

Sequence Analysis of Poly(ethylene terephthalate)/Poly(butylene terephthalate) Copolymer Prepared by Ester-Interchange Reactions

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ABSTRACT: The molecular structure of the copolyester formed through the interchange reaction in poly(ethylene terephthalate)/poly(butylene terephthalate) blends was investigated with ¹³C-NMR spectroscopy. The molar fractions of heterolinkage triads in the copolyesters were lower than the values calculated by Bernoullian statistics; this indicates that the sequence of heterolinkages was far from a random distribution at the initial stage of the interchange reaction. However, the randomness increased and the number-average sequence length decreased with reaction time. The solubility of the blend decreased with increasing sequence length, resulting from the formation of block copolymers with long sequence lengths at the initial stage of the interchange reaction. The solubility of the copolyester formed by a dibutyltin dilaurate (DBTDL)-catalyzed reaction was higher than that of the copolyester formed by a titanium tetrabutoxide-catalyzed reaction; this is related to the fact that alcoholysis prevailed in the DBTDL-catalyzed reaction. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 159–168, 2001

Key words: copolyester; interchange reaction; poly(ethylene terephthalate) (PET); poly(butylene terephthalate) (PBT); blend; randomness; sequence length

INTRODUCTION

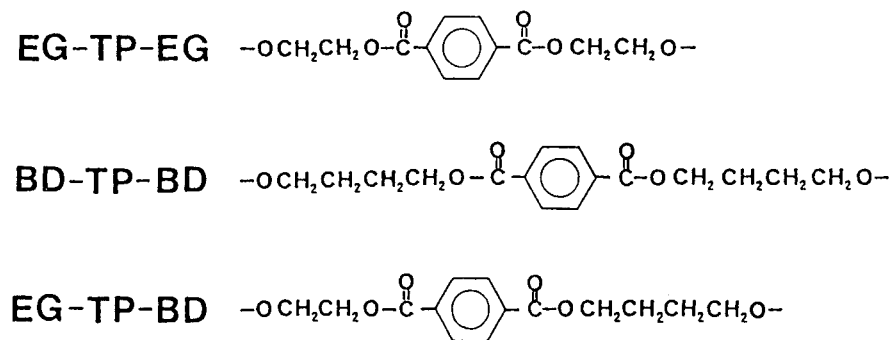
Polyester is one of the most widely used polymers for engineering plastics and synthetic fibers, having excellent mechanical and thermal properties. Among polyesters, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) have a variety of industrial uses as representative fiber-forming polymers. In particular, PBT has the advantages of a very high crystallization rate to reduce the molding period and elastic recovery and dyeability and flexibility superior to those of PET.¹ In contrast, the mechanical properties of PET are superior to those of PBT.^{1,2} Thus, copo-

lymerizations and polymer blends of PBT and PET are actively in progress.^{1–10} Misra and Garg^{1,2} synthesized PET/PBT block copolymers to enhance the crystallization rate of PET. The improvement and complement of properties of polymeric materials are also achieved by blending. For a PET/PBT blend, miscibility in the amorphous region was confirmed for the entire blend composition.¹¹

It is well known that chemical interchange reactions between polyester molecules occur above the melting temperature. A uniform distribution of molecular weight is achieved by the interchange reaction for the homopolymer mixture. Meanwhile, in the blend system of polyesters, block copolymers are formed preferentially in the initial stage of the interchange reaction. The block length of the copolymers becomes shorter

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Scheme 1 Triad sequences of the interchange-reacted PET/PBT blend.

with the progress of the reaction, and random copolymers prevail in the later stage of the reaction.^{12,13}

The interchange reaction of polyester is classified into three types: intermolecular alcoholysis between hydroxyl end group and ester group, intermolecular acidolysis between carboxyl end group and ester group, and direct transesterification between ester groups. The interchange reaction in PET/PBT blends results in the formation of heterolinkages. As presented in Scheme 1,

there are three kinds of triad sequences in a PET/PBT blend system having undergone the interchange reactions. However, because of the structural similarity of PET and PBT, ¹H-NMR spectroscopy reveals only the compositions of the blend pairs.

In a ¹³C-NMR spectrum, the chemical shift of the ester carbonyl group in the copolyester was found by Kricheldorf.¹⁴ Only one peak was observed with the protons attached to the phenylene ring, regardless of the methylene group linked to

