# Kinetics of Copolycondensation of Bis(4-hydroxybutyl) Terephthalate and Bis(2-hydroxyethyl) Terephthalate by Ester-Interchange Reaction

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## SYNOPSIS

The kinetics of polycondensation and copolycondensation reactions were investigated using bis(4-hydroxybutyl) terephthalate (BHBT) and bis(2-hydroxyethyl) terephthalate (BHET) as monomers. BHBT was prepared by ester interchange reaction of dimethyl terephthalate and 1,4-butanediol. BHBT and BHET were polymerized at 270°C in the presence of titanium tetrabutoxide (TBT) as a catalyst. Applying second-order kinetics for polycondensation, the rate constants of polycondensation of BHBT and BHET, $k_{11}$ and $k_{22}$, were calculated as 3.872 min$^{-1}$ and 2.238 min$^{-1}$, respectively. BHBT and BHET were also copolymerized at 270°C using TBT. The rate constants of crossreactions in the copolycondensation of BHBT and BHET, $k_{12}$ and $k_{21}$, were obtained by using the results obtained from a proton nuclear magnetic resonance ($^1$H-NMR) spectroscopy and a high-performance liquid chromatography (HPLC). It was found that the rate constants during the copolycondensation of BHBT and BHET at 270°C decreased in the order $k_{21} > k_{11} > k_{22} > k_{12}$ and the monomer reactivity ratio of BHBT was four or five times larger than that of BHET. In calculating the crossreactions, the method by the $^1$H-NMR spectroscopy gave more accurate results than that by the HPLC. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Various methods were introduced to evaluate the monomer reactivity in addition copolymerization system. The method using kinetic equation derived by Dostal and Alfrey[1] is examplified as one of the well-defined analytical techniques. In comparison with the active research on the relative reactivity of vinyl type monomers in the addition copolymerization system, a few comparative study of the monomer reactivity was carried out in the copolycondensation system. Han[2] synthesized poly(ethylene terephthalate) (PET), poly(propylene terephthalate) (PPT), and PET–PPT copolyester. He calculated the monomer reactivity ratio of bis(2-hydroxyethyl) terephthalate (BHET) and bis(2-hydroxy-n-propyl)

terephthalate (BHPT) in their copolymerization applying the copolymerization kinetic equation and using a gas chromatography to obtain the rate constants of crossreactions. However, because those polymerizations had been conducted at much lower temperature than general industrial polycondensation and copolycondensation temperatures of BHET and BHPT such as 260, 270, or 280°C, it was difficult to apply monomer reactivity ratio claculated by Han with processible copolymerization conditions in order to control various molecular parameters of copolyesters like blockiness, randomness, and type and amount of end group, etc., to some extent.

In the case of poly(butylene terephthalate) (PBT) and PET used widely as commercial fibers and engineering plastics,[3] its copolymerization and polymer blend are in progress actively.[4-9] However, kinetic approachs to the reactivity of its monomeric forms such as bis(4-hydroxybutyl) terephthalate (BHBT) and BHET have been rare up to now.

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In the present study, BHBT and BHET were homopolymerized and copolymerized in the presence of titanium tetrabutoxide (TBT) as a catalyst at 270°C, respectively, and the rate constants of the crossreactions and the monomer reactivity ratios for BHBT and BHET were calculated by using the results obtained from a proton nuclear magnetic resonance ($^1$H-NMR) spectroscopy and a high performance liquid chromatography (HPLC).

## EXPERIMENTAL

### Purification of BHET[10]

BHET from Nisso was dissolved in water at 67–68°C, and this was crystallized by cooling. A white needle shape crystal [melting point (m.p.) 109.5°C; lit. value: 109–110°C) was obtained by recrystallizing the above crystallized BHET from 1,1,2,2-tetrachloroethane (TCE).

### Synthesis and Purification of BHBT[11,12]

The transesterification of dimethyl terephthalate (DMT) (78 g: 0.4 mol) with 1,4-butanediol (1,4-BD) (710 mL: 7.9 mol) in the presence of TBT (7.8 × 10$^{-2}$: 2.29 × 10$^{-4}$ mol) as a catalyst 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, 1,4-BD and catalyst was heated at 160°C for 5 h. After the reaction has been completed, the product was washed with water and rewashed with ethylether to remove residual 1,4-BD. The crude product was crystallized from water. A white needle shaped crystal (m.p.: 79–80°C) was obtained. The purity of crystallized BHBT was characterized by a CHN corder (Yanaco-MT-2), a differential scanning calorimeter (Dupont-910), and a melting temperature apparatus (Yamato). m.p.: 79.9°C, lit. value, 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%.

