

# Study on Co[poly(butylene terephthalate-*p*-oxybenzoate)] Thermotropic Copolyester. II. Thermal Behavior and Crystalline Morphology

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Received 3 August 1999; accepted 21 March 2000

**ABSTRACT:** The POB/PBT copolyesters, designated B28, B46, B64, and B82, were prepared from *p*-acetoxybenzoic acid (PAB) and poly(butylene terephthalate) (PBT). The polymeric products obtained were then ground and subjected to solid-state polymerization under vacuum for 4 h. The melting and crystallization behaviors of these copolyesters have been studied by differential scanning calorimetry (DSC). In the DSC scan of the POB-rich composition, the endothermic peak shows obscurely, and enthalpy of fusion becomes small due to the change in the crystalline morphology from isotropic to anisotropic. In general, the melting point of the copolyester is increased by the solid-state polymerization reaction. Also, thermogravimetric analysis (TGA) were performed with these samples obtained. It was found that the decomposition temperature ( $T_d$ ) is increased as the POB content is increased. Effects of composition and solid-state polymerization on the decomposition temperature of copolyesters are also discussed. The crystalline morphology of copolyester was investigated with a Zeiss polarized optical microscope. It was found that the POB/PBT copolyesters with 60 mol % POB was shown to be highly anisotropic. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2363–2368, 2000

**Key words:** liquid crystalline polymers; copolyester; differential scanning calorimetry; thermogravimetric analysis; crystalline morphology

## INTRODUCTION

For a polymer to exhibit thermotropic liquid crystalline behavior, it must be able to melt or become liquid-like, and the oriented aggregates of rod-like moieties must be stable in the melt state. The series of copolyesters, based upon poly(ethylene terephthalate) (PET) that has been copolymerized with *p*-acetoxybenzoic acid (PAB) or *p*-hydroxybenzoic acid (PHB), has been investigated for their structure and properties by several researchers.<sup>1–10</sup> The co[poly(ethylene terephthalate-*p*-oxybenzoate)] copolyesters, called POB/PET, have been shown to exhibit liquid crystallinity at or above 35 mol % POB. In our previous research on blends of PET with POB/PET, we reported on the crystallization kinetics by DSC<sup>11,12</sup> and morphologic observation by polarized light microscopy<sup>13</sup> and compatibility by scanning electron microscopy (SEM)<sup>14</sup> and also on the interchange reaction between PET and POB/PET by proton NMR.<sup>15,16</sup>

Poly(butylene terephthalate) (PBT) has a similar structure to that of PET, and poly(*p*-oxybenzoate) incorporated with PBT would be expected to exhibit liquid crystalline behavior at certain compositions. The series of POB/PBT copolyesters has not been investigated to as great an extent as POB/PET copolyesters. The solubility, thermal properties, and liquid crystalline properties of

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Contract grant sponsor: National Science Foundation; contract grant number: NSC88-2216-E-167-002.

*Journal of Applied Polymer Science*, Vol. 78, 2363–2368 (2000)  
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POB/PBT copolyesters have been reported by Chen and coworkers.<sup>17</sup> They found that POB/PBT copolyesters with 40–60 mol % POB content exhibited a continuous nematic phase. In my previous article,<sup>18</sup> the exact composition and sequence distribution of the copolyester were investigated. For this article, we present the results of melting and crystallization behaviors, thermol stability, and crystalline morphology of POB/PBT copolyesters.

## EXPERIMENTAL

### Materials

The POB/PBT copolyesters with various POB/PBT compositions have been synthesized according to the procedure as reported in my previous article.<sup>18</sup> These copolyesters contain different POB/PBT mol ratios: 20/80 in B28, 40/60 in B46, 60/40 in B64, and 80/20 in B82. PBT was a commercial product from the Far East Textile Co. (Taoyuan, Taiwan), having an intrinsic viscosity of 1.0 (dL/g) measured at 30°C in 60/40 by weight phenol/tetrachloroethane solvent.

