

Effect of the Copolycondensation Temperature on the Reactivities of Bis(3-hydroxypropyl)terephthalate and Bis(2-hydroxyethyl)terephthalate

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ABSTRACT: The rate constants of cross reactions in the copolycondensation of bis(3-hydroxypropyl)terephthalate (BHPT) and bis(2-hydroxyethyl)terephthalate (BHET), k_{12} and k_{21} , were determined with the results obtained from ¹H NMR spectroscopy analysis. BHPT and BHET were polymerized and copolymerized at 260, 270, and 280°C with titanium tetrabutoxide as a catalyst. With the adoption of second-order kinetics to the polycondensation, k_{11} and k_{22}

were calculated. The monomer reactivity ratios of BHPT were much larger than those of BHET, indicating the block nature of the copolycondensation, but the difference between the reactivity ratios was lowest at the highest polycondensation temperature of 280°C. This indicated that the probability of randomization was increased. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1890–1895, 2003

INTRODUCTION

The industrially important polyesters poly(ethylene terephthalate) (PET) and poly(trimethylene terephthalate) (PTT) have widely been used as commercial fibers, polymeric films, and engineering plastics.^{1–7} So that the processability, crystallization rate, and elastic properties of PET might be enhanced, and so that the mechanical and thermal properties of PTT might be improved, their copolymerization with both oligomeric and monomeric forms as reactants and their usage as polymer blends have actively been studied.^{8–17} However, the effects of the polycondensation temperatures on the reactivities of pure monomeric forms, such as bis(3-hydroxypropyl)terephthalate (BHPT) and bis(2-hydroxyethyl)terephthalate (BHET), have rarely been studied.

Various methods are known for determining the monomer reactivity in addition to the copolymerization system. A method with a kinetic equation derived by Dostrál and Alfrey¹⁸ is exemplified as one of the well-known theoretical techniques. Comparing active research on addition copolymerization systems, a few comparative studies of the monomer reactivity have been carried out in copolycondensation systems. Han¹⁹ synthesized PET, poly(propylene terephthalate) (PPT), and PET–PPT copolymers. He calculated the

monomer reactivity ratios of BHET and bis(2-hydroxyl-*n*-propyl)terephthalate in their copolymerization with gas chromatography to obtain the rate constants of the cross reaction. However, because the polymerizations were conducted at much lower temperatures than general industrial polycondensation temperatures of BHET and bis(2-hydroxyl-*n*-propyl)terephthalate, such as 260, 270, or 280°C, it was difficult to apply the monomer reactivity ratios calculated by Han to real copolycondensation systems to control for various molecular parameters such as blockiness and randomness.

In this study, BHPT and BHET were homopolymerized and copolymerized in the presence of titanium tetrabutoxide (TBT) as a catalyst at 260, 270, or 280°C, and the effect of the copolycondensation temperature on the monomer reactivity and the blockiness of the copolyester synthesized was identified. The rate constants of the cross reactions and the monomer reactivity ratios for BHPT and BHET were calculated with results obtained from ¹H-NMR spectroscopy analysis.

EXPERIMENTAL

Materials

BHET from Nisso was dissolved in water at 67–68°C, and this solution was crystallized by cooling. A white, needle-shaped crystal (melting point = 109.5°C, lit. 109–110°C²⁰) was obtained by recrystallization of the crystallized BHET from 1,1,2,2-tetrachloroethane (TCE).²⁰

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TABLE I
Feed Ratios of the Monomer and Catalyst for Copolycondensation

