for the FR-PBTs and PBT. The oxygen index increases with increasing DOP-MBDA content, reaching a LOI value of 31 for FR-PBT-15. Aufmuth *et al.*¹³ found that the LOI value of the blended flame retardant PBT with a 20 wt% content of 1,4-diisobutylene-2,3,5,6-tetrahydroxy-1,4-diphosphineoxide (trade name Cyagard) was 23, and that the LOI value was independent of the amount of Cyagard. However, when employed in combination with a charrable polymer, poly(dimethyl-phenyl oxide) (PPO), and charring catalyst Fe₂O₃, Cyagard can help to increase the LOI value of the blended flame retardant PBT to 28. Levchik *et al.*⁸ reported that the

LOI value of the blended flame retardant PBT with phosphorus oxynitride increased from 28 to 32 on increasing the phosphorus oxynitride content from 20 to 30 wt%. Thus, in comparison to the FR-PBTs with DOP-MBDA reported here, the blended flame retardant PBT with phosphorus oxynitride requires twice the amount of the flame retardant to achieve an equivalent LOI value. This result leads us to conclude that the blending process does not fully disperse the flame retardant in blended flame retardant PBTs, which means that the carbonaceous char that acts as a physical barrier to heat transfer from the flame to the polymer does not completely protect the PBT.¹⁴

It is clear from the results in Table IV that the flame retardancy of FR-PBTs increases with increasing phosphorus content in the copolymers. FR-PBTs also generated less fumes and fewer drips than PBT. On increasing the phosphorus content above 8 wt%, the average burning time decreased remarkably and the amount of dripping diminished markedly. The difference between FR-PBT-8 and FR-PBT-10 in terms of UL 94 V classification lay in the tendency of the burning polymer to drip flaming particles. Because it was difficult to visually distinguish between flaming polymer and glowing polymer, a small piece of surgical cotton was used as an indicator for UL 94 V Test. Ignition of the cotton is indicative of flaming of the polymer. The drips from FR-PBT-8 ignited the cotton indicator but those from FR-PBT-10 did not, indicating that FR-PBT-10 was glowing but not flaming under burning. Hence, FR-PBT-10 was classified as 94V-1. These phenomena can be explained in terms of the flame retardancy mechanism referred to as solid phase inhibition.^{14,15} Under this mechanism, phosphorus compounds

generally lower the initial decomposition temperature of polymer, increase char formation at high temperatures, and this char insulates the polymer from the heat of the flame and prevents further burning. The present results show that the incorporation of a small amount of DOP-MBDA into PBT enhances the flame retardancy of the polymer.

Conclusions

The novel flame retardant PBT can be prepared by polymerizing DMT, BD, and DOP-MBDA. A phosphorus compound, DOP-MBDA is synthesized by an addition reaction of DMI with DOP. The flame retardancy of prepared novel PBT was excellent, that is, the novel flame retardant PBT containing a phosphorus content as low as 0.5 wt% can achieve the UL 94-V2. The novel flame retardant PBT also exhibited good thermal and mechanical properties.

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References

- (1) A. G. Hoechst, US Patent, 3.941.752 (1992).
- (2) A. G. Hoechst, US Patent, 4.033.936 (1977).
- (3) Toyobo Co. Ltd., Germany Patent, 2.646.218 (1977).
- (4) C. S. Wang, J. Y. Shieh, and Y. M. Sun, *Eur. Polym. J.*, **35**, 1465 (1999).
- (5) S. J. Chang, Y. C. Sheen, R. S. Chang, and F. C. Chang, *Polym. Degrad. Stab.*, **54**, 365 (1996).
- (6) D. Derouet, F. Morvan, and C. Brosse, *J. Appl. Polym. Sci.*, **62**, 1855 (1996).
- (7) S. Maiti, S. Banerjee, and S. K. Palit, *Prog. Polym. Sci.*, **18**, 227 (1993).
- (8) J. Y. Kim, E. S. Seo, S. H. Kim, and T. Kikutani, *Macromol. Res.*, **11**, 62 (2003).
- (9) S. V. Levchik, G. F. Levchik, A. I. Balabanovich, E. D. Weil, and M. Klatt, *Angew. Makromol. Chem.*, **264**, 48 (1998).
- (10) G. F. Levchik, Y. V. Grigoriev, A. I. Balabanovich, S. V. Levchik, and M. Klatt, *Polym. Int.*, **49**, 1095 (2000).
- (11) LG Chemicals. KP Patent, 0231063 (1999).
- (12) J. Yu, D. Zhou, W. Chai, B. Lee, S. W. Lee, J. Yoon, and M. Rhee, *Macromol. Res.*, **11**, 25 (2003).
- (13) W. Aufmuth, S. V. Levchik, G. F. Levchik, and M. Klatt, *Fire Mater.*, **23**, 1 (1999).
- (14) G. L. Nelson, *Fire and Polymers: Materials and Tests for Hazard Prevention*, ACS, Washington D. C., 1995.
- (15) W. C. Kuryla and A. J. Papa, *Flame Retardancy of Polymeric Materials*, Marcel Dekker, New York, 1975, vol. 3.