### DSC Measurement

The weight of all samples was kept between 10 and 11 mg for DSC evaluation. DSC measurements were carried out in a DuPont DSC cell equipped with a DuPont 2000 thermal analyst system. The reference material used was a blank aluminum pan. Samples were heated to 300°C at a heating rate of 10°C/min under a nitrogen atmosphere, held for 3 min to destroy anisotropy, and then cooled at 10°C/min to 30°C. Both thermal and crystallization parameters were obtained from the heating and cooling scans.  $T_m$  was considered to be the maximum of the endothermic melting peak from the heating scans, and  $T_c$  that of the exothermic peak of the crystallization from the cooling scans. The heat of fusion ( $\Delta H_f$ ) and crystallization heats ( $\Delta H_c$ ) were determined from the areas of melting peaks and crystallization peaks. All results are the average of three samples.

### Thermogravimetric Analysis (TGA)

The thermogravimetric analysis for all samples was performed by a DuPont 2950 TGA system. The TGA measured weight change of the material was a function of temperature at a heating rate of 10°C/min under a nitrogen atmosphere.

### Polarized Optical Microscopy (POM)

Specimens were observed using a Zeiss polarized microscope (III), equipped with a programmable Mettler FP82 HT hot stage. The specimens held between two thin microscope cover slips were prepared in a hot stage preheated at 250°C. When the blends melted, they were pressed on the upper cover slip and then immediately quenched by liquid nitrogen. The sequence of heating, pressing, and quenching was always accomplished in under 20 s.

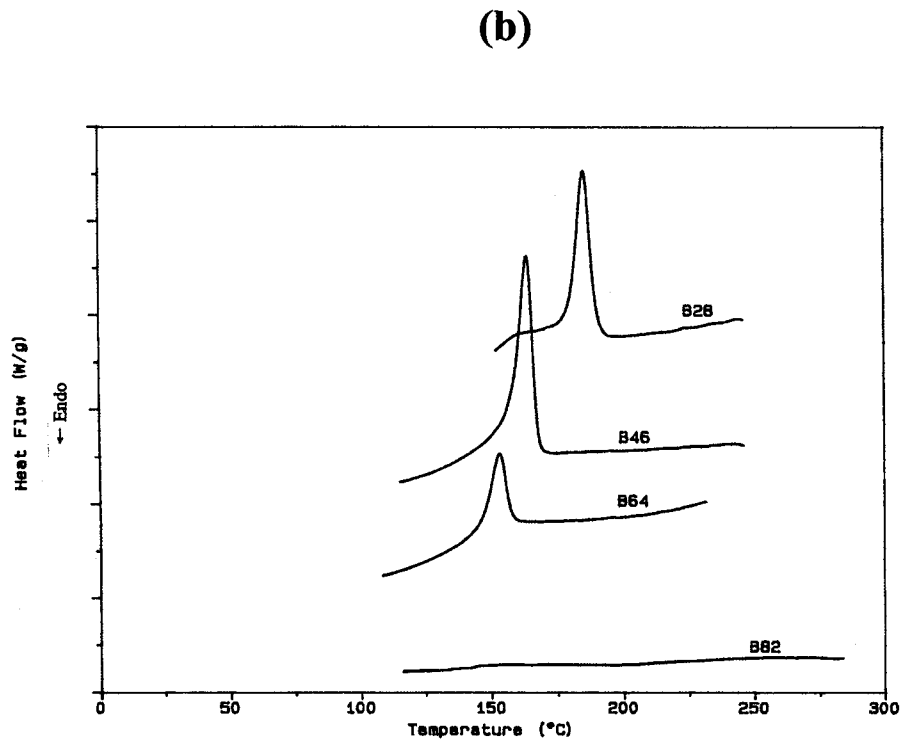
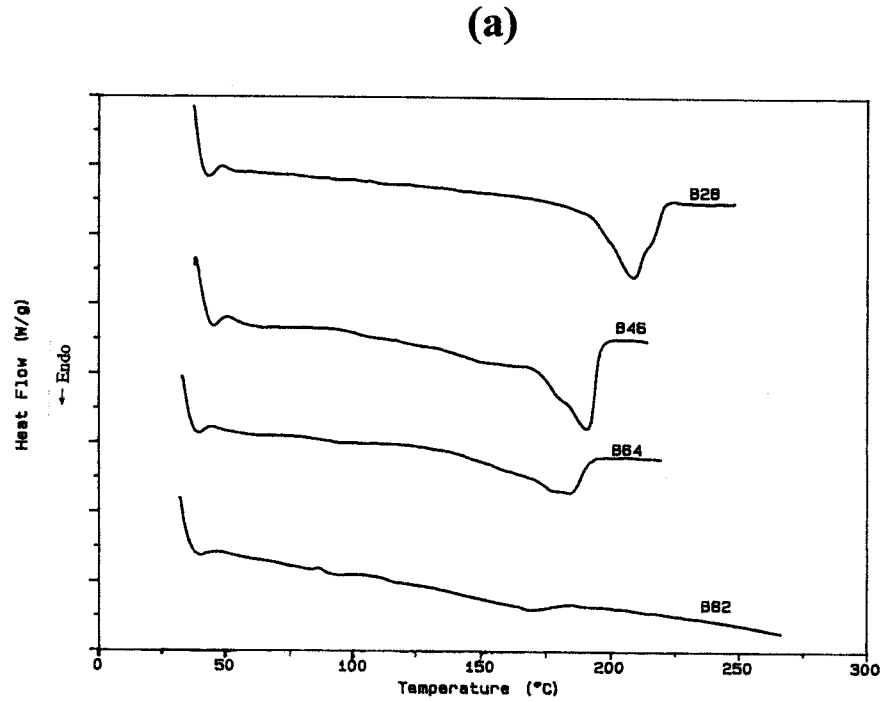
## RESULTS AND DISCUSSION