No.	BHPT		BHET		TBT catalyst	
	g	mol	g	mol	g	mol
1	10	0.0354	0	0	0.0034	1.05×10^{-5}
2	8	0.0284	2	0.0079	0.0035	1.08×10^{-5}
3	7	0.0248	3	0.0118	0.0035	1.08×10^{-5}
4	6	0.0213	4	0.0157	0.0036	1.11×10^{-5}
5	5.261	0.0187	4.739	0.0187	0.0036	1.11×10^{-5}
6	4	0.0142	6	0.0236	0.0037	1.14×10^{-5}
7	3	0.0106	7	0.0276	0.0038	1.17×10^{-5}
8	2	0.0071	8	0.0315	0.0039	1.20×10^{-5}
9	0	0	10	0.0394	0.0040	1.23×10^{-5}

BHPT was synthesized by the transesterification reaction of dimethyl terephthalate (DMT) with 1,3-propanediol (1,3-PD) with zinc acetate as a catalyst.^{16,21} The transesterification of DMT (97 g, 0.5 mol) with 1,3-PD (83.6 mL, 1.1 mol) in the presence of zinc acetate (0.054 g, 2.97×10^{-4} mol) was performed in a three-necked, round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a distillation column. The mixture of DMT, 1,3-PD, and catalyst was purged with nitrogen and stirred continuously throughout the reaction at 190°C. After 1 h, the temperature was gradually raised to 210°C and was maintained for 30–40 min with stirring. After the reaction was completed, the product was washed and dissolved in hot water. A white, needle-shaped crystal was obtained by recrystallization of the crystallized BHPT from TCE.

Homopolycondensation and polycondensation

Purified BHET (10 g, 0.0394 mol) was melted under a nitrogen flow in a polycondensation tube 30 cm long and 5 cm in diameter that was equipped with a mechanical stirrer and a silicon sealing apparatus. Molten BHET was stirred at 50 rpm. At 200°C, the nitrogen flow stopped, and a TBT catalyst (0.0040 g, 1.23×10^{-5} mol) was added to the polycondensation tube. It was decompressed to about 20 mmHg with a vacuum pump, and this pressure was maintained for a given polycondensation time. The reaction temperature was increased with decompression to 260, 270, or 280°C and maintained. The polycondensed material was quenched in cold water immediately after the reaction stopped and dried in a vacuum oven at 100°C for 1 day. BHPT (10 g, 0.0354 mol) was also polymerized under the same conditions (TBT, 0.0034 g, 1.05×10^{-5} mol).

The copolycondensation was conducted for 10 min under the same conditions used in the homopolycondensation. The amount of the TBT catalyst was regulated according to the molar ratio of BHET and BHPT, as listed in Table I.

Characterization

The number-average degree of polymerization (P_n) was determined by the viscosity method.²² For PTT, a phenol/TCE (50/50 w/w) solution was used as a solvent. The intrinsic viscosity ($[\eta]$) at 25°C was obtained by the usual method. With eq. (1), the number-average molecular weight (M_n) was calculated with $[\eta]$. P_n was calculated by the substitution of M_n in eq. (2):

$$[\eta] = 8.2 \times 10^{-2} [M_n]^{0.63} \quad (1)$$

$$P_n = (M_n - 77) / 206 \quad (2)$$

For PET, eqs. (3)²¹ and (4) were used. A phenol/TCE (40/60 w/w) solution was used as a solvent. $[\eta]$ at 25°C was obtained by the usual method. With eq. (3), $[\eta]$ at 25°C was obtained and with eq. (4), M_n and P_n of PET were obtained:

$$[\eta] = 1.4 \times 10^{-3} [M_n]^{0.64} \quad (3)$$

$$P_n = (M_n - 62) / 192 \quad (4)$$

¹H-NMR spectra of PTT, PET, and the copolyester formed through the polycondensation and copolycondensation were obtained with NMR spectrophotometers (JNM-MH-100, JEOL, Tokyo, Japan) with trifluoroacetic acid.