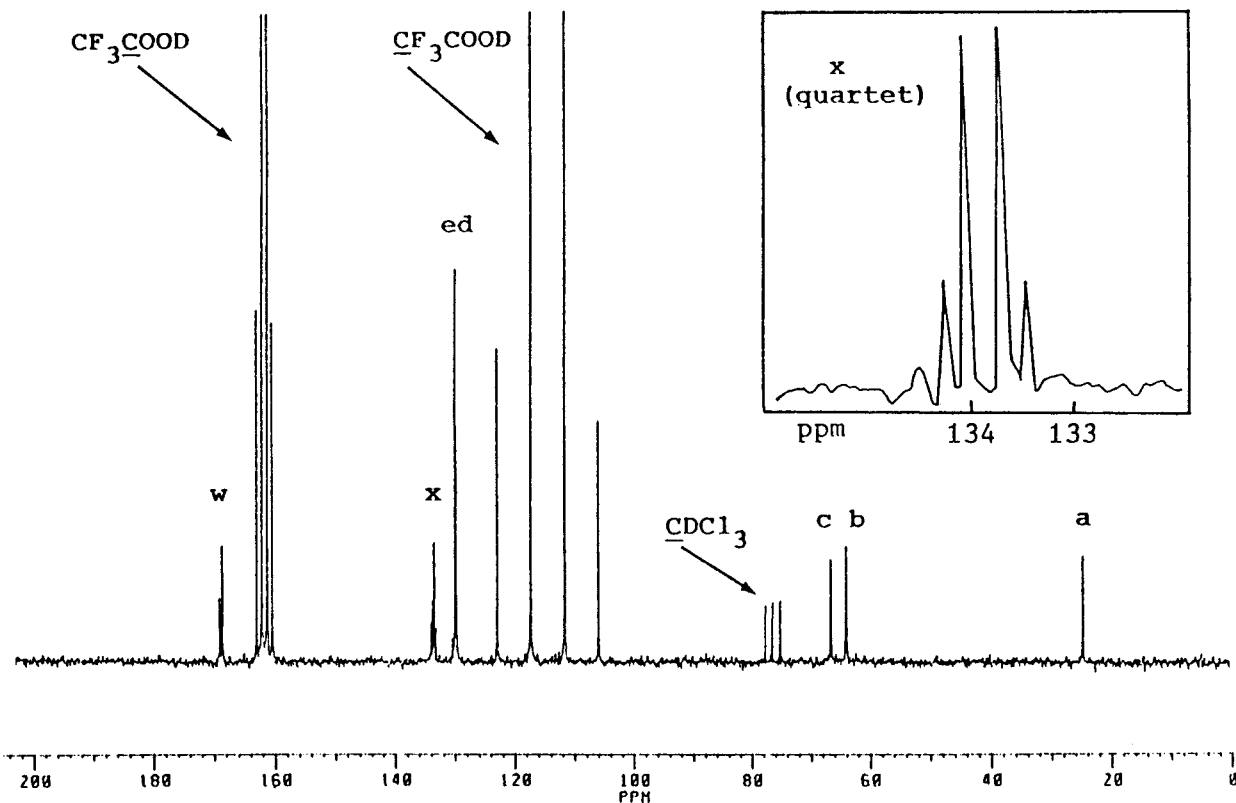


Figure 1 Typical ¹³C-NMR spectrum of the interchange reaction product of the PET/PBT blend.

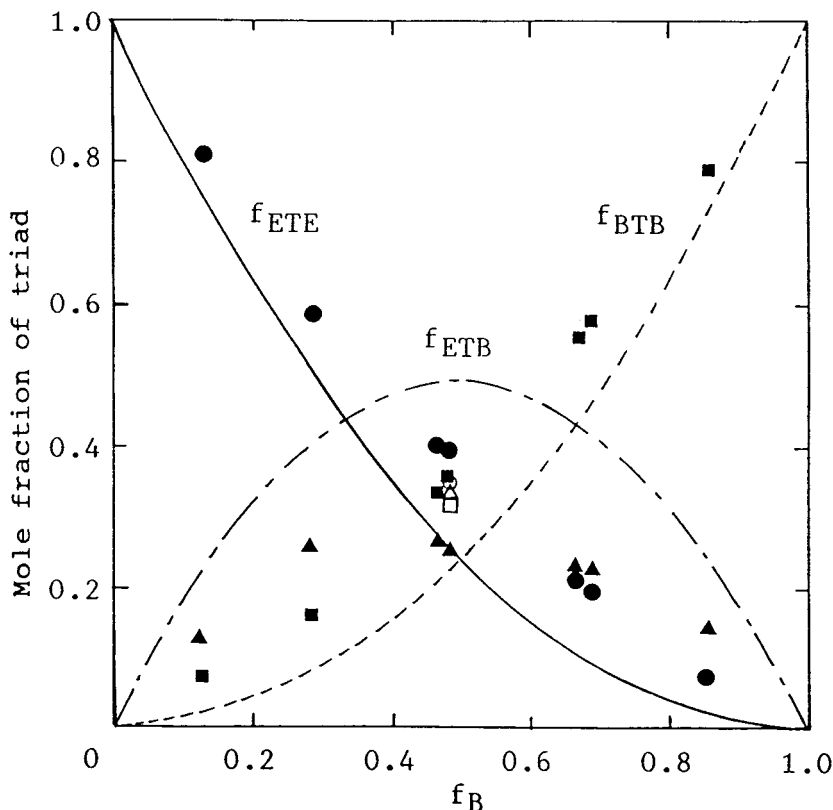


Figure 2 Molar fractions of homolinkage and heterolinkage triads for the copolyester formed by the interchange reaction of the PET/PBT blend for 90 min as a function of f_B : (■) f_{BTB} , (●) f_{ETE} , and (▲) f_{ETB} for the TBT-catalyzed reaction; (□) f_{BTB} , (○) f_{ETE} , and (△) f_{ETB} for the DBTDL-catalyzed reaction; and (···) f_{BTB} , (—) f_{ETE} , and (-·-) f_{ETB} by Bernoullian statistics.

terephthalate (TP) in a $^1\text{H-NMR}$ spectrum. In contrast, the long-range effect on the chemical shift of ester carbonyl carbons and quaternary carbons in TP was identified with $^{13}\text{C-NMR}$ spectroscopy. Thus, the sequential analyses of various copolyesters were achieved successfully with $^{13}\text{C-NMR}$ spectroscopy.^{15,16} In this study, the differences in the molecular structures of copolymers formed through the interchange reactions of PET/PBT blends with titanium tetrabutoxide (TBT) and dibutyltin dilaurate (DBTDL) were elucidated with $^{13}\text{C-NMR}$ spectroscopy. In addition, the sequential changes during the interchange reaction were investigated on the basis of the sequence distribution, randomness, and sequence length.

