Effect of copolycondensation temperature
on the reactivity ratios of bis(4-hydroxybutyl) terephthalate
and bis(2-hydroxyethyl) terephthalate

Won Seok Lyoo[1,*], Se Geun Lee[2], Wan Shik Ha[2], Jinwon Lee[3], Joon Ho Kim[4]

[1] Electronic Materials and Devices Research Center, Korea Institute of Science
and Technology, P.O. Box 131, Cheongryang, Seoul, Korea
[2] Department of Fiber and Polymer Science, Seoul National University,
Seoul 151-742, Korea
[3] Department of Chemical Engineering, Kwangwoon University, Wolgye-dong,
Nowon-gu, Seoul 139-701, Korea
[4] School of Textiles, Yeungnam University, Kyongsan 712-749, Korea

Summary

The effect of copolycondensation temperature on the monomer reactivity ratios of bis(4-hydroxybutyl) terephthalate (BHBT) and bis(2-hydroxyethyl) terephthalate (BHET) was investigated at 260, 270, and 280 °C, in the presence of titanium tetrabutoxide as a catalyst. Adopting 2nd order kinetics to polycondensation, the rate constants of polycondensation of BHBT and BHET, k_{11} and k_{22}, were calculated to be 2.58, 1.30; 3.87, 2.24; and 5.29, 4.06 min^{-1}. In addition, the rate constants k_{12} and k_{21} of cross reactions could be determined as 0.91, 3.00; 1.49, 4.42; and 2.13, 5.85 min^{-1} from a proton nuclear magnetic resonance spectroscopic analysis. The monomer reactivity ratios of BHBT were much larger than those of BHET, indicating the block nature of the copolycondensation, but the differences between monomer reactivity ratios were decreased with increasing polycondensation temperature, indicating that a probability of randomization was increased.

Introduction

Industrially important polyesters, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) have been widely used as commercial fibers, polymeric films, and engineering plastics [1]. To enhance the processibility and crystallization rate of PET and to improve the mechanical and thermal properties of PBT, their copolymerization using both oligomeric and monomeric forms as reactants or usage of them as polymer blend are actively studied [2-7]. But the effect of polycondensation temperatures on the reactivities of its pure monomeric forms such as bis(4-hydroxybutyl) terephthalate (BHBT) and bis(2-hydroxyethyl) terephthalate (BHET) have been rarely studied.

Various methods were known to determine the monomer reactivity in addition copolymerization system. The method using kinetic equation derived by Dostral and Alfrey [8] is exemplified as one of the well known theoretical techniques. Comparing with the active research on the addition copolymerization system, a few comparative study of the monomer reactivity was carried out in the copolycondensation system. Han [9] synthesized PET, poly(propylene terephthalate) (PPT) and PET-PPT copolymers. He calculated the monomer reactivity ratios of BHET and bis(2-hydoxyl-n-propyl)

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* Corresponding author

terephthalate (BHPT) in their copolymerization using a gas chromatography to obtain the rate constants of cross reaction. However, because those polymerizations had been conducted at much lower temperature than general industrial polycondensation temperatures of BHET and BHPT 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 various molecular parameters like blockiness and randomness.

In the present study, BHBT and BHET were homopolymerized and copolymerized in the presence of titanium tetrabutoxide (TBT) as a catalyst at 260, 270, or 280 °C, respectively to identify the effect of copolycondensation temperature on the relative reactivities of BHBT and BHET.

Experimental

Materials
BHET from Nisso was purified by recrystallization. White needle shape crystal (m.p. 109.5 °C; lit.: 109-110°C [10]) was obtained.