### Polarized Optical Microscope (POM)

Polarized optical microscope was used to obscure the crystalline texture of polymer crystalline. As seen in our previous report [Fig. (3a)],<sup>19</sup> it is obvious that the texture of PBT shows the typical spherulites texture. B28 is a random copolymer with a low POB content, and the POB sequences are short. Under polarized light, the B28 melt showed no explicit melt birefringence. Yet POB sequences of B46 are longer than that of B28. The patterns of B46 show a dispersed anisotropic phase in a continuous isotropic phase, yet keep the isotropic and anisotropic biphases. We believe that the structure of POB/PBT is similar to that of POB/PET. The shapes of the crystalline in this composition begin to exhibit the general mesophase, but a similar type of PBT spherulites. For B64, the mesophase become continuous, and the patterns show the typical threaded texture, which is consistent with a nematic phase. B82 could not melt or become liquid-like on the hot stage. Its crystalline morphology could not be observed by a polarized optical microscope.

### Thermal Behaviors

The results of DSC heating and cooling scans for POB/PBT copolyesters are shown in Figure 1(a) and 1(b), respectively. It is evident that there is an endothermic melting peak in all of the heating scans, and there is a distinct exothermic crystallization peak in all of the cooling scans except for B82. The various thermal and crystallization parameters determined from heating and cooling scans for all copolyesters are given in Table I. The melting temperatures ( $T_m$ ) and the heat of fusion ( $\Delta H_f$ ) of PBT are 223°C and 36.9 J/g, respectively. It has been shown in Table I that the  $T_m$  of B28 is lower than that of PBT, and the  $\Delta H_f$  of B28 is



**Figure 1** DSC thermograms of POB/PBT copolyesters (a) heating scans, (b) cooling scans.

smaller than that of PBT. The depression in the  $T_m$  and  $\Delta H_f$  are attributable to the destruction of the PBT isotropic crystal domain by the incorpo-

ration of POB moiety. The  $T_m$  of the copolyesters decreased as the POB content increased in the range from 20 to 80 mol %. The  $\Delta H_f$  of the copoly-

**Table I DSC Data of PBT and POB/PBT Copolyesters**

Composition	Melting (From Heating Scans)			Crystallization (From Cooling Scans)			
	Onset (°C)	$T_m$ (°C)	$\Delta H_f$ (J/g)	Onset (°C)	$T_c$ (°C)	$\Delta T_c$ (°C)	$\Delta H_c$ (J/g)
PBT	203	223	36.9	203	189	22	37.2
B28	179	209	23.3	196	185	25	21.5
B46	169	191	19.0	172	164	32	18.5
B64	131	183	12.1	161	154	23	10.7
B82	144	169	2.0	—	—	—	— <sup>a</sup>