EXPERIMENTAL

Materials

Commercial chips of PET and PBT were obtained from Tongyang Polyester Co. (Ulsan, Korea) and

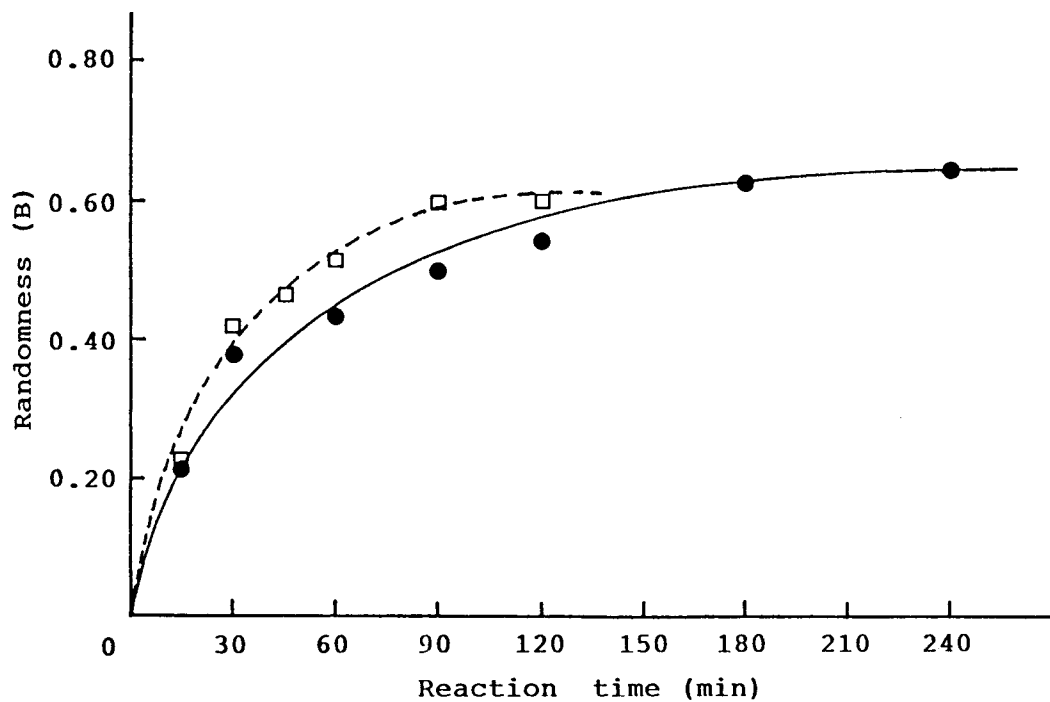
Toray Industry Inc. (Tokyo, Japan), respectively. The intrinsic viscosities in the mixed solvent of phenol/1,1,2,2-tetrachloroethane (TCE) with a weight ratio of 6/4 were 0.55 and 0.82, respectively. The number-average molecular weights of the polymers were 22,000 and 23,000, respectively. Other extra-pure-grade reagents were used without further purifications.

Preparation of the PET/PBT Blend

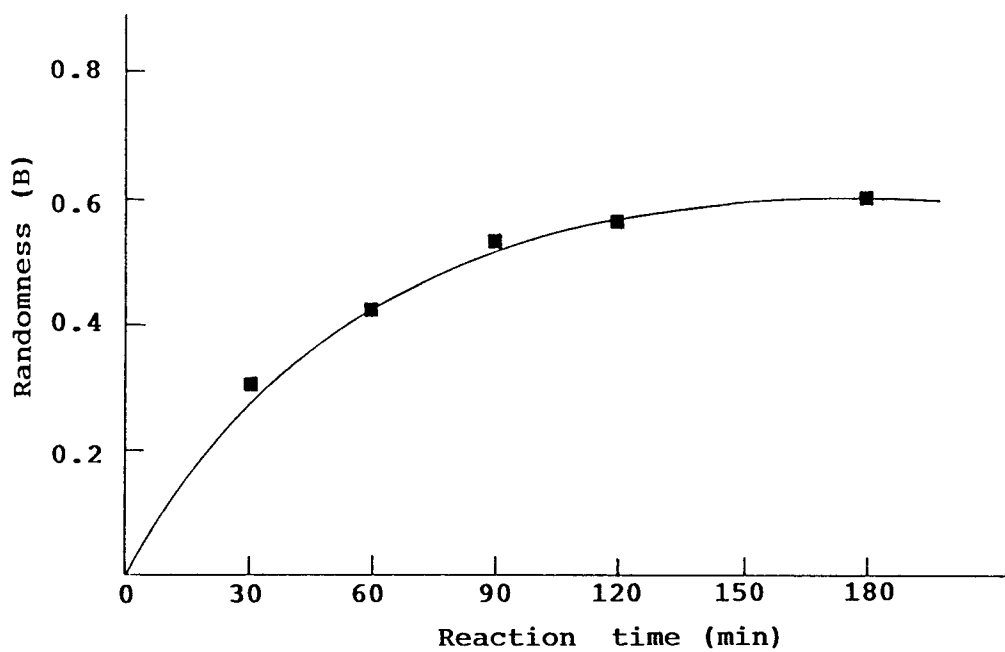
Mixtures of PET and PBT with compositions of 100/0, 95/5, 75/25, 50/50, 25/75, 10/90, 5/95, and 0/100 (w/w) were dissolved in a mixed solvent of phenol and TCE with a weight ratio of 6/4 at 60°C for 4 h. The solution was precipitated in cold methanol to yield a white, solid product. After the removal of the residual solvent from the precipitates and subsequent drying under vacuum, the final product was obtained.