BHBT was synthesized by the transesterification reaction of dimethyl terephthalate with 1,4-butanediol (1,4-BD) using TBT as a catalyst [11, 12]. (m.p. 79.9 °C; lit.: 79-80 °C; Elementary analysis: Found, C, 62.3, H, 7.2 %; calculated for $C_{16}H_{22}O_6$, C, 62.0, H, 7.1 %)

Polycondensation
Purified BHBT (10 g ; 0.032 mol) and 0.0063 g of TBT catalyst (1.85×10^{-5} mol) were melted under nitrogen flow in polycondensation tube of 30 cm length and 5 cm diameter, equipped with mechanical stirrer and silicon sealing apparatus. Molten BHBT was stirred at 60 rpm. At 200 °C nitrogen flow was stopped and decompression was started to reach highly reduced pressure of 0.3 mmHg after 10 min, and the pressure was maintained during a given polycondensation time. The reaction temperature was increased with decompression to 270 °C and maintained. Polycondensed material was quenched in cold water immediately after reaction stopped, and dried in a vacuum oven at 100 °C for 1 day. BHET (10 g: 0.039 mol) was also polymerized under the same conditions (TBT: 0.0076 g: 2.24×10^{-5} mol).

The copolycondensation was conducted for 10 min under the same conditions as used in homopolycondensation. The amount of TBT catalyst was regulated according to the mole ratio of BHBT and BHET as listed in Table 1.

Characterization
The number-average degree of polymerization (P_n) was determined by the viscosity method [13]. For PBT, phenol/TCE (60/40 wt.) mixture solution was used as a solvent. The intrinsic viscosity [η] at 25 °C was obtained by usual method. From eq. (1), number-average molecular weight (M_n) was calculated by using [η]. The P_n was calculated by substituting M_n for eq. (2).

$$[\eta] = 2.15 \times 10^{-4} [M_n]^{0.82} \tag{1}$$
$$P_n = (M_n - 90)/220 \tag{2}$$

In the case of PET, equation (3) [14] and (4) were used. Phenol/TCE(40/60 wt.) mixture solution was used as a solvent. [η] at 25 °C was obtained by usual method.

From eq. (3), $[\eta]$ at 25 °C and eq. (4), M_n and P_n of PET were obtained.

$$[\eta] = 1.40 \times 10^{-3} [M_n]^{0.64} \tag{3}$$
$$P_n = (M_n\text{-}62)/192 \tag{4}$$

Table 1. Feed ratios of monomer and catalyst for copolycondensation

BHBT		BHET		TBT catalyst	
G	mol	G	mol	g	Mol
10	0.032	0	0	0.0063	1.85×10^{-5}
8	0.026	2	0.008	0.0066	1.94×10^{-5}
7	0.023	3	0.012	0.0067	1.97×10^{-5}
6	0.019	4	0.016	0.0068	2.00×10^{-5}
5.497	0.018	4.503	0.018	0.0069	2.03×10^{-5}
5	0.016	5	0.019	0.0070	2.06×10^{-5}
4	0.013	6	0.024	0.0071	2.09×10^{-5}
2	0.006	8	0.031	0.0073	2.15×10^{-5}
0	0	10	0.039	0.0076	2.24×10^{-5}

^{1}H-NMR spectra of PBT, PET, and copolyester formed through the polycondensation and the copolycondensation were obtained by NMR spectrophotometers (Jeol, JNM-MH-100) using trifluoroacetic acid.

Result and Discussion

Polycondensation of BHET has been known as 1st order [15] or 2nd order [16] reaction to the mole number of chains. Because this study is for the chain growth reaction without thermal decomposition reaction, it can be thought that 2nd order reaction kinetics of Cefelin and Malek [16] like eq. (5) is more proper.

