

Thermotropic liquid crystalline copolyesters of poly(butylene terephthalate) and *p*-hydroxybenzoic acid

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The PBT/PHB copolyesters were prepared by reacting poly (butylene terephthalate) with *p*-acetoxybenzoic acid. The liquid crystalline properties, thermal properties and solubility in phenol/TCE of PBT/PHB copolyesters were different to those of PET/PHB copolyesters to some extent. The PBT/PHB copolyesters exhibited considerably lower solubility in phenol/TCE. The PBT/PHB copolyesters with PHB content ranging from 20 to 60 mol% showed melt birefringence, while the PET/PHB copolyesters with 40–80 mol% PHB content exhibited liquid crystalline behaviour.

(Keywords: liquid crystalline polymers; copolyesters of poly(butylene terephthalate) and *p*-acetoxybenzoic acid; solubility; melting temperature; melt birefringence)

INTRODUCTION

For a polymer to exhibit thermotropic liquid crystalline behaviour, 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. Some *para*-linked aromatic polyesters such as poly(*p*-hydroxybenzoate) decompose before melt. If flexible aliphatic groups are incorporated into the main chain, the melting temperature of the *para*-linked aromatic polymers are depressed and liquid crystalline polymers may be obtained. Poly(ethylene terephthalate) (PET) was incorporated into various *para*-linked aromatic polymers to give thermotropic liquid crystalline polymers^{1–4}. Among these liquid crystalline polymers, copolyesters of PET and *p*-hydroxybenzoic acid (PHB) have been investigated to a great extent by some researchers^{2,5–32}.

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 behaviour at certain suitable compositions. In this paper, copolyesters of PBT and PHB were prepared, and the liquid crystalline properties of these copolyesters were studied and compared with those of copolyesters of PET and PHB.

EXPERIMENTAL

PET was obtained from Far Eastern Textile Ltd, Taiwan, and PBT (B-4500) was supplied by BASF. *p*-Acetoxybenzoic acid was prepared by reacting *p*-hydroxybenzoic acid (San Fu Chemical Co. Ltd, Taiwan) with acetic anhydride at 100°C, and the product was recrystallized from acetone solution. Zinc acetate and Sb₂O₃ were both Merck reagent grade and used as catalysts for melt condensation method. Copolyesters of PET and PHB were prepared by melt polycondensation²

at 275°C in the presence of 0.5 wt% of catalysts. The copolyesters of PBT and PHB were prepared in a similar manner. The composition of these copolyesters was characterized by the mol% of PHB, and thus PBT/PHB50 represents a copolyester of PBT and PHB with 50 mol% of PHB.

The thermal properties of PBT/PHB copolyesters were determined using a Du Pont Instruments 910 DSC. The melt birefringence was investigated with a Leitz polarizing microscope equipped with a hot stage.

RESULTS AND DISCUSSION

Solubility

The solubility of PBT/PHB copolyesters and PET/PHB copolyesters in phenol/TCE (syn-tetrachloroethane) (60/40 wt/wt) is shown in Table 1. The solubility of PBT/PHB copolyesters was considerably lower than that of corresponding PET/PHB copolyesters.

The PET/PHB copolyesters were proposed to be random copolymers^{1,2}, and soluble in phenol/TCE with content of PHB less than 70 mol%. When the content of PHB was higher, e.g. PET/PHB80, the longer PHB sequences were rendered insoluble.

The solubility behaviour of PBT/PHB copolyesters was different than PET/PHB copolyesters. PBT/PHB10 and PBT/PHB20 were soluble in phenol/TCE, but PBT/PHB copolyesters with PHB content ranging from 30 to 70 mol% were found to be partially soluble or insoluble as described in Table 1. The nondissolved parts of PBT/PHB copolyesters (30–60 mol% PHB) were swollen by the solvent to some extent. The PHB sequence length of PBT/PHB copolyesters should be longer (as compared to PET/PHB copolyesters) and thus low solubility was found. In other words, PBT/PHB copolyesters were not random copolymers.