RESULTS AND DISCUSSION

The polycondensation of BHET has been known as a first-order²³ or second-order²⁴ reaction to the molar number of chains. Because this study concerns the chain-growth reaction without the thermal decomposition reaction, we think that the second-order reaction kinetics of Cefelin and Malek²⁴ are more proper:

$$- (dN/dt) = k_{22} N^2 \quad (0 < t < t_c) \quad (5)$$

where N is the molar number of PET chains, t is the polycondensation time of BHET, k_{22} is the rate constant of polycondensation of BHET, and t_c is the time at which degradation of PET chains occurs. Integrating eq. (5) gives eq. (6):

$$(1/N) = k_{22}t + (1/N_0) \quad (6)$$

where N_0 is the initial molar number of PET chains. If N_0 is 1, eq. (4) can be converted into the following expression: $N = 192/(M_n - 62)$. Therefore, eq. (6) can be expressed as follows:

$$P_n = k_{22}t + 1 \quad (7)$$

If we apply eq. (6) to the case of BHPT and convert eq. (2) into $N = 260/(M_n - 77)$, eq. (8) can be derived:

$$P_n = k_{11}t + 1 \quad (8)$$

where k_{11} is the rate constant of polycondensation of BHPT.

To obtain the polycondensation rate constants k_{11} for PTT and k_{22} for PET, we determined P_n of a sample polymerized for a given time by the viscometry. Figure 1 presents P_n with the polycondensation time at three different polycondensation temperatures. The polycondensation rates of BHPT were higher than those of BHET at all polycondensation temperatures. Moreover, the polycondensation rates increased with an increase in the polycondensation temperature. As we reported concerning the kinetics of polycondensation of BHET,²⁵ an initial linear region in the relationship between the polycondensation time and P_n existed, exhibiting a second-order reaction with respect to the molar number of chains. From the slope of the straight line in Figure 1, the growth rate constants of polycondensation of BHPT (k_{11}) were calculated to be 2.48 min^{-1} at 260°C , 3.98 min^{-1} at 270°C , and 5.10 min^{-1} at 280°C . Moreover, the growth rate constants of polycondensation of BHET (k_{22}) were calculated to be 1.22 min^{-1} at 260°C , 2.06 min^{-1} at 270°C , and 3.90 min^{-1} at 280°C , respectively. The linearity was lost after a certain polycondensation time (Fig. 1). This happened presumably because a midterm ester interchange¹⁸ and a decomposition reaction occurred.

Han¹⁹ applied the expressions for addition copolymerization systems derived by Dostrál and Alfrey¹⁸ to