<sup>a</sup> Cannot be detected.

esters were always smaller than that of pure PBT, and decreased as the POB content increased. The POB/PBT copolyesters are random copolyesters, as confirmed by my previous article.<sup>18</sup> The decrease of the  $T_m$  and  $\Delta H_f$  was attributed to the inclusion of the rigid POB unit in the PBT chain, which causes a decrease in their crystallizable segment length. B64 showed a broad and obscurely melting peak at 183°C, and a small  $\Delta H_f$  due to the change in the crystalline morphology from isotropic to anisotropic. The mesophase of B64 observed by POM becomes the continuous phase, resulting in a broad peak during the thermal process because the heating process deals with a rigid chain-softening process of the liquid crystalline polymer.

The crystallization peak temperature ( $T_c$ ) and crystallization peak width ( $\Delta T_c$ ) of PBT are 189 and 22°C, respectively. The  $T_c$  of the copolyesters are always lower than that of pure PBT, and decreased as the POB content increased in the range from 20 to 80 mol %. Changes in the crystallization peak width ( $\Delta T_c$ ) and the heat of crystallization ( $\Delta H_c$ ) are related to the overall crystallization rate and the extent of crystallization, respectively. The  $\Delta T_c$  and the values of  $\Delta H_c$  for the POB/PBT copolyesters are broader and smaller than those of pure PBT. These results reveal that the overall crystallization rate and the extent of crystallization of POB/PBT copolyesters are smaller than those of pure PBT.

The heat of fusion,  $\Delta H_f$ , normalized per gram of PBT homopolymer, is seen in Table II to decrease with an increase in the POB content. The degree of crystallinity (PBT component) of POB/PBT copolyesters could be obtained from the heat of fusion of fully crystalline PBT (34.5 cal/g).<sup>20</sup> The degree of crystallinity shown in Table II decreases with an increase in the POB content also. This result was attributed to the inclusion of a POB

unit in the PBT chain. From the NMR analysis,<sup>18</sup> the POB/PBT copolyesters with a higher POB content exhibit a longer POB–POB sequence (a shorter PET–PET sequence).

### Thermogravimetric Analysis

Figure 2 shows the thermogravimetric curve of PBT. The thermogravimetric curves of the POB/PBT copolyesters are like that of PBT. The category of a thermogravimetric curve in TGA is determined by the average decomposition temperature ( $T_d$ ) as well as the lower decomposition temperature ( $T_l$ ) and the upper decomposition temperature ( $T_u$ ). The experimental data obtained from thermogravimetric curve are summarized in Table III. It is clear that the decomposition temperature of POB/PBT copolyesters depends primarily on the POB content. It is shown in Table III that the decomposition temperature is increased as the ratio of POB moiety is increased. This is may be explained by the fact that the decomposition temperature of poly(*p*-oxybenzoate) (515°C)<sup>21</sup> is higher than that of PBT (419°C). From the results of the previous report,<sup>21</sup> the higher degree of polymerization of the same chemical segment may be less stable under the

**Table II The Crystallinity of POB/PBT Copolyesters**

Copolyester	$\Delta H_f$ (J/g · PBT)	Crystallinity (%) <sup>a</sup>
B28	25.6	17.3
B46	25.0	16.9
B64	18.8	12.7
B82	— <sup>b</sup>	—

<sup>a</sup> Calculated by the heat of fusion of fully crystalline PBT (34.5 cal/g).<sup>20</sup>

<sup>b</sup> Cannot be detected.

