

# Study on Co[poly(butylene terephthalate-*p*-oxybenzoate)] Thermotropic Copolyester. I. Composition Analysis and Sequence Distribution

CHENG-FANG OU

National Chin-Yi Institute of Technology, Department of Chemical Engineering, Taichung, Taiwan, Republic of China

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**ABSTRACT:** Copolyesters made from Poly(butylene terephthalate) (PBT) and *p*-acetoxybenzoic acid (PAB) have been examined in solution by proton nuclear magnetic resonance (NMR) spectroscopy. Proton NMR spectra of solutions have shown that the sequence distribution for POB/PBT copolyesters can be described in terms of a probability model in which POB (*p*-oxybenzoate) has a chance that is almost random of being bonded to another POB in the copolyesters, with POB content ranging from 20 to 40 mol %. From the experimental data, we can predict that the higher the content of POB in copolyester is, the larger the deviation from randomness of sequence distribution is. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 949–954, 2000

**Key words:** liquid crystalline polymers; copolyester; nuclear magnetic resonance; sequence distribution; randomness

## INTRODUCTION

Many of the stiff-chain aromatic polymers that are used as high-strength and high-modulus materials exhibit liquid crystalline behavior. For practical purposes, there is a need for nematic mesophases processible at relatively low temperature. 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 scan-

ning 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 POB/PBT copolyesters have been reported by Chen and coworkers.<sup>17</sup> They found that POB/PBT copolyesters exhibited liquid crystalline behavior with 20–60 mol % POB content. They suggested the reason why the POB/PBT copolyesters exhibit liquid crystalline behavior at lower POB content compared to the POB/PET copolyesters is that POB/PBT copolyesters are more blocky than POB/PET copolyesters. For this article, POB/PBT copolyesters were prepared by melt polycondensation of PBT with PAB. The exact compositions of the copolyesters and sequence

distribution as determined by proton NMR were studied.

## EXPERIMENTAL

### Materials

PBT resin was generously supplied by Far East Textile Co (Taoyuan, Taiwan) having an intrinsic viscosity of 1.0 (dL/g) in 60/40 (w/w) phenol/tetrachloroethane at 30°C. *p*-Acetoxybenzoic acid was supplied by BASF. Sb<sub>2</sub>O<sub>3</sub> was Merck reagent grade and was used as catalyst for melt condensation. Trifluoroacetic acid (Aldrich Chemical Co.) was used as a solvent for proton NMR analysis.

POB/PBT copolyesters were prepared by the Kuhfuss and Jackson melt polycondensation method,<sup>1</sup> in which a mixture of the *p*-acetoxybenzoic acid, PET, and 1 wt % catalyst were placed in a flask equipped with a stirrer and short head with an inlet and an outlet for nitrogen. The nitrogen outlet was connected to a glass tube (distillation column), which led to a receiver with provision for applying vacuum. After the reaction flask was evacuated and purged with nitrogen three times to remove all air, it was heated to 260°C and held for 1 h under nitrogen atmosphere in a eutectic salt bath of sodium nitrite and potassium nitrate. After the initial polymer fragmentation reaction was completed, a vacuum of about 0.5 mmHg was slowly applied and the polymerization reaction was allowed to occur for 6 h at 260°C. The composition of these copolyesters was characterized by the mol % of POB, and thus 60POB/PBT represents a copolyester having 60 mol % POB moiety.

### Copolymer Composition Analyses and Sequence Distribution

Proton NMR analysis was used to determine the compositions of the POB/PBT copolyesters. For the NMR spectra, 5 to 10 wt % solutions of copolyester in cold (room temperature) deuterated trifluoroacetic acid (TFA) were prepared. With the exception of 80POB/PBT, all solutions were clear. 80POB/PBT would not dissolve and could not be measured by NMR spectroscopy. The spectra were obtained by using a Varian Model Unity-300 NMR spectrometer operating at 300 MHz under usual conditions and with tetramethylsilane (TMS) as the internal standard. The dyads fractions or the mol % of POB bonded to PET unit

were determined from the NMR spectra by integration of specific peak areas as described in Lenz<sup>18</sup> and Nicely<sup>19</sup> et al. and our previous article.<sup>14,15</sup>