Ester-Interchange Reaction

The blend of PET/PBT was melted under a nitrogen flow for the interchange reaction. TBT or



(a)



(b)

Figure 3 (a) Randomness during the interchange reaction of the PET/PBT blend (50 wt % PBT) at 280°C with the interchange reaction time: (●) TBT-catalyzed reaction and (□) DBTDL-catalyzed reaction. (b) Randomness of the chloroform-insoluble fraction with the interchange reaction time; the PBT content was 25 wt %, the reaction temperature was 280°C, and the catalyst was TBT.

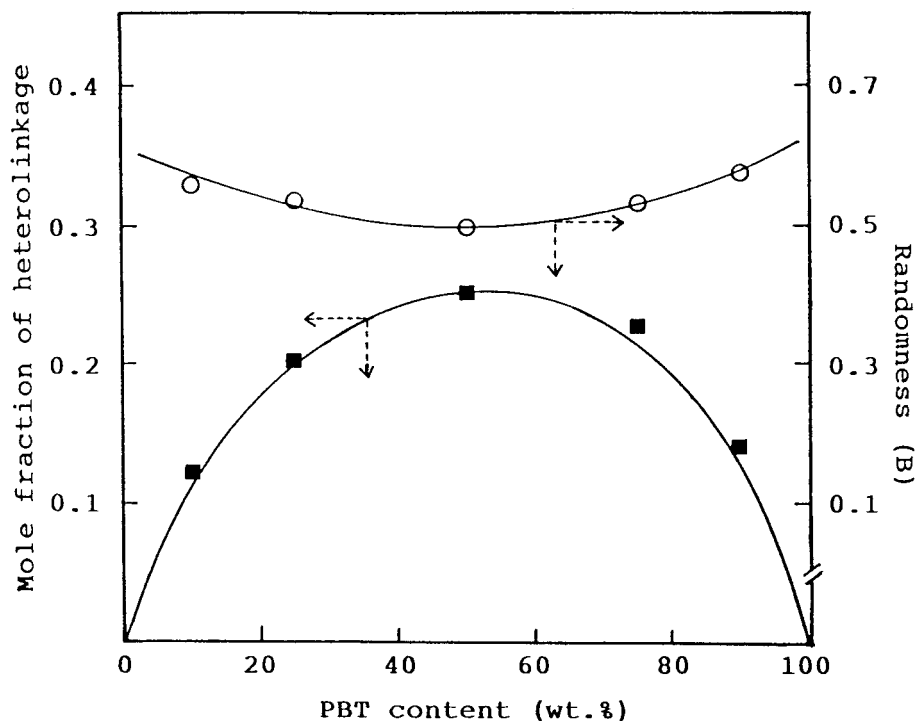


Figure 4 Changes in the molar fraction of (■) heterolinkage and (○) randomness with the PBT content. The reaction temperature was 280°C, the reaction time was 90 min, and the catalyst was TBT.

DBTDL (0.02 wt %) was added as a catalyst. After the reaction, the reactants were quenched in cold water and dried.

Extraction of the PET/PBT Copolymer

The product obtained from the interchange reaction was reprecipitated by the same method adopted in the blend preparation. The copolymer was extracted in chloroform from the reprecipitates for 24 h with a Soxhlet apparatus and reprecipitated in cold methanol. The solubility in chloroform was determined from the weight fraction of the extracted product to the product obtained from the ester-interchange reaction.

¹³C-NMR Spectroscopy

The products were dissolved in trifluoroacetic acid/chloroform-*d*₆ with a volume ratio of 7/3 to obtain ¹³C-NMR spectra with a Bruker AM-100 FT-NMR spectrometer (Rheinstetten, Germany). The measurement was carried out at a sweep width of 5000 Hz and an acquisition time of 0.8 s.