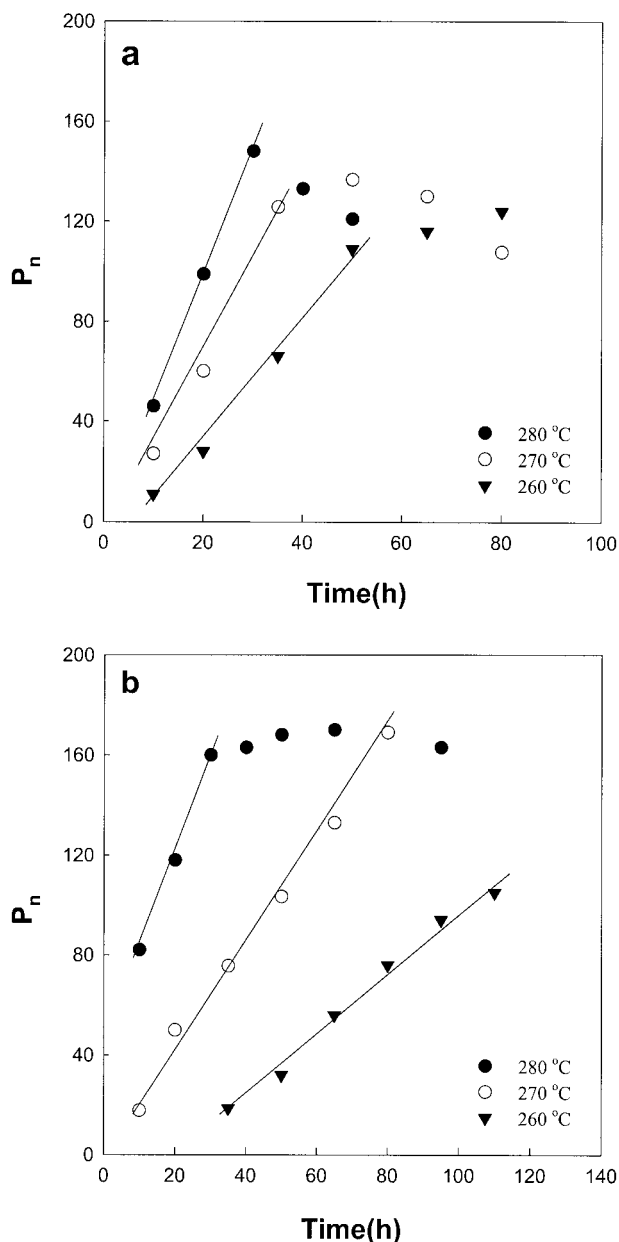
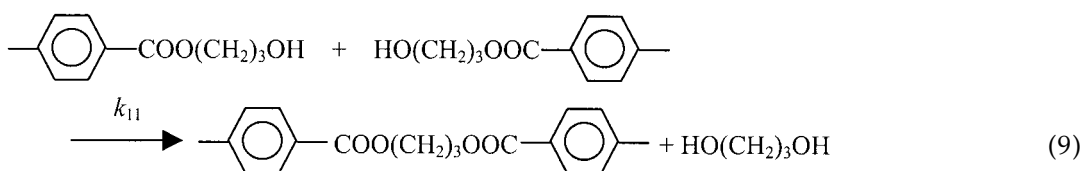
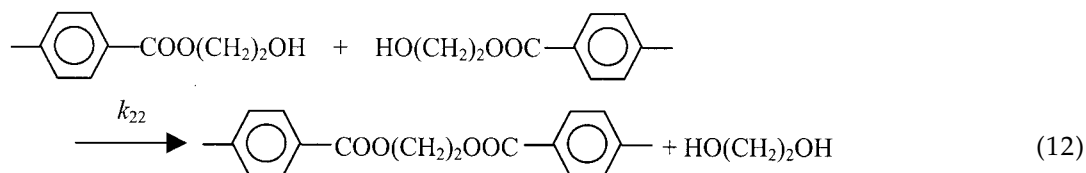
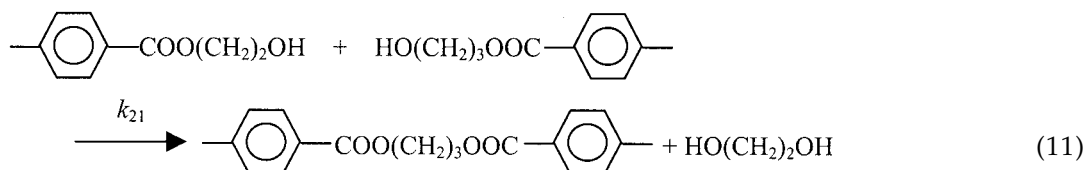
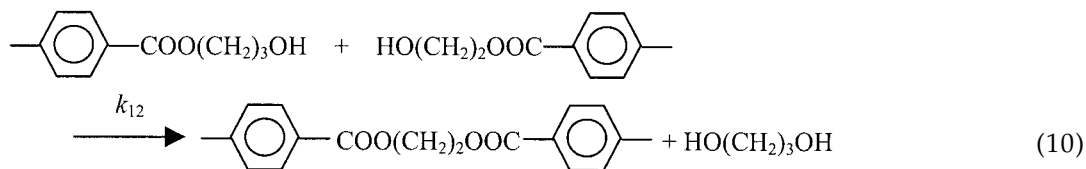