Calculation of rate constants;

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

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

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

where N_0 is initial mole number of PET chains. By supposing N_0 to be 1, eq. (4) can be converted to a expression that N is $192/(M_n\text{-}62)$. Thus eq. (6) can be expressed as following eq. (7):

$$P_n = k_{22}t + 1 \tag{7}$$

By applying eq. (6) to the case of BHBT and by converting eq. (2) that N is $220/(M_n-90)$, eq. (8) can be derived:

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

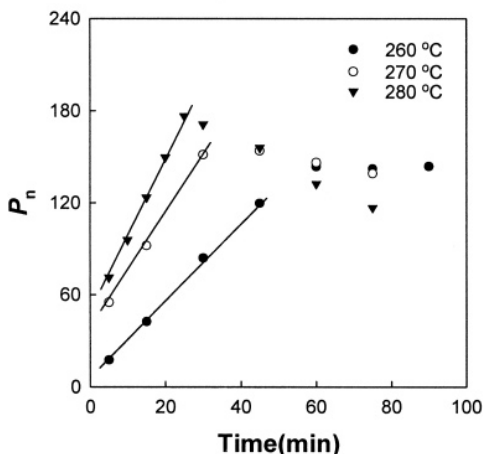where k_{11} is rate constant of polycondensation of BHBT.

Figure 1. (P_n)s of PBT obtained by polycondensation of BHBT at 260, 270, and 280 °C using TBT catalyst with polycondensation times.
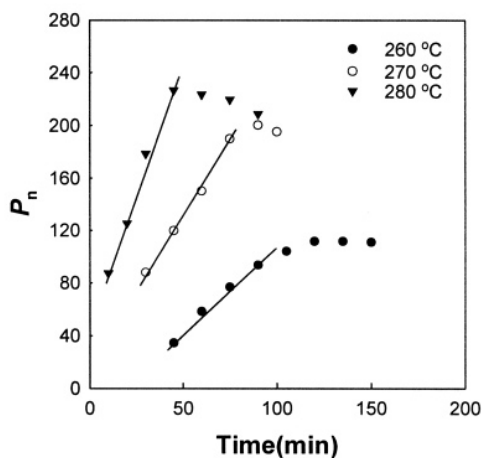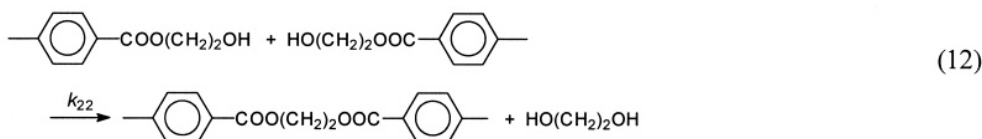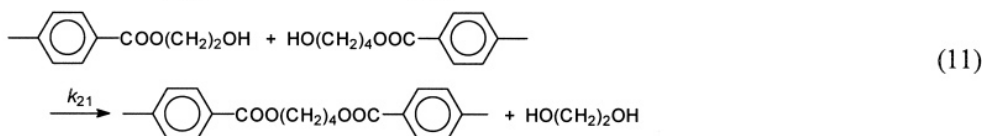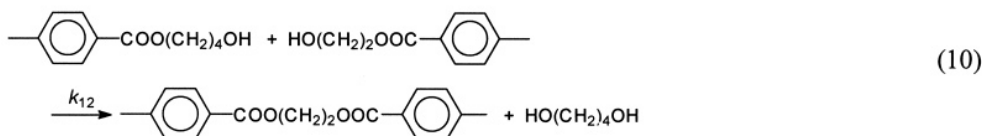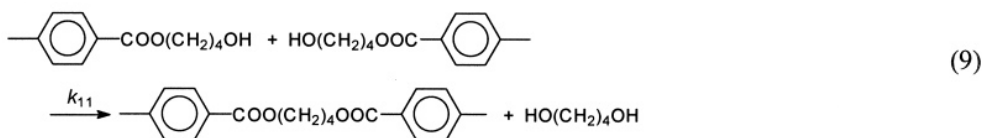
Figure 2. (P_n)s of PET obtained by polycondensation of BHET at 260, 270, and 280 °C using TBT catalyst with polycondensation times.