The studies of PET/PHB80 (obtained from Tennessee Eastman Kodak) conducted by Zachariades *et al.*¹⁰

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Table 1 Solubility of PET/PHB copolyesters and PBT/PHB copolyesters in phenol/TCE

Copolyester	PET/PHB30	PRY/PHB40	PET/PHB50	PET/PHB60	PET/PHB70	PET/PHB80	
Solubility	YES	YES	YES	YES	Partial ^a	Insoluble	
$[\eta]^b$ (dl/g)	0.27	0.35	0.41	0.67	—	—	
Copolyester	PBT/PHB10	PBT/PHB20	PBT/PHB30	PBT/PHB40	PBT/PHB50	PBT/PHB60	PBT/PHB70
Solubility	YES	YES	Partial ^c	Partial ^c	Partial ^c	Partial ^c	Insoluble
$[\eta]^b$ (dl/g)	0.27	0.40	—	—	—	—	—

^a Almost soluble^b Determined in phenol/TCE at 30°C^c The samples were partially soluble, the nondissolved parts were swollen by the solvent

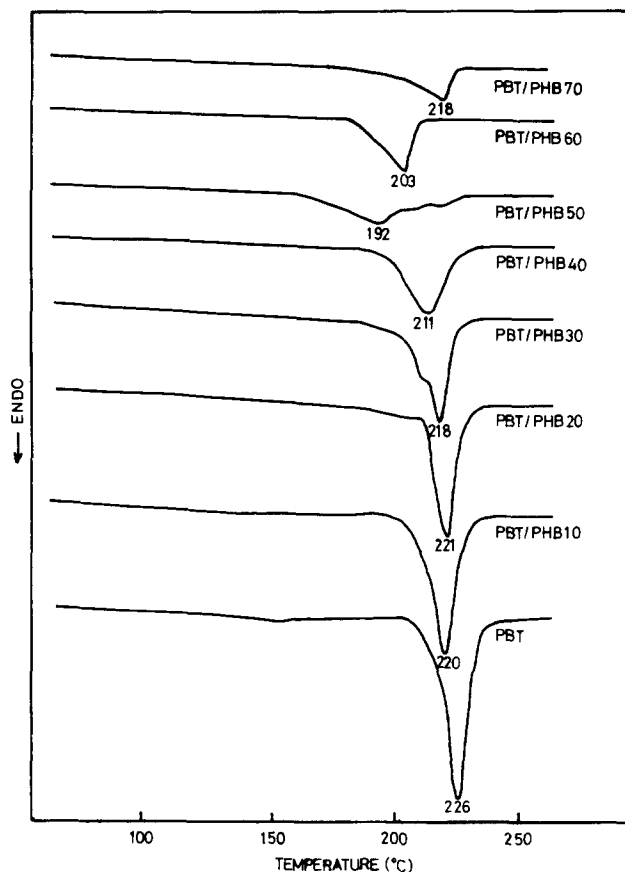
suggested that the reaction was heterogeneous in the later stages of reaction, and PHB blocks with long sequences were similar to PHB homopolymer, which is insoluble. The situation of PBT/PHB copolyester may be similar to the heterogeneous nature of the later stages of polymerization described by Zachariades *et al.* The reaction of PBT and *p*-acetoxybenzoic acid might be heterogeneous and more blocky copolymers could be obtained.

Thermal properties

The d.s.c. thermograms of PBT/PHB copolyesters are shown in Figure 1. The melting peaks of PBT/PHB10, PBT/PHB20 and PBT/PHB30 were found to be about 220°C and were close to that of PBT. This behaviour is different from PET/PHB copolyesters. It has been shown that the melting peaks of PET/PHB copolyesters were broadened and shifted to lower temperature^{2,14}. Taking PET/PHB30 as an example, its T_m was found to be 226°C and was considerably lower than PET (245°C)². The PET/PHB copolyesters are random copolymers, thus T_m was depressed due to the presence of the PHB unit. As described above, PBT/PHB copolyesters are not random copolymers, instead, they are more like block copolymers. Because the content of PHB was low, PBT sequences were long enough to render their crystalline behaviour similar to PBT and T_m was found to be close to PBT for PBT/PHB copolyesters with 10–30 mol% PHB.

PBT/PHB40 showed a broad melting peak at 211°C. The peak of PBT/PHB50 was much more broad and was shifted to 192°C. Although PBT/PHB copolymers are more blocky, the presence of higher content of PHB lowered the sequence length of PBT blocks. Thus a lower T_m and a more broad peak were found for PBT/PHB50. PBT/PHB60 reached T_m at 203°C and the melting peak was also broadened. PBT/PHB70 had a broad melting peak at 218°C which is close to the T_m of PBT. This behaviour can be explained as the heterogeneous reaction nature of polymerization.