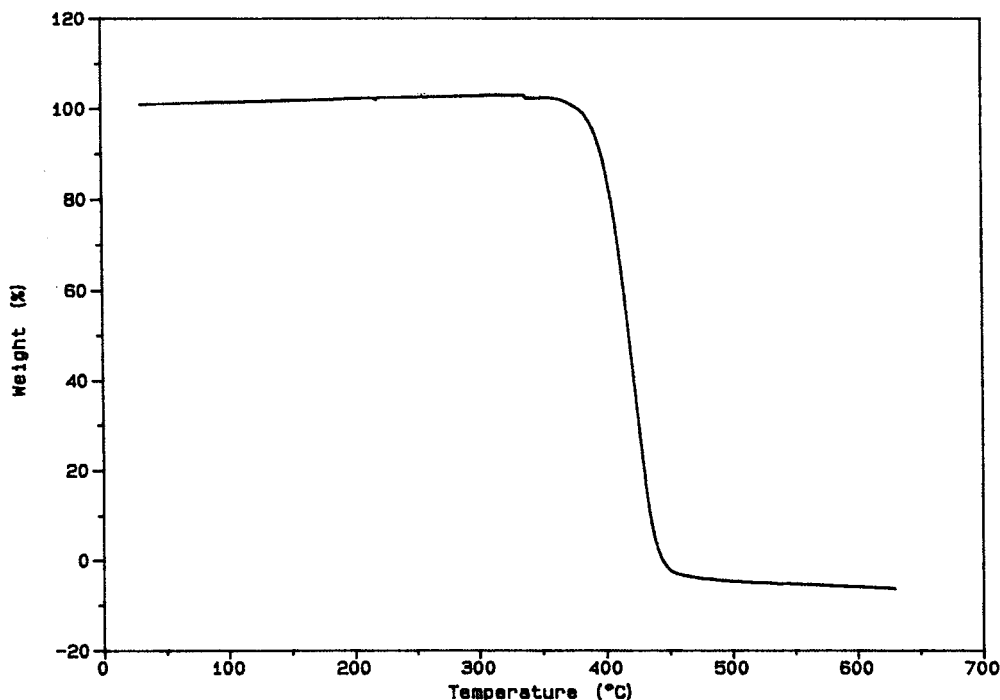


Figure 2 TGA curve for PBT.

thermal decomposition temperature in POB/PET copolyesters. For POB/PBT copolyesters, the lower decomposition temperature is related to the PBT moiety, and the upper decomposition temperature is related to the POB moiety. The lower decomposition temperature of POB/PBT copolyesters are higher than that of pure PBT (400°C) by 1 to 2°C. This result reveals that the chain length of the PBT unit in the POB/PBT copolyesters is slightly shorter than that of the pure PBT. In contrast, the upper decomposition temperatures of POB/PBT copolyesters are significantly larger than that of PBT (438°C). The reason is that the upper decomposition temperature is related to the POB moiety, which is hard segment. The in-

roduction of POB moiety into the structure composition causes the increase in the upper decomposition temperature for the POB/PBT copolyesters. The upper decomposition temperatures of B28, B46, and B64 are about at 450°C, indicating that they exhibit about the same chain length as that of the POB unit. The upper decomposition temperatures of B82 show an upper temperature of 498°C, a jump of 48°C from the 450°C of B64, and are larger than that of pure PBT by 60°C. The reason for this jump in the upper decomposition temperature is not clear at this point. One of the possible explanations is that the content of POB unit in B82 is 80%, and the upper decomposition temperature must be close to the the upper de-

Table III TGA Data of PBT and POB/PBT Copolyesters

Composition	$T_l$ (°C)	$T_d$ (°C)	$T_u$ (°C)	$\Delta T$ (°C)	$T_{da}$ (°C)
PBT	400	419	438	38	—
B28	401	421	452	52	423
B46	401	423	448	43	424
B64	402	426	450	48	428
B82	402	458	498	96	496

$T_l$ : lower decomposition temperature,  $T_d$ : decomposition temperature.

$T_u$ : upper decomposition temperature,  $\Delta T = T_u - T_l$ .

$T_{da}$ : decomposition temperature after 4-h solid-state polymerization.

composition temperature of poly(*p*-oxybenzoate) (532°C).<sup>21</sup> Moreover, the difference between upper and lower decomposition temperatures ( $\Delta T$ ) of POB/PBT copolyesters are larger than that of pure PBT (38°C). This means that the POB/PBT copolyesters exhibit more uniform thermal characteristics over the broad heating temperature interval. The value of  $\Delta T$  of B82 is about two times that for those of another three copolyesters. This fact means that B82 has the most uniform thermal characteristics.