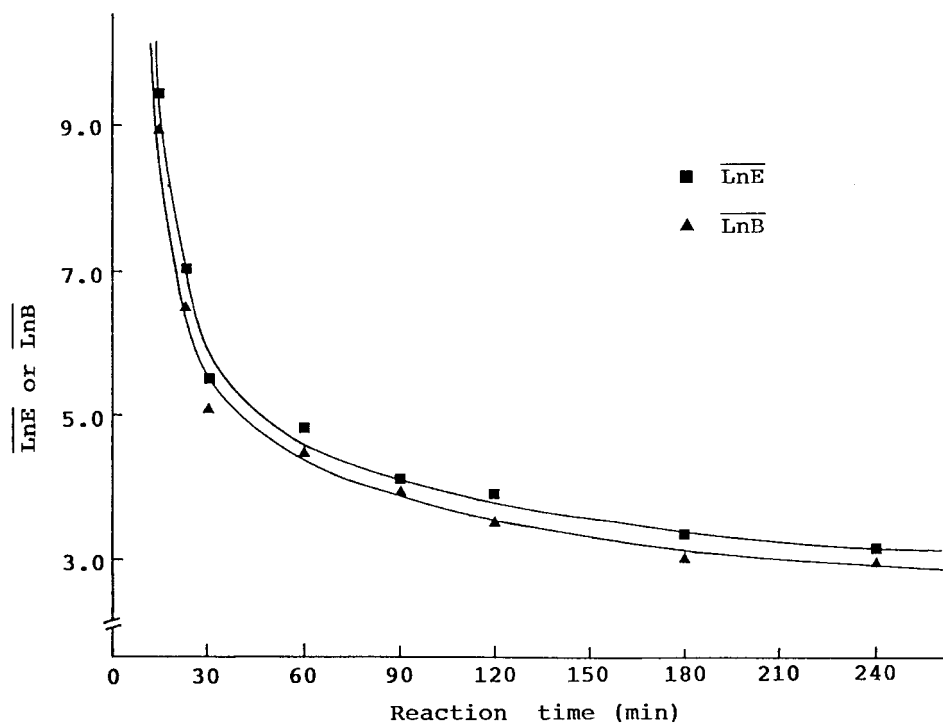
RESULTS AND DISCUSSION

Sequence Distribution

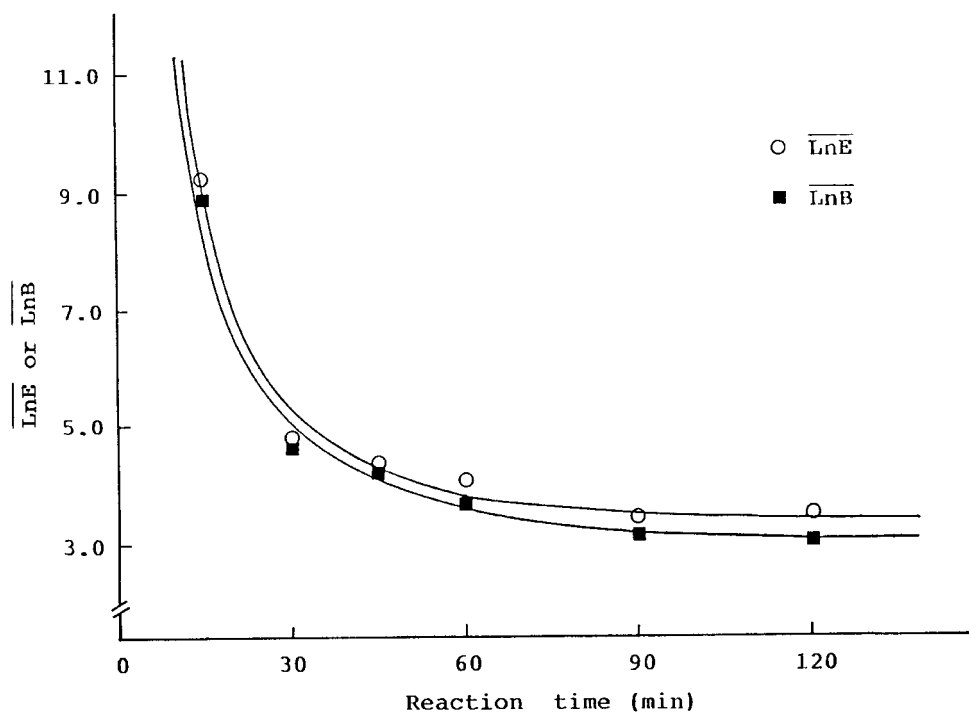
For a quantitative analysis of the ¹³C-NMR spectrum, the spin-lattice relaxation time (*T*₁) and nu-

clear Overhauser enhancement (NOE) should be unchangeable.^{15,16} It has been reported that *T*₁'s and NOEs of quaternary carbon in TP and carbonyl carbon of PET/PBT copolymer synthesized from ethylene glycol (EG), 1,4-butandiol (BD), and dimethyl terephthalate are fixed and fairly reproducible through a number of experiments.¹⁶ Hence, the aromatic quaternary carbons in PET/PBT blends can be compared with one another quantitatively by peak area in a ¹³C-NMR spectrum.

A typical ¹³C-NMR spectrum of a PET/PBT copolymer prepared by ester-interchange reaction is shown in Figure 1. The peaks at 26 (a), 66 (b), 68 (c), and 132 ppm (d and e) are assigned to 2,3-carbons in the butylene unit, two carbons in the ethylene unit, 1,4-carbons in the butylene unit, and four carbons in the phenylene ring, except for quaternary carbons, respectively. The quartet peak (x) at 134 ppm is for the quaternary carbon in TP. Another quartet peak (w) at 170 ppm is the resonance of the carbonyl carbon. In this study, the quartet peak (x) of the quaternary carbon in the TP unit was used for the sequence quantification. This peak is divided into four subordinate ones assigned to the sequences of EG-TP-BD, EG-TP-EG, BD-TP-BD, and BD-TP-EG, respectively. The



(a)



(b)

Figure 5 \overline{LnE} and \overline{LnB} during (a) TBT-catalyzed and (b) DBTDL-catalyzed inter-change reactions of PET/PBT blends (50 wt % PBT) at 280°C with interchange reaction times.