### Homopolycondensation of BHBT and BHET

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 silicone sealing apparatus. As a heating apparatus, salt bath with $NaNO_3$/$KNO_3$ (mol ratio of 1 : 1) mixture was used. Molten BHBT was stirred at 60 rpm. At 200°C nitrogen flow stopped and de-

compression started by vacuum pump. By using a teflon valve it was slowly decompressed so that highly reduced pressure of 0.3 mmHg reached 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 same conditions (TBT: 0.0076 g: 2.24 × 10$^{-5}$ mol).

### Measurement of Number-Average Degree of Polymerization ($P_n$)

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

$$[\eta] = 2.15 \times 10^{-4}[M_n]^{0.82} \tag{1}$$

$$P_n = (M_n - 90)/220 \tag{2}$$

On the other hand, in case of PET, phenol/TCE (40/60 wt) mixture solution was used as a solvent. [$\eta$] at 25°C was obtained by the usual method. From eq. (3),[14] [$\eta$] at 25°C and eq. (4), $M_n$ and $P_n$ of PET were obtained.

$$[\eta] = 1.40 \times 10^{-3}[M_n]^{0.64} \tag{3}$$

$$P_n = (M_n - 62)/192 \tag{4}$$

### Copolycondensation of BHBT and BHET

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 I.

### $^1$H-NMR Spectroscopy Analysis of Copolyester

$^1$H-NMR spectra of PBT, PET, and copolyester formed through polycondensation, and the copolycondensation were obtained by NMR spectrophotometers (JEOL, JNM-MH-100). Trifluoroacetic acid was used as a solvent of the samples.
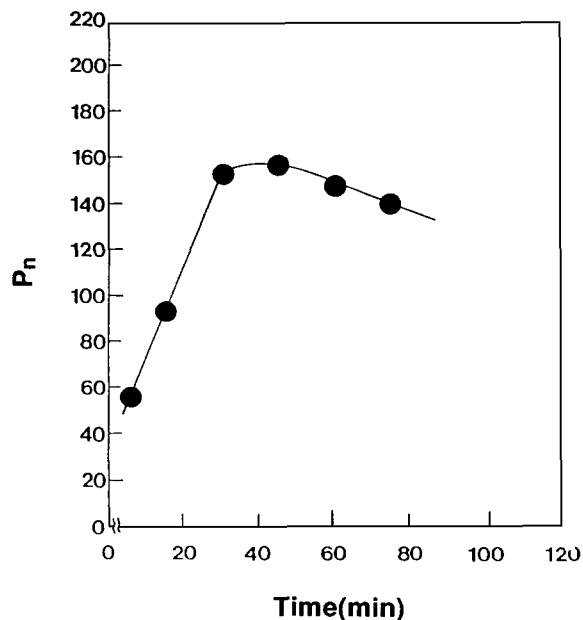
**Figure 1** Plot of $P_n$ of PBT obtained by polycondensation of BHBT at 270°C using TBT catalyst vs. polycondensation time.

## HPLC Analysis

The mixture solution of ethylene glycol (EG), 1,4-BD, tetrahydrofuran (THF), and water formed during the copolycondensation was analyzed quantitatively using a high-performance liquid chromatograph (Waters).
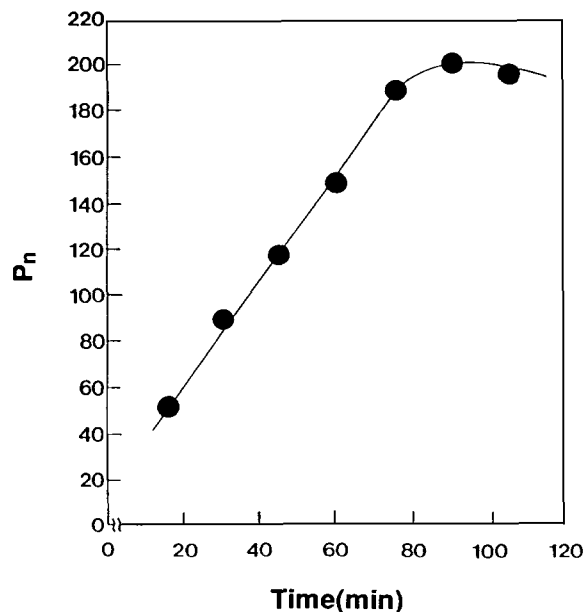


**Figure 2** Plot of $P_n$ of PET obtained by polycondensation of BHET at 270°C using TBT catalyst vs. polycondensation time.

**Table I  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 | $1.85 \times 10^{-5}$ |
| 8 | 0.026 | 2 | 0.008 | 0.0066 | $1.94 \times 10^{-5}$ |
| 7 | 0.023 | 3 | 0.012 | 0.0067 | $1.97 \times 10^{-5}$ |
| 6 | 0.019 | 4 | 0.016 | 0.0068 | $2.00 \times 10^{-5}$ |
| 5.497 | 0.018 | 4.503 | 0.018 | 0.0069 | $2.03 \times 10^{-5}$ |
| 5 | 0.016 | 5 | 0.019 | 0.0070 | $2.06 \times 10^{-5}$ |
| 4 | 0.013 | 6 | 0.024 | 0.0071 | $2.09 \times 10^{-5}$ |
| 2 | 0.006 | 8 | 0.031 | 0.0073 | $2.15 \times 10^{-5}$ |
| 0 | 0 | 10 | 0.039 | 0.0076 | $2.24 \times 10^{-5}$ |

The operating conditions of high-performance liquid chromatograph are listed in Table II.