## RESULTS AND DISCUSSION

### Copolyester Composition Analyses

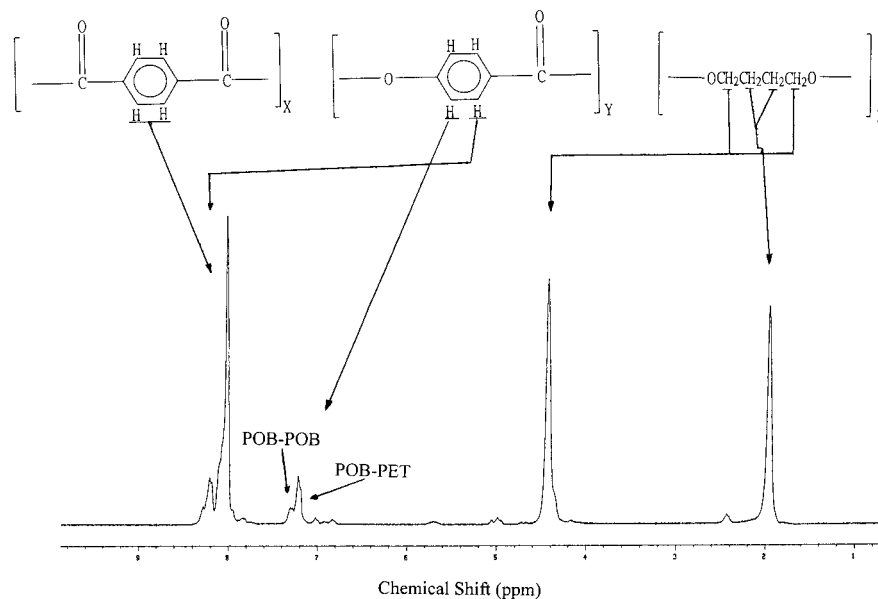
Figure 1 illustrates the 300-MHz proton NMR spectrum for 60POB/PBT in trifluoroacetic acid solution, and shows the assignments for the resonances. The sharp signal at 8.0 ppm corresponds to the proton of the terephthalate proton. The peaks at 2.0 and 4.4 ppm correspond to the methylene proton of PBT. According to Lenz<sup>18</sup> and Nicely<sup>19</sup> et al., the peaks at higher magnetic field (7.3 ppm) correspond to the POB–POB dyad, while the other (7.2 ppm) is due to the POB–PBT dyad. The dyads fraction or the mol fraction of POB bonded to another POB unit were determined from the integration of the two peaks. Integrations of each of the resulting peaks were taken to calculate the mole fraction of POB unit in the copolyester as described in the following. From the assignments for various protons in the POB/PBT copolyesters in Figure 1, we designate the integrations of the peaks at 8.0 and 8.2 ppm as A1 and A2. The peaks at 7.2 and 7.3 ppm are designated as B1 and B2. The peaks at 2.0 and 4.4 ppm are designated as C1 and C2, respectively.

The POB/PBT copolyester composition was calculated by the following equation from the data of Figure 1:

$$X_{\text{POB}} = \frac{\frac{B}{2}}{\frac{A1}{4} + \frac{A2}{2}} = \frac{2B}{A1 + 2A2} \\ = \frac{2B}{(A1 + A2) + A2} = \frac{2B}{A + B} \quad (1)$$

where  $X_{\text{POB}}$  is the mol fraction of POB units in the copolyester;  $A = A1 + A2$ , and  $B = B1 + B2$ .