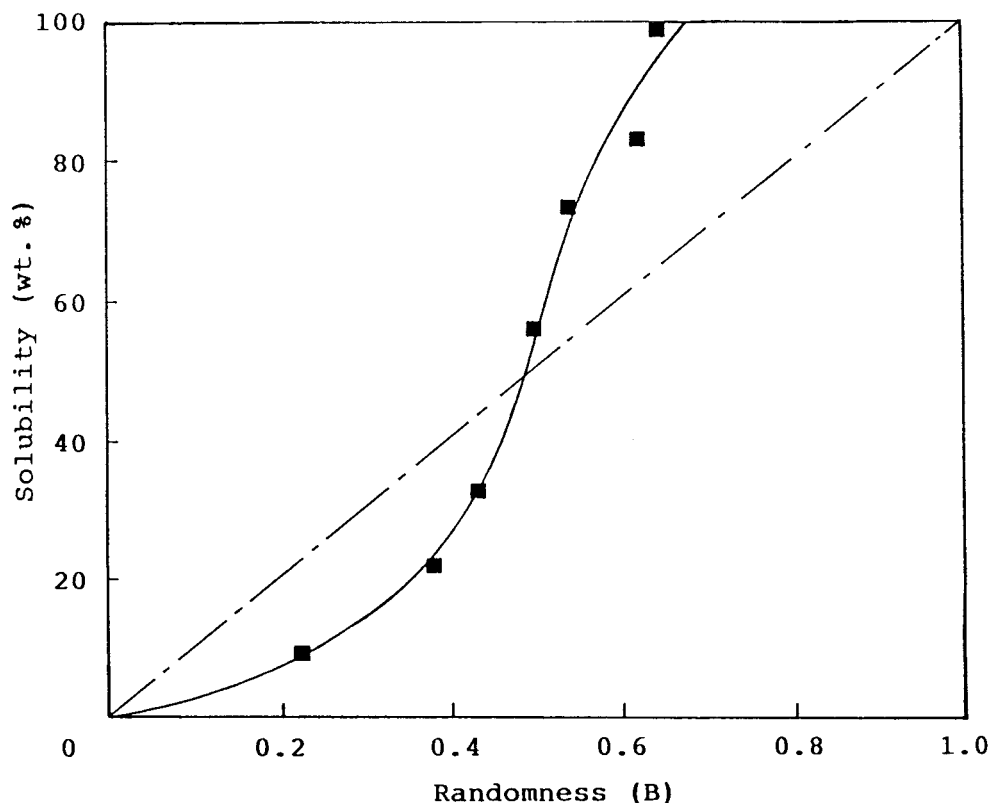


Figure 6 Solubility in chloroform as a function of randomness of the PET/PBT blend (50 wt % PBT) interchange-reacted at 280°C.

molar fractions of EG (f_E) and BD (f_D) were calculated from eqs. (1) and (2):

$$f_E = f_{ETE} + \frac{1}{2} f_{ETB} \quad (1)$$

$$f_B = f_{BTB} + \frac{1}{2} f_{ETB} \quad (2)$$

where f_{ETE} , f_{BTB} , and f_{ETB} are the molar fractions of EG-TP-EG, BD-TP-BD, and EG-TP-BD with respect to the total TP unit calculated from the peak area.

Figure 2 shows the molar fractions of homolinkage and heterolinkage triads for the copolyester formed by the interchange reaction in the PET/PBT blend as a function of f_B . The curve obtained from Bernoullian statistics implies a perfectly random sequence distribution of the monomers with the same reactivity. Considering EG-TP or BD-TP as a monomeric unit, we calculate the molar fractions from the dyad distributions according to Bernoullian statistics as follows:¹⁷

$$f_{ETE} = f_E^2 \quad (3)$$

$$f_{ETB} = 2f_E(1 - f_E) = 2f_E f_B \quad (4)$$

$$f_{BTB} = f_B^2 \quad (5)$$

As shown in Figure 2, both f_{ETE} and f_{BTB} were higher than the values obtained from Bernoullian statistics, whereas f_{ETB} was lower, which indicates that the heterolinkage sequence is not described by a random distribution at the initial stage (90 min) of the interchange reaction. A sequence distribution close to Bernoullian was found in the copolymer formed by the interchange reaction of PET/poly(ethylene sebacate) for 180 min.¹⁸ The heterolinkage formation in the interchange reaction with DBTDL was more favored than that with TBT, which was far from the Bernoullian distribution.

Degree of Randomness (B) and Sequence Length

The probability that a butylene terephthalate (BT) unit is placed next to an ethylene terephtha-