To get polycondensation rate constant k_{11} for PBT and k_{22} for PET, P_n of the sample polymerized for a given time was determined by the viscometry. Figures 1 and 2 present P_n with polycondensation time at three different polycondensation temperatures. In both Figures, it is particularly noteworthy in two points. First, the polycondensation rates of BHBT were higher than those of BHET at all polycondensation temperatures. Second, the polycondensation rates were increased with an increase in the polycondensation temperature. As we has reported on the kinetics of polycondensation of BHET [17], it was recognized that an initial linear region in the relation between the polycondensation time and P_n exists, exhibiting 2nd order reaction with respect to the mole number of chains. From the slope of the straight line in Figure 1, the growth rate constants of polycondensation of BHBT, k_{11} was calculated as 2.58 min^{-1} at 260 °C, 3.87 min^{-1} at 270 °C and 5.29 min^{-1} at 280 °C, respectively. Also, the growth rate constants of polycondensation of BHET, k_{22}, were calculated as 1.30 min^{-1} at 260 °C, 2.24 min^{-1} at 270 °C and 4.06 min^{-1} at 280 °C, respectively. The linearity was lost after a certain polycondensation time in Figures 1 and 2. The reason of this was supposed that mid-term ester interchange reaction [18] and decomposition reaction occurred.

Han [9] applied the expressions for addition copolymerization system driven by Dostral and Alfrey [8] to the copolycondensation of polyesters. Now applying this to the copolycondensation of BHBT and BHET gave following reactions:

$$\text{—} \bigcirc \text{—COO(CH}_2)_4\text{OH} + \text{HO(CH}_2)_4\text{OOC—} \bigcirc \text{—}$$

$$\xrightarrow{k_{11}} \text{—} \bigcirc \text{—COO(CH}_2)_4\text{OOC—} \bigcirc \text{—} + \text{HO(CH}_2)_4\text{OH}$$

(9)

$$\text{—} \bigcirc \text{—COO(CH}_2)_4\text{OH} + \text{HO(CH}_2)_2\text{OOC—} \bigcirc \text{—}$$

$$\xrightarrow{k_{12}} \text{—} \bigcirc \text{—COO(CH}_2)_2\text{OOC—} \bigcirc \text{—} + \text{HO(CH}_2)_4\text{OH}$$

(10)

$$\text{—} \bigcirc \text{—COO(CH}_2)_2\text{OH} + \text{HO(CH}_2)_4\text{OOC—} \bigcirc \text{—}$$

$$\xrightarrow{k_{21}} \text{—} \bigcirc \text{—COO(CH}_2)_4\text{OOC—} \bigcirc \text{—} + \text{HO(CH}_2)_2\text{OH}$$

(11)

$$\text{—} \bigcirc \text{—COO(CH}_2)_2\text{OH} + \text{HO(CH}_2)_2\text{OOC—} \bigcirc \text{—}$$

$$\xrightarrow{k_{22}} \text{—} \bigcirc \text{—COO(CH}_2)_2\text{OOC—} \bigcirc \text{—} + \text{HO(CH}_2)_2\text{OH}$$

(12)

The rate constants of the cross reactions in the copolycondensation of BHBT and BHET, k_{12} and k_{21}, can be calculated from eq. (13) [9],

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

where α is the ratio of monomers in the copolycondensation ([BHBT]/[BHET]) and b is the ratio of diol in the copolyester ($d[-O(CH_2)_4O-]/d[-O(CH_2)_2O-]$). From eq. (13), if b is determined experimentally, k_{12} and k_{21} can be easily obtained. To get the value of b in eq. (13), ^{1}H-NMR spectroscopy was applied. Figure 3 shows an example of ^{1}H-NMR spectrum of copolyester which was copolymerized using the same mole ratio of BHBT and BHET at 260 °C. The diol unit ratio of the copolyester was determined by obtaining the area ratio of the $-O(CH_2)_4O-$ peak integration (δ of 4.6 ppm) to the $-O(CH_2)_2O-$ peak integration (δ of 4.9 ppm) [3, 19]. Figure 3 apparently showed that the peak area of the 1,4-BD units was much larger than that of the EG units regardless of the ^{1}H-NMR spectrum of the copolyester copolymerized using the same mole ratio of BHBT and BHET. This fact had the important meaning in the calculation of the reactivity ratios of BHBT and BHET.