The compositions of the copolyesters, as determined by NMR analysis, are given in Table I. The compositions were always lower in POB unit content than the calculated amount based on monomer composition in the copolymerizations. 20POB/PBT copolyester contains 18.6 mol % POB unit. 60POB/PBT copolyester contains 50.4 mol % POB unit. The POB content in POB/PBT



**Figure 1** Proton NMR spectrum at 300 MHz with the assignments of the absorptions for 60POB/PBT copolyester dissolved in trifluoroacetic acid.

copolyester is always smaller than the calculated amount. It seems that copolyesters containing higher POB content exhibit larger composition deviations from the calculated amount. The result is similar to the data of POB/PET copolyesters presented by Nicely et al.<sup>19</sup> and Olbrich et al.<sup>21</sup> 80POB/PBT would not dissolve in trifluoroacetic acid, and its composition could not be determined by NMR spectroscopy. The reason for this discrepancy appears to be twofold: (1) the loss of *p*-acetoxybenzoic acid by hydrolysis and sublimation during copolymerization; and (2) *p*-acetoxybenzoic acid monomer forms an insoluble, infusible polymer by homopolymerization during copolymerization.

### Sequence Distribution

The fraction of the POB repeat units that are bonded to another POB or to a PBT unit can be

**Table I** The Code and Compositions of POB/PBT Copolyesters

POB/PBT (Mol Ratio)	Code	$X_{\text{POB}}$
20/80	20POB/PBT	0.186
40/60	40POB/PBT	0.367
60/40	60POB/PBT	0.504
80/20	80POB/PBT	—

determined by integrating the two peaks of 7.2 and 7.3 ppm.

$$f_{\text{POB-POB}} = \frac{B_2}{B_1 + B_2} \quad (2)$$

where  $f_{\text{POB-POB}}$  is the fraction of POB units that are connected directly to another POB unit in a copolyester with a  $X_{\text{POB}}$  mol fraction of POB units. For the case of a purely random copolymer, the probability of a POB being bonded to another POB is given by<sup>20</sup>

$$P(\text{POB/POB}) = P(\text{POB}) / (P(\text{POB}) + 2P(\text{PBT})) \\ = \frac{X_{\text{POB}}}{X_{\text{POB}} + 2(1 - X_{\text{POB}})} = a \quad (3)$$

In the nonrandom copolymer, if the POB has a composition-independent preference for bonding to itself, then we might find<sup>20</sup>

$$P(\text{POB/POB}) = ma \quad (4)$$

where  $m$  is the preference factor that is one for a purely random copolymer. The fraction of the POB units that are connected directly to another POB unit in a copolyester with a  $X_{\text{POB}}$  mol fraction of POB units is given by<sup>20</sup>

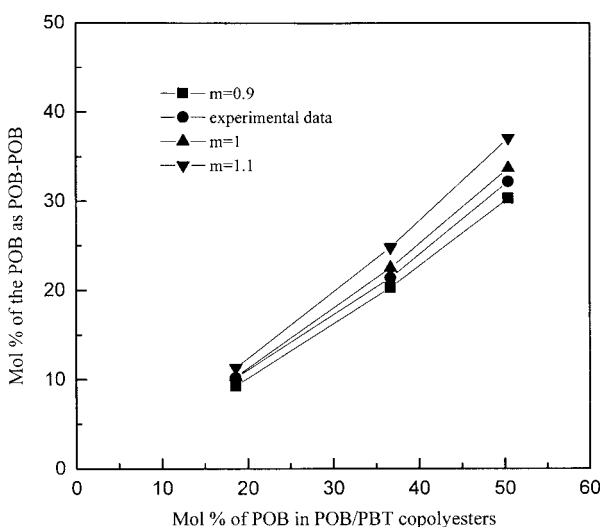
**Table II The Characteristics of POB/PBT Copolyesters**

Sample	$X_{\text{POB}}$	$f_{\text{POB-POB}}$	$a$	$m$
20POB/PBT	0.186	0.102	0.103	0.990
40POB/PBT	0.367	0.214	0.225	0.951
60POB/PBT	0.504	0.322	0.337	0.956