Figure 1 P_n values of (a) PTB obtained by the polycondensation of BHPT at 260, 270, and 280°C with TBT as a catalyst and (b) PET obtained by the polycondensation of BHET at 260, 270, and 280°C with TBT as a catalyst with the polycondensation times.

the copolycondensation of polyesters. Applying this to the copolycondensation of BHPT and BHET yielded the following reactions:





The rate constants of the cross reactions in the copolycondensation of BHPT and BHET, k_{12} and k_{21} , were calculated with eq. (13):¹⁹

$$ak_{11} - (b/a)k_{22} = bk_{12} - k_{21} \quad (13)$$

where a is the ratio of monomers in the copolycondensation ($[\text{BHPT}]/[\text{BHET}]$) and b is the ratio of diols in

the copolyester ($d[-\text{O}(\text{CH}_2)_3\text{O}-]/d[-\text{O}(\text{CH}_2)_2\text{O}-]$). With eq. (13), if b is determined experimentally, k_{12} and k_{21} can easily be obtained. To obtain the value of b in eq. (13), we applied $^1\text{H-NMR}$ spectroscopy. Figure 2 shows the $^1\text{H-NMR}$ spectrum of a copolyester that was copolymerized with the same molar ratio of BHPT and BHET at 270°C. The diol unit ratio of the copolyester was determined from the area ratio of the

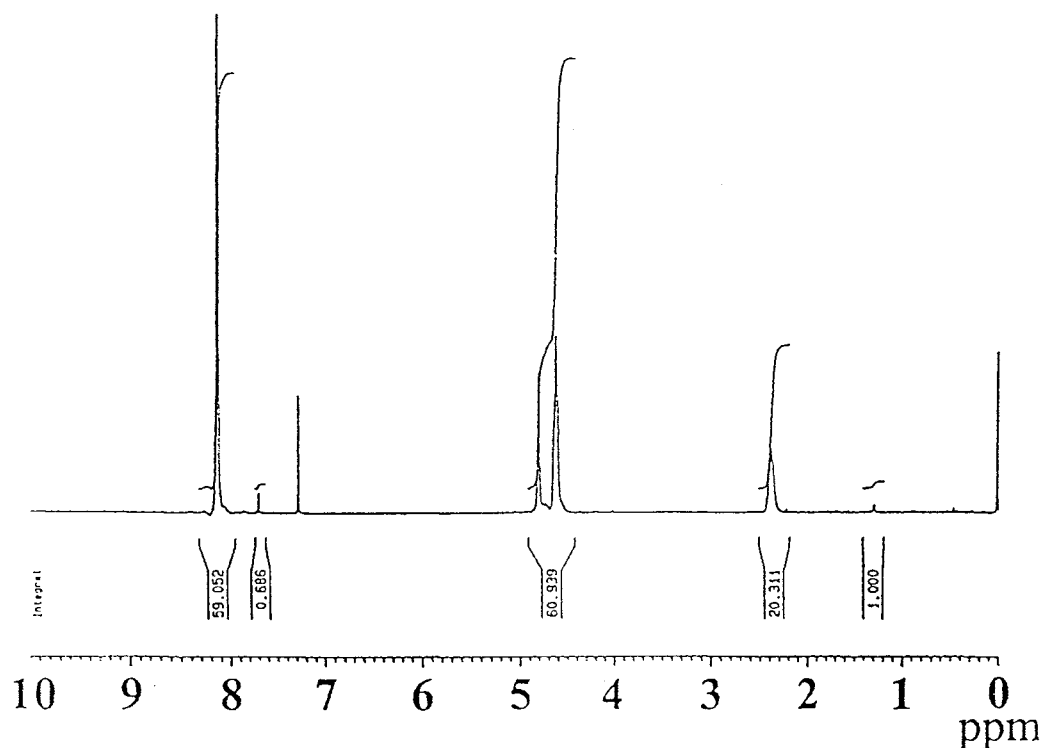


Figure 2 $^1\text{H-NMR}$ spectrum of the PTT-PET copolyester prepared by the copolycondensation of BHPT and BHET with a molar ratio of 1/1 at 270°C for 10 min with TBT as a catalyst.