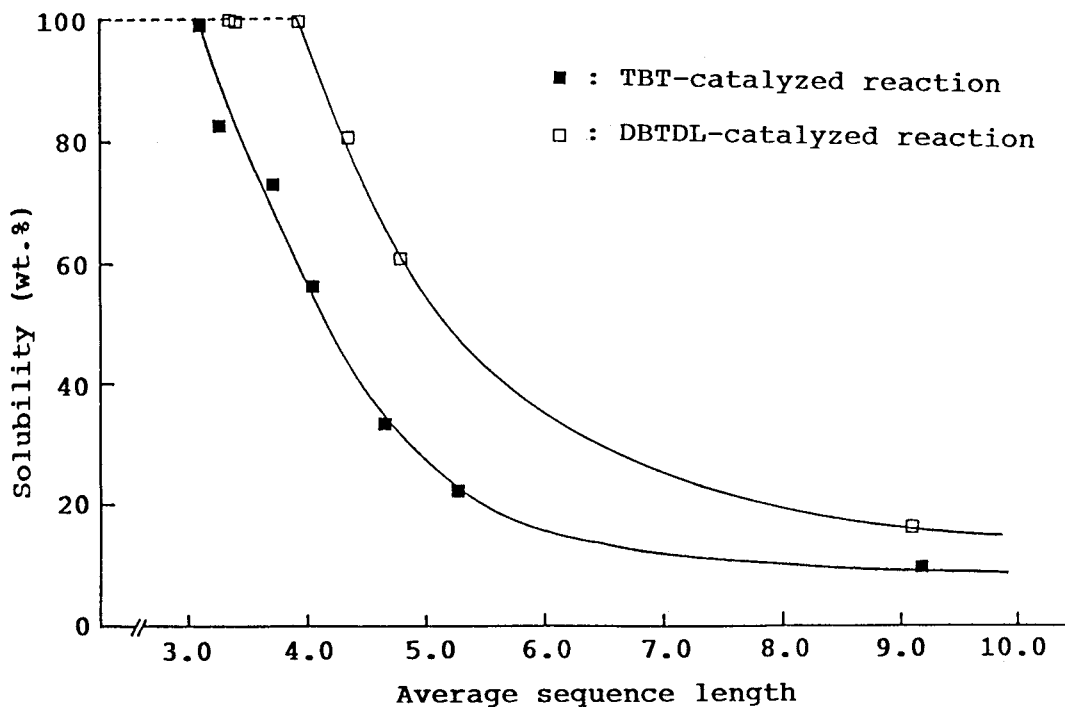


Figure 7 Solubility in chloroform as a function of the average sequence length of the PET/PBT blend (50 wt % PBT) interchange-reacted at 280°C.

late (ET) unit (P_{EB}) and the probability that a BT unit exists next to an ET unit (P_{BE}) are given as follows:

$$P_{EB} = \frac{f_{ETB}}{2f_E} \quad (6)$$

$$P_{BE} = \frac{f_{ETB}}{2f_B} \quad (7)$$

B is defined by eq. (8).¹⁹ If $B = 1$, a random distribution of ET and BD units is achieved. A copolymer is blocky if B is smaller than 1. In contrast, the sequence length becomes shorter when B is larger than 1 and the copolymer is completely alternating if B reaches 2:

$$B = P_{EB} + P_{BE} \quad (8)$$

The number-average sequence length is calculated from eqs. (9) and (10):¹⁹

$$\overline{L_n E} = \frac{2f_E}{f_{ETB}} = \frac{1}{P_{EB}} \quad (9)$$

$$\overline{L_n B} = \frac{2f_B}{f_{ETB}} = \frac{1}{P_{BE}} \quad (10)$$

where $\overline{L_n E}$ and $\overline{L_n B}$ are the number-average sequence lengths of ET and BT units, respectively.

B of the PET/PBT blend during the interchange reaction as a function of reaction time is presented in Figure 3(a). B increased gradually and leveled off after 180 min in the TBT-catalyzed reaction, whereas B reached its maximum after 90 min when DBTDL was used. The activation energy of alcoholysis is lower than that of the ester-ester-interchange reaction.²⁰ Also, B obtained from the DBTDL-catalyzed reaction was higher than that obtained from the TBT-catalyzed reaction at the early stage of the interchange reaction. Hence, the increase of B at the initial reaction stage is thought to be due to the alcoholysis reaction between hydroxyl end groups in PET (or PBT) and ester groups in PBT (or PET). A similar trend was found in the chloroform-insoluble fraction, as shown in Figure 3(b).

Figure 4 denotes the changes in the molar fraction of heterolinkage and B as a function of PBT content in the blend. The different B values were obtained according to the blend composition, implying that B should be compared at the same blend composition.

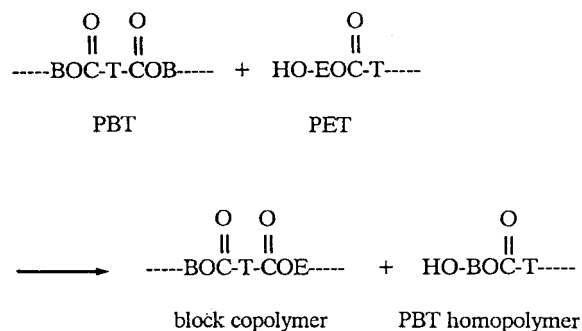
The number-average sequence length during the TBT-catalyzed interchange reaction fell off

abruptly at the initial stage of the reaction and leveled off after 180 min, as shown in Figure 5(a). Considering that the number-average sequence length of a perfectly random copolymer ($B = 1$) is 2, we found that the copolymer remained blocky and the reaction did not reach equilibrium after 180 min. The DBTDL-catalyzed reaction reached equilibrium faster than the TBT-catalyzed reaction [Fig. 5(b)]. $\overline{L_n E}$ was always larger than $\overline{L_n B}$, which might be explained by the fact that the reactivity ratio of the ET unit was larger than that of the BT unit and the molar fraction of the ET unit was larger than that of the BT unit.