The effect of 4-h solid-state polymerization on the decomposition temperature of the POB/PBT copolyesters is shown in Table III. The decomposition temperature after 4-h solid-state polymerization ( $T_{da}$ ) are always higher than those of decomposition temperature before 4-h solid-state polymerization. The result is similar to the result of POB/PET copolyesters after 4-h solid-state polymerization.<sup>21</sup>

The POB/PBT copolyesters were made from the hard segment of *p*-oxybenzoate (POB) moiety and soft segment of poly(butylene terephthalate) (PBT) moiety. The introduction of POB moiety into the structure composition causes the increase in the decomposition and the upper decomposition temperature. The decomposition temperature and the upper decomposition temperature are increased as the ratio of the POB moiety is increased.

## CONCLUSIONS

Under polarized light, the B28 melt showed no explicit melt birefringence. The POB/PBT copolyesters with 40–60 mol % POB content exhibited an anisotropic phase, and B64 exhibited the typical threaded texture of nematic liquid crystalline.

The  $\Delta H_f$  of the copolyesters were always smaller than that of pure PBT, and decreased as the POB content increased. The  $\Delta T_c$  and the values of  $\Delta H_c$  for the POB/PBT copolyesters are broader and smaller than those of pure PBT. B64 showed a broad and obscurely melting peak at 183°C and a small  $\Delta H_f$  due to the change in the crystalline morphology from isotropic to anisotropic.

The decomposition temperature and upper decomposition temperature of the POB/PBT copolyesters were increased as the POB content increased. The thermal stability of POB/PBT copolyesters will be increased by 4-h solid-state polymerization.

We gratefully acknowledge support from the National Science Foundation Grant No. NSC88-2216-E-167-002.

## REFERENCES

1. Jackson, W. J., Jr.; Kuhfuss, H. F. *J Polym Sci Polym Chem Ed* 1976, 14, 2043.
2. Krigbaum, W. R.; Salaris, F. *J Polym Sci Polym Phys Ed* 1978, 16, 883.
3. Menczel, J.; Wunderlich, B. *J Polym Sci Polym Phys Ed* 1980, 18, 1433.
4. Meesiri, W.; Menczel, J.; Gaur, U.; Wunderlich, B. *J Polym Sci Polym Phys Ed* 1982, 20, 719.
5. Viney, C.; Windle, A. H. *J Mat Sci* 1982, 17, 2661.
6. Blackwell, J.; Lieser, G.; Gutierrez, G. A. *Macromolecules* 1983, 16, 1418.
7. Done, D.; Baird, D. G. *Polym Eng Sci* 1987, 27, 816.
8. Cuculo, J. A.; Chen, G. Y. *J Polym Sci Polym Phys Ed* 1988, 26, 179.
9. Sun, T.; Porter, R. S. *Polym Commun* 1990, 31, 70.
10. Brostow, W.; Hess, M.; Lopez, B. L. *Macromolecules* 1994, 27, 2262.
11. Ou, C. F.; Lin, C. C. *J Appl Polym Sci* 1994, 54, 1223.
12. Ou, C. F.; Lin, C. C. *J Appl Polym Sci* 1995, 56, 1107.
13. Ou, C. F.; Lin, C. C. *J Appl Polym Sci* 1996, 61, 1447.
14. Ou, C. F.; Lin, C. C. *J Appl Polym Sci* 1996, 59, 1379.
15. Ou, C. F.; Lin, C. C. *J Appl Polym Sci* 1996, 61, 1455.
16. Ou, C. F. *J Appl Polym Sci* 1998, 68, 1591.
17. Chen, M. S.; Lee, C.; Chang, N. H.; Chang, B. C.; Tsai, H. B. *Polymer* 1989, 30, 1472.
18. Ou, C. F. *J Appl Polym Sci* 2000, 77, 949.
19. Song, W. J.; Ou, C. F.; Lin, C. C. *J Appl Polym Sci* 1996, 60, 1505.
20. Miller, R. L. In *Polymer Handbook*; Brandrup, J.; Immergut, E. H., Eds.; Wiley: New York, 1975, p. III-35, 2nd ed.
21. Shinn, T. H.; Chen, J. Y.; Lin, C. C. *J Appl Polym Sci* 1993, 47, 1233.