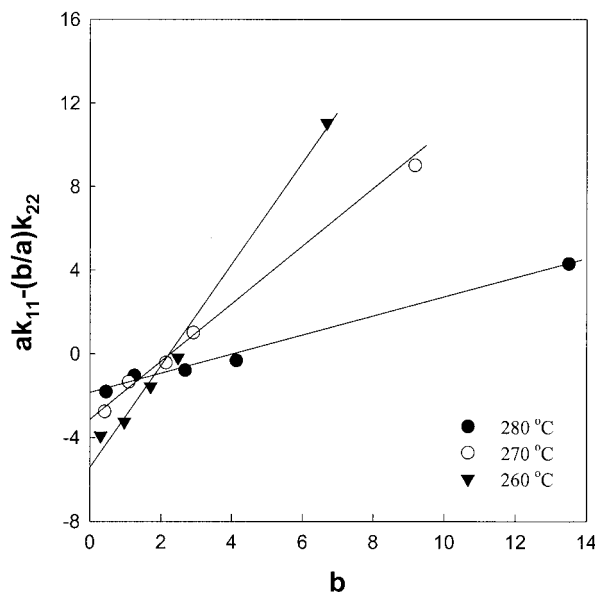


Figure 3 $ak_{11} - (b/a)k_{22}$ versus b for the PTT-PET copolyesters prepared by copolycondensation at 260, 270, and 280°C for 10 min with TBT as a catalyst.

— $\text{O}(\text{CH}_2)_3\text{O}$ — peak integration ($\delta = 4.6$ ppm) to the — $\text{O}(\text{CH}_2)_2\text{O}$ — peak integration ($\delta = 4.8$ ppm). Figure 2 apparently shows that the peak area of the 1,3-PD units was much larger than that of the ethylene glycol (EG) units, regardless of the $^1\text{H-NMR}$ spectrum of the copolyester copolymerized with the same molar ratio of BHPT and BHET. This was important for the calculation of the reactivity ratios of BHPT and BHET.

To obtain the rate constants of the cross reactions, we calculated the left terms of eq. (13) by introducing the ratio of diol units in the copolyester. Figure 3 presents these calculated values plotted against b according to eq. (13). The plots give a straight line. Because all the plots in Figure 3 show good correlation coefficients (0.991–0.997) of straight lines, it is thought that $^1\text{H-NMR}$ spectroscopy is an effective method for determining the monomer reactivity ratios of BHPT and BHET during copolycondensation. From the slope and intercept of the straight line in Figure 3, k_{12} and k_{21} were calculated to be 0.96 and 1.46 at 260°C, 1.32 and 3.06 at 270°C, and 2.42 and 5.45 at 280°C, as presented in Table II. Finally, the monomer reactivity ratios of BHPT and BHET, r_1 (k_{11}/k_{12}) and r_2 (k_{22}/k_{21}), were calculated to be 2.58 and 0.84 at 260°C, 3.02 and 0.67 at

270°C, and 2.11 and 0.72 at 280°C. r_1 was much larger than r_2 . Because r was a relative value, it could be determined that the reactivity of BHPT was predominant when BHPT and BHET were copolymerized at 260–280°C.

k_{11} and k_{21} were largest and k_{12} was smallest at all polycondensation temperatures. That is, the reaction in which the 1,3-PD unit formed occurred as soon as possible, and the reaction in which the 1,3-PD unit was missed during the formation of the EG unit occurred as slowly as possible. Therefore, on the basis of these results, the molecular type of the precondensate synthesized might be thought to be a series of block copolymers composed of smaller blocky 1,3-PD units. In this reaction system, r_1 was greater than 1, and r_2 was smaller than 1. Therefore, it was thought that the copolyester with more 1,3-PD units than EG units was produced in the early reaction stage, and the EG units in the copolyester increased as the reaction proceeded. The differences between the monomer reactivity ratios decreased with increasing polycondensation temperatures. It was thought that the probability of randomization reactions might have increased with increasing polycondensation temperatures.