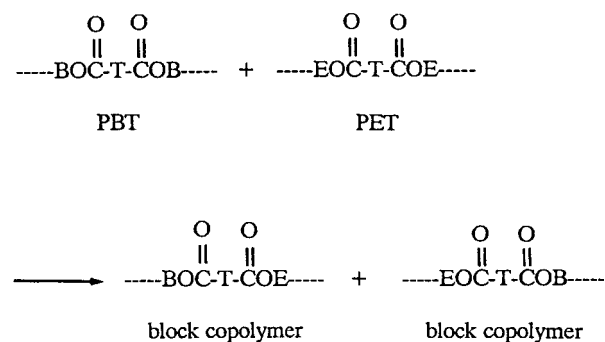
Figure 6 shows the relationship between the solubility and B of the copolyester formed by the interchange reaction in the PET/PBT blend. The solubility increased with an increase in B . At the initial stage of reaction, a block copolymer with long sequences was formed, which led to a low degree of solubility, although the preferred heterolinkage formation at a 50/50 blend composition facilitated dissolution. On the contrary, with progress in the interchange reaction, the solubility increased significantly as the average sequence length, $(\overline{L_n E} + \overline{L_n B})/2$, decreased, as depicted in Figure 7. The difference in the solubilities of the copolyesters formed by TBT- and DBTDL-catalyzed reactions can be explained by the reaction mechanism shown in Scheme 2. In the alcoholysis reaction, one block copolymer is formed through one interchange reaction, whereas two block copolymers are formed in an ester-ester-interchange reaction. Therefore, if the amount of heterolinkages formed by alcoholysis is equivalent to that formed by ester-ester interchange, the copolymers with short block lengths prevail in alcoholysis. For this reason, the sequence length distribution of the block copolymer formed by alcoholysis is less uniform than that formed by the ester-ester-interchange reaction, although the number-average values are almost identical. Also, the solubility increased because of the larger amount of copolymers with short blocks easily soluble in the solvent. Consequently, it is suggested that alcoholysis was preferred in the DBTDL-catalyzed reaction in comparison with the TBT-catalyzed reaction.

Figure 8 shows B and the molar fraction of heterolinkages in the PET/PBT copolyester extracted in chloroform with the reaction time. f_{ETB} and B increased slightly and leveled off after 180 min. An f_{ETB} value of 0.332 was regarded as the maximum value obtained in this system.

(a) Alcoholysis



(b) Ester-ester interchange reaction



Scheme 2 Comparison of the alcoholysis and ester-ester-interchange reactions.

CONCLUSION

The interchange reaction led PET/PBT blends to form copolyesters with various sequence distributions, randomnesses, and sequence lengths. Such parameters were influenced significantly by reaction time. At the initial stage of reaction time, block copolymer was formed preferentially, which was confirmed by a deviation from Bernoullian statistics. However, the randomness increased and the sequence length became shorter with the progression of reaction time. The solubility of the interchange-reacted blend decreased with sequence length, which supports the formation of block copolymers with long sequence lengths at the initial stage of reaction time. The solubility of the copolyester was affected by the catalysts in the interchange reaction. The DBTDL-catalyzed interchange reaction promoted the formation of copolymers with short block lengths by alcoholysis to cause good solubility with respect to the DBTDL-catalyzed interchange reaction.

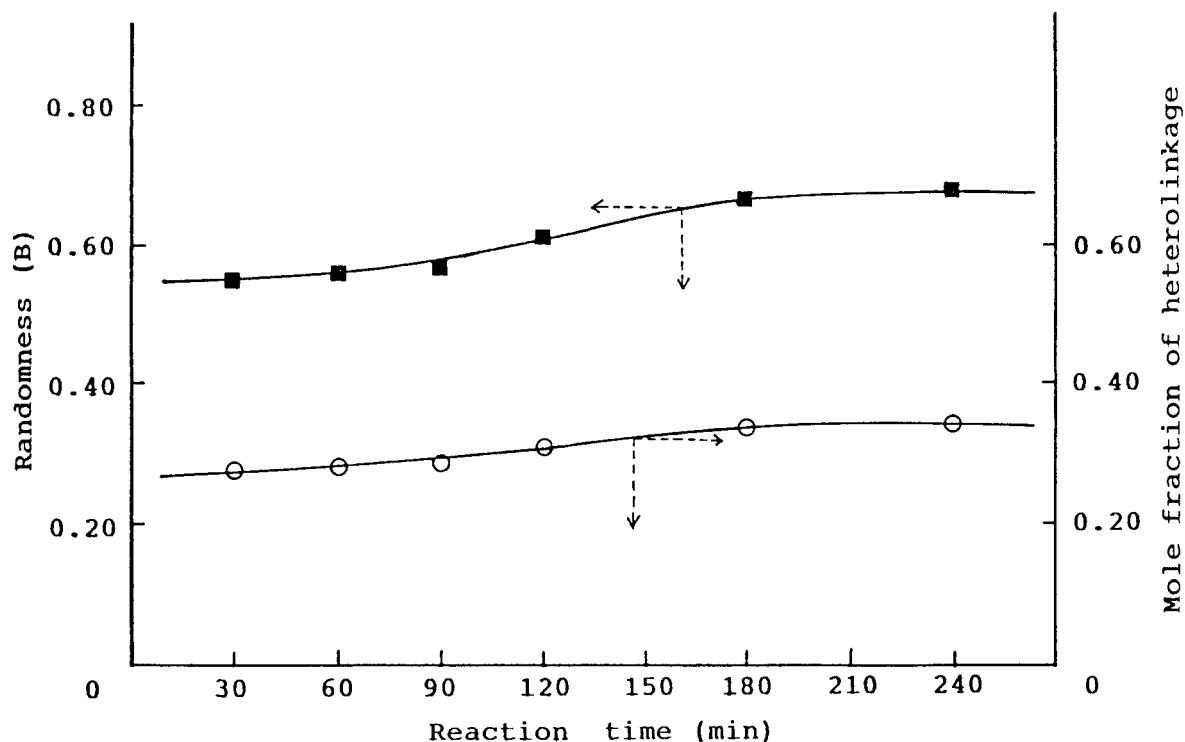


Figure 8 Changes in the randomness and molar fraction of heterolinkage in the chloroform-soluble fraction with interchange reaction times. The PBT content was 25 wt %, the reaction temperature was 280°C, and the catalyst was TBT.

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