In our interpretation of the reaction of PET and *p*-acetoxybenzoic acid², *p*-acetoxybenzoic acid can react with PET through transesterification and PHB units can be incorporated into the PET chain. The *p*-acetoxybenzoic acid can react with itself to form dimers or oligomers at the same time. The reactivity of these two types of reaction may be close enough for random copolymers to be obtained. In the reaction of PBT and *p*-acetoxybenzoic acid, the reactivity of PBT with *p*-acetoxybenzoic acid may be lower than that of *p*-acetoxybenzoic acid with itself. Thus, more PHB dimer

**Figure 1** D.s.c. thermograms of PBT/PHB copolyesters

or oligomers were formed at the initial stage. As the reaction proceeded, copolyesters with longer PHB sequences were obtained. When the PHB content was low (e.g. < 30 mol%), the PHB sequences were shorter and PBT sequences were longer. Thus the resulting PBT/PHB copolyesters were soluble and exhibited a melting peak close to PBT. As the content of PHB was higher (e.g. 50 mol%), PHB sequences were longer and PBT sequences were shorter. Thus, low solubility and lower and bordered melting peak were found. When the content of PHB was high, as in the case of PBT/PHB70, even longer PHB sequences formed initially. As reaction proceeded, the PHB sequences of some blocks might have been long enough so that some parts precipitated and could not react further, and the probability of transesterification of PBT blocks with PHB units was lowered. The PBT sequences of PBT/PHB70 may be longer than PBT/PHB50. Thus PBT/PHB70 exhibited a higher melting point.

Table 2 The crystallinity of PBT/PHB copolyesters

Copolyester	Crystallinity (%) [*]
PBT/PHB10	34
PBT/PHB20	30
PBT/PHB30	27
PBT/PHB40	24
PBT/PHB50	19
PBT/PHB60	17
PBT/PHB70	14

^{*} Obtained by dividing the heat of fusion of copolyester by that of fully crystalline PBT(34.5 cal/g)³³

The crystallinity (PBT component) of PBT/PHB copolyesters could be obtained from their heat of fusion. Table 2 lists the results. The crystallinity decreased as the PHB content increased (PBT content decreased) as was expected.

Liquid crystalline properties

The liquid crystalline behaviour was investigated with a polarizing microscope. PET/PHB30 is a random copolymer with a low PHB content and the PHB sequences are short. Under polarized light, the PET/PHB30 melt showed no explicit melt birefringence. The PHB sequences of PET/PHB40 are longer, thus, PET/PHB40 exhibited liquid crystallinity explicitly. Under polarized light, the PET/PHB40 showed an anisotropic phase in an isotropic phase. As the content of PHB increased, the nematic phase of the PET/PHB copolyesters became continuous.

Because the PBT/PHB copolyesters are more blocky, the PHB sequences are longer than the corresponding PET/PHB copolyesters. Thus, only 20 mol% of PHB would cause PBT/PHB copolyester to exhibit liquid crystalline behaviour and show melt birefringence. Under polarized light, the nematic phase of PBT/PHB20 and PBT/PHB30 was found to be disperse and that of PBT/PHB40, PBT/PHB50, and PBT/PHB60 became continuous. Although PBT/PHB70 had a melting peak in the d.s.c. thermogram, it could not melt (or become liquid-like) on the hot stage. Degradation was observed when it was heated to about 340°C.

Since the PBT/PHB copolyesters are more blocky, they exhibit liquid crystallinity at a lower content of PHB as compared to the PET/PHB copolyesters.

CONCLUSIONS

The PBT/PHB copolyesters exhibited different properties than PET/PHB copolyesters. The PBT/PHB copolyesters are more blocky in contrast to PET/PHB copolyesters which are random. Thus, the PBT/PHB copolyesters exhibit lower solubility and exhibit liquid crystalline

behaviour at lower PHB content as compared to the PET/PHB copolyesters. The PBT/PHB copolyesters exhibited liquid crystalline behaviour with 20–60 mol% PHB content, while the PET/PHB copolyesters showed liquid crystalline behaviour with a PHB content of 40–80 mol%.

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