Figure 4 presents a composition diagram of copolyesters plotted with the b value determined by $^1\text{H-NMR}$ analysis. The composition diagram was plotted by the standardization of BHPT, which was predominant in reactivity. As presented in Figure 4, there was no azeotropic composition presented in eq. (14) for this reaction system, and this indicated that a series of block copolymers were synthesized. This agrees well with the previous monomer reactivity ratio data:

$$a = c = (k_{21} - k_{22}) / (k_{12} - k_{11}) \quad (14)$$

CONCLUSIONS

The effect of the copolycondensation temperature on the monomer reactivity ratios of BHPT and BHET was investigated at 260, 270, and 280°C in the presence of TBT as a catalyst. With the adoption of second-order kinetics to the polycondensation, the rate constants of polycondensation of BHPT and BHET, k_{11} and k_{22} , were calculated to be 2.48 and 1.22 min^{-1} at 260°C, 3.98 and 2.06 min^{-1} at 270°C, and 5.10 and 3.90 min^{-1} at 280°C. In addition, the rate constants k_{12} and k_{21} of

TABLE II
Rate Constants and Reactivity Ratios of Copolycondensation of BHPT and BHET at Three Copolycondensation Temperatures for 10 min, Calculated from $^1\text{H-NMR}$ Spectroscopy Data

Copolycondensation temperature (°C)	k_{11} (min^{-1})	k_{12} (min^{-1})	k_{21} (min^{-1})	k_{22} (min^{-1})	r_1	r_2
260	2.48	0.96	1.46	1.22	2.58	0.84
270	3.98	1.32	3.06	2.06	3.02	0.67
280	5.10	2.42	5.45	3.90	2.11	0.72

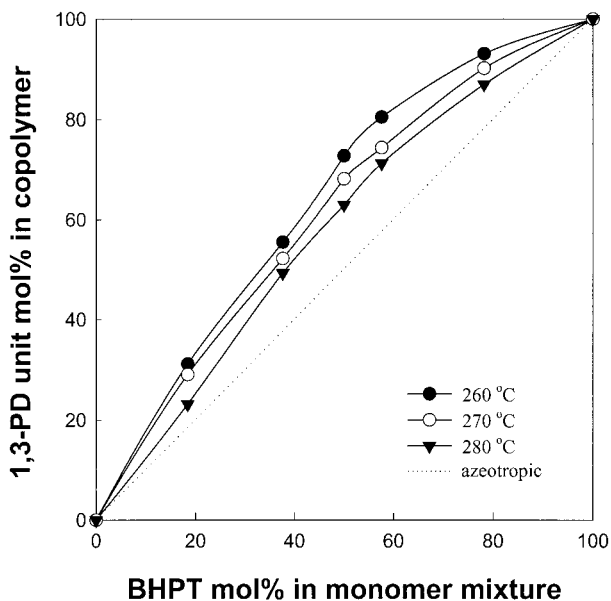


Figure 4 Compositions of the PTT-PET copolyesters as a function of the monomer ratio. The copolyesters were prepared by copolycondensation at 260, 270, and 280°C for 10 min with TBT as a catalyst.

the cross reaction were determined to be 0.96 and 1.46 min^{-1} at 260°C, 1.32 and 3.06 min^{-1} at 270°C, and 2.42 and 5.45 min^{-1} at 280°C from ^1H NMR spectroscopy analysis. The monomer reactivity ratios of BHPT were much larger than those of BHET; this indicated the block nature of the copolycondensation.

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