In order to obtain the rate constants of the cross reactions, the left terms of eq. (13) were calculated by introducing the ratio of diol units in the copolyester. Figure 4 presents these calculated values plotted against b according to eq. (13). The plot gives a straight line. Because all plots in Figure 4 showed good correlation coefficients (0.994-1.000) of straight lines, it is thought that the method by ^{1}H-NMR spectroscopy is an effective method to determine the monomer reactivity ratios of BHBT and BHET during the copolycondensation. From the slope and the intercept of the straight line in Figure 4, k_{12} and k_{21} were calculated to be 0.91 and 3.00 at 260 °C, 1.49 and 4.42 at 270 °C, and 2.13 and 5.85 at 280 °C, respectively, as presented in Table 2. Finally, the monomer reactivity ratios of BHBT and BHET, r_1 ($= k_{11}/k_{12}$) and r_2 ($= k_{22}/k_{21}$), were calculated to be 2.84 and 0.43 at 260 °C, 2.59 and 0.51 at 270 °C, and 2.48 and 0.69 at 280 °C,

respectively. The r_1 was much larger than the r_2. Because r is relative value, it can be identified that the reactivity of BHBT is predominant when BHBT and BHET are copolymerized at 260-280 °C.
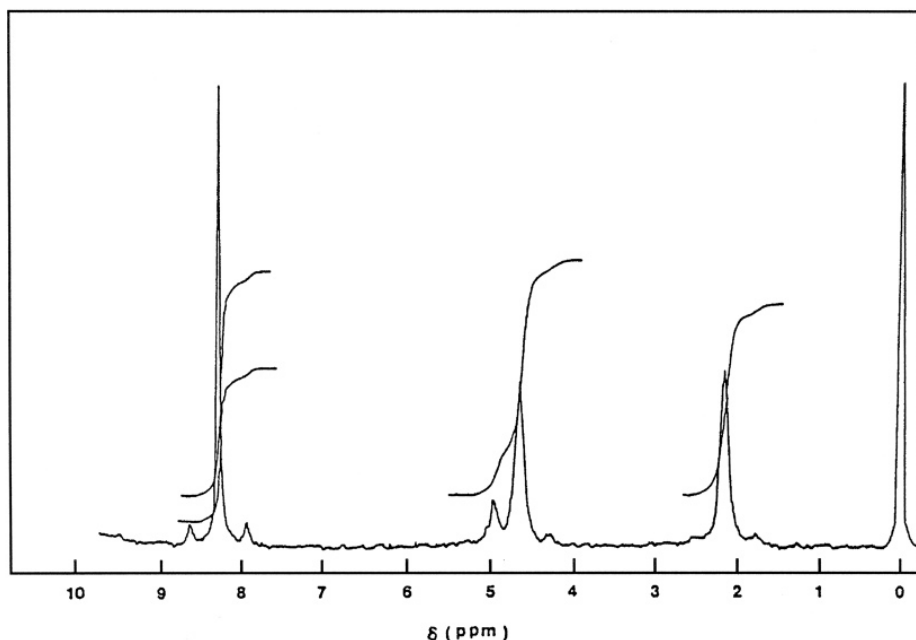

Figure 3. ^{1}H-NMR spectrum of P(BT/ET) copolymer obtained by copolycondensation of BHBT and BHET with the mole ratio of 1.0 for 10 min at 260 °C using TBT catalyst.