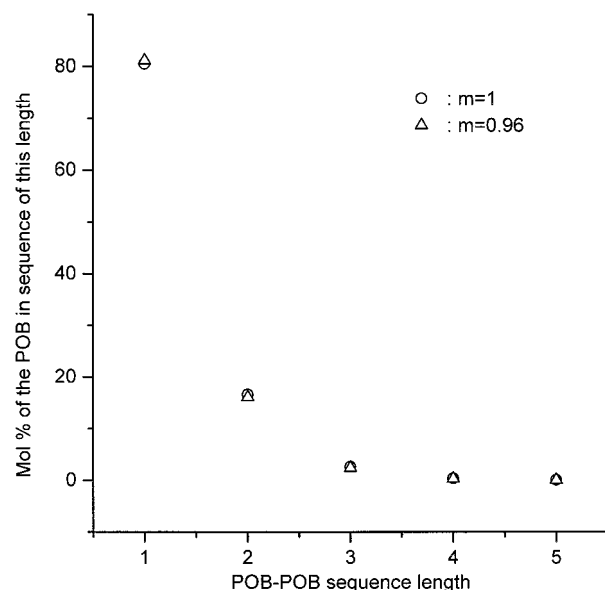
$$f_{\text{POB-POB}} = ma \quad (5)$$

The value of  $m$  might be calculated from the values of  $f_{\text{POB-POB}}$  and  $a$ , which are determined from NMR measurements.

The values of  $X_{\text{POB}}$ ,  $f_{\text{POB-POB}}$ ,  $a$ , and  $m$  are shown in Table II. The value of  $m$  of 20POB/PBT copolyester containing 18.6 mol % POB units is 0.990. This result reveals that 20POB/PBT is almost nearly a pure random copolymer. The values of  $m$  of 40POB/PBT containing 36.7 mol % POB units and 60POB/PBT containing 50.4 mol % POB units are 0.951 and 0.956, respectively. Although the values of  $m$  of these POB/PBT copolyesters are slightly smaller than 1.0 for a purely random copolymer, the deviations compared to the random model are small. Figure 2 shows the mol % of the POB unit bonded to another POB unit for several POB/PBT copolyesters with POB content ranging from 20 to 60 mol % POB. Also included in Figure 2 are the data calculated from a probability model for  $m$  of 0.9, 1.0, and 1.1



**Figure 2** Mol % of POB connected directly to another POB for several POB/PBT copolyesters. Lines were calculated from a probability model described in the text.