It was found that the (k_{21})s were the largest and the (k_{12})s were smallest at all polycondensation temperatures. That is, the reaction in which the EG unit was missed during the formation of the 1,4-BD unit occurred as soon as possible, and the reaction in which the 1,4-BD unit was missed during the formation of the EG unit occurred as slowly as possible. Thus, from these results, the molecular type of the precondensate synthesized might be supposed to be a series of block copolymer composed of smaller

Table 2. Rate constants and reactivity ratios of copolycondensation of BHBT and BHET at three different copolycondensation temperatures for 10 min, calculated from ^{1}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	2.58	0.91	3.00	1.30	2.84	0.43
270	3.87	1.49	4.42	2.24	2.59	0.51
280	5.29	2.13	5.85	4.06	2.48	0.69

blocky 1,4-BD units. In this reaction system, r_1 was larger than 1 and r_2 was smaller than 1. Therefore, it was thought that the copolyester which had richer 1,4-BD units than EG units was produced in the early reaction stage, and the EG units in copolyester increased as a reaction proceeded. It is interesting to see that the differences between monomer reactivity ratios were decreased with increasing polycondensation

temperature. This was supposed that a probability of randomization reactions might be increased with increasing the polycondensation temperature.
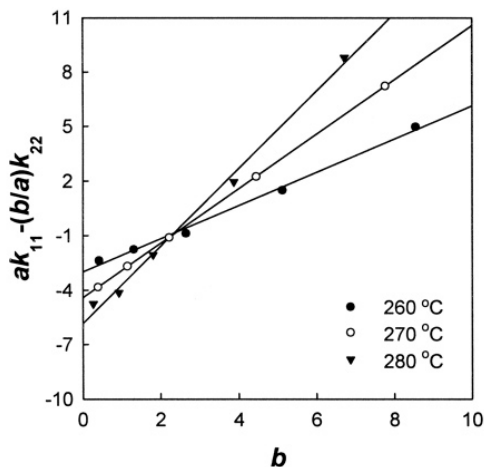

Figure 4. Plots of ak_{11}-$(b/a)k_{22}$ vs. b from P(BT/ET) copolymers obtained by copolycondensation at 260, 270, and 280 °C for 10 min.
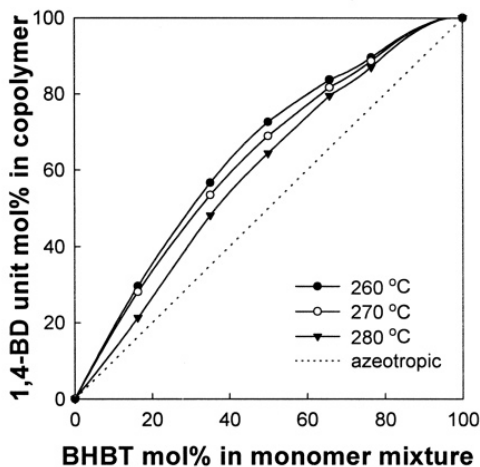
Figure 5. Composition in P(BT/ET) copolymers as a function of monomer ratio: the copolymer was obtained by copolycondensation at 260, 270, 280 °C for 10 min and 1,4-BD unit mol% was calculated from ^{1}H-NMR.

Figure 5 presents composition diagram of copolyester plotted with b value determined from ^{1}H-MNR analysis. The composition diagram was plotted by standardizing BHBT which was predominant in reactivity. As presented in Figure 5, there was no azeotropic composition presented in eq. (14) in this reaction system, indicating that a series of block copolymer were synthesized. These are well coincident with the previous monomer reactivity ratio data.

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

Conclusions

The kinetics of polycondensation and copolycondensation reactions at 260, 270 and 280 °C were investigated using BHBT and BHET as monomers. BHBT was prepared by ester interchange reaction of DMT and 1,4-BD. BHBT and BHET were polymerized and copolymerized in the presence of TBT as a catalyst. Adopting 2nd order kinetics to polycondensation, the rate constants of polycondensation of BHBT and BHET, k_{11} and k_{22}, were calculated. In addition, the rate constants of cross reactions in the copolycondensation of BHBT and BHET, k_{12} and k_{21}, were determined by using the results obtained from ^{1}H-NMR spectrum. The monomer reactivity ratios of BHBT were much larger than those of BHET. So the molecular type of the precondensate synthesized might be supposed to be a series of block copolymer. The differences between monomer reactivity ratios were decreased with increasing polycondensation temperature, indicating that a probability of randomization was increased.

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