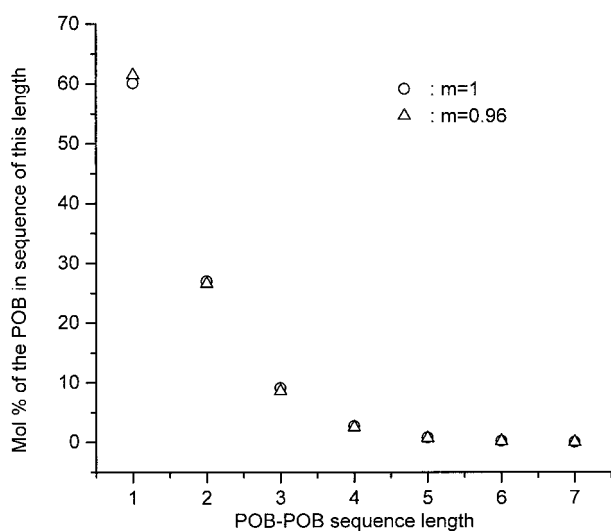


**Figure 3** Mol % of POB units in 20POB/PBT in sequences of various lengths as calculated from a probability model.

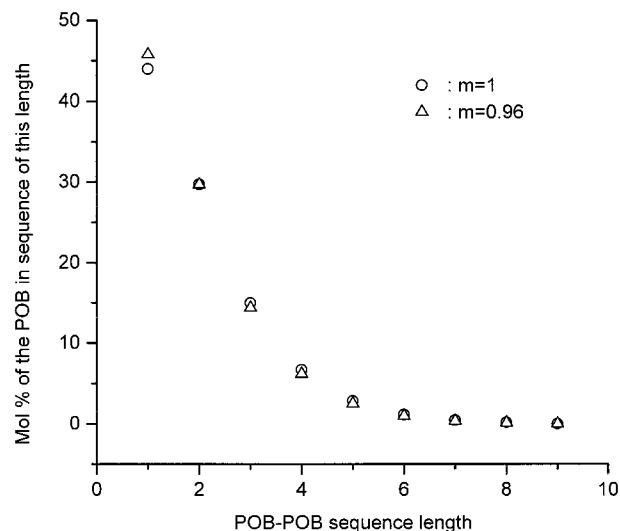
described in the preceding text. A preference factor of about 0.96 for  $m$  was obtained from the line near each of the experimental data points. The ability of the model to place a line near each data point while using a single value for  $m$  gives some support to the appropriateness of the model and the assumption that a single mechanism accounts for the sequencing of repeat units in the series of copolymers. The value for  $m$  of 1.3 was found for the POB/PET copolyesters in the previous report by Lenz et al.<sup>18</sup> The value for  $m$  of 0.96 obtained in this research for the POB/PBT copolyesters. This result indicates that POB/PBT copolyesters in this research are more nearly random copolymers than the POB/PET copolyester synthesized by Lenz et al.<sup>18</sup> In other words, the POB sequence length of POB/PET copolyesters should be longer compared to POB/PBT copolyesters.

Figures 3–5 show the probability model prediction for the sequence length distribution<sup>20</sup> in three copolyesters. Figure 3 shows the probability model of 20POB/PBT for  $m$  of 0.96 compared to the random model with  $m$  of 1. Both of them are almost the same. The mol % of POB in the POB–POB sequence length  $n = 1$  of about 80% is much larger than that of  $n = 2$  at about 16%. The mol % of POB in the POB–POB sequence length  $n > 3$  is near to zero. This result reveals that 20POB/PBT exhibits short POB–POB sequences and is nearly a pure random copolymer. Figure 4 shows the

probability model of 40POB/PBT for  $m$  of 0.96 and 1. Both of them are almost the same as each other except for  $n = 1$ . The sequence distribution is similar to that of 20POB/PBT. The mol % of POB in the POB-POB sequence lengths  $n = 1$  and  $n = 2$  are about 60 and 27%, respectively. The mol % of POB in the POB-POB sequence length  $n = 3$  at about 9% in 40POB/PBT is larger than that of 2.5% in 20POB/PBT. This result reveals that 40POB/PBT is still nearly a pure random copolymer but exhibits more long POB-POB sequences than 20POB/PBT. Figure 5 shows that 60POB/PBT exhibits a significant deviation with an  $m$  of 0.96 compared to the random distribution with  $m$  of 1 at the POB-POB sequence length  $n = 1$ . On the other hand, the mol % of POB in the POB-POB sequence length  $n = 5$  at about 2.5% is not as small as to be negligible. These results reveal that 60POB/PBT exhibits much longer POB-POB sequences than those of 20POB/PBT and 40POB/PBT. From these data, the probability model of the sequence shows that the deviation of the sequences from those for a random sequence for POB contents below 60 mol % is so small as to be negligible. In other words, the deviations from randomness of the sequence distributions are small at lower POB contents (20POB/PBT and 40POB/PBT) and become more significant at higher POB content in the POB/PBT copolyesters. Although 80POB/PBT is not dissolvable in trifluoroacetic acid, we predict that it will exhibit longer sequences and larger deviation from randomness than 40POB/PBT and 60POB/PBT.



**Figure 4** Mol % of POB units in 40POB/PBT in sequences of various lengths as calculated from a probability model.



**Figure 5** Mol % of POB units in 60POB/PBT in sequences of various lengths as calculated from a probability model.

## CONCLUSIONS

Proton NMR spectra of solutions have shown that the sequence distributions for POB/PBT copolyesters can be described in terms of a probability model in which POB has a chance that is almost random of being bonded to another POB in 20POB/PBT and 40POB/PBT. The POB/PBT copolyesters with higher POB contents exhibit a longer POB-POB sequence and more significant deviations from randomness of sequence distributions.

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