## RESULTS AND DISCUSSION

### Kinetics of Polycondensation

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

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

where $N$ is mol number of PET chains, $t$ is polycondensation time of BHET, $k_{22}$ is rate constant of polycondensation of BHET, and $t_c$ is the time at which degradation of the PET chains occurs, respectively.

**Table II  Operating Conditions of High-Performance Liquid Chromatograph for Analyzing the Composition of Glycol Mixture Formed during the Copolycondensation**

| | |
|---|---|
| Column | $\mu$-Bondapak $C_{18}$ (3.9 mm $\times$ 30 cm) |
| Detector | differential refractometer (RI-401) |
| Column temperature | 20°C (regulated with circulating water bath (Haake FE-2) |
| Eluent | water/methanol (8 : 2 in volumn ratio) |
| Flow ratio | 1.0 mL/min |
| Sample | glycol mixture |
| Solvent | none |

**d (ppm)**
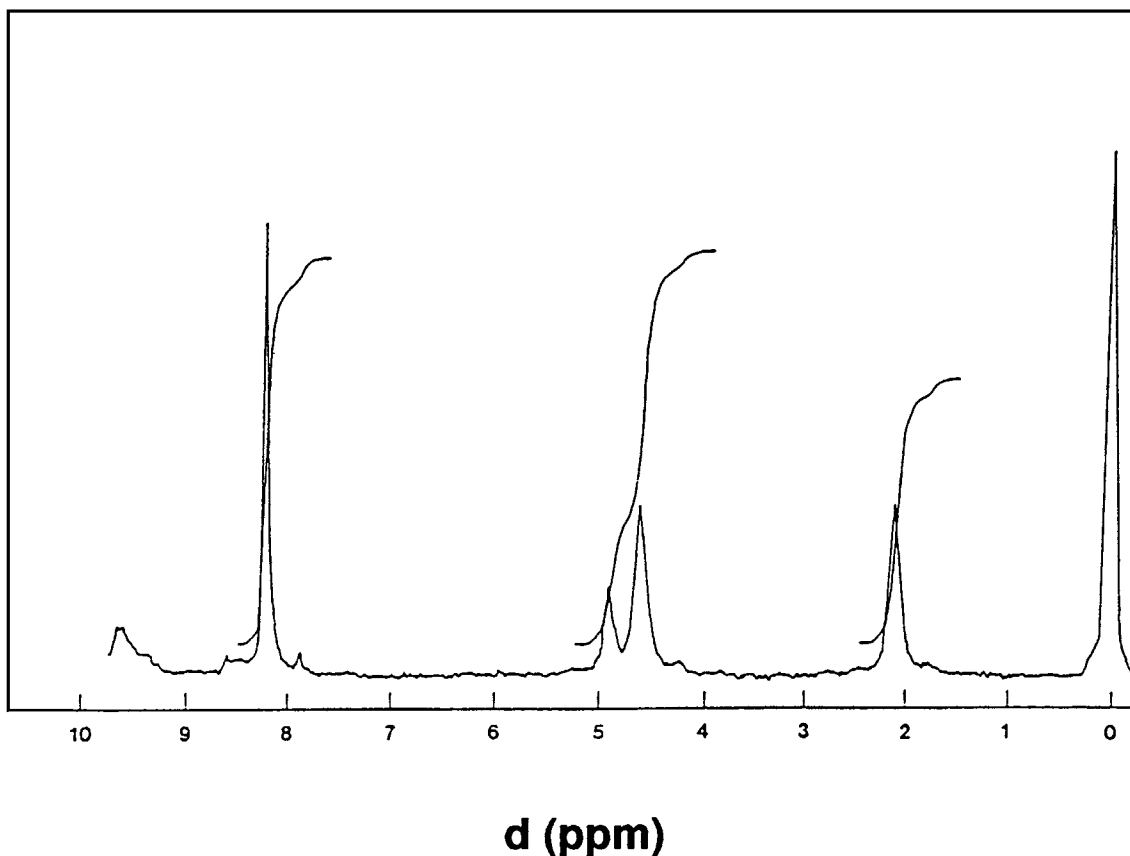
**Figure 3**   $^1$H-NMR spectrum of P(BT/ET) copolymer obtained by copolycondensation of BHBT and BHET with the mol ratio of 1.0 for 10 min at 270°C using TBT catalyst.

Integrating eq. (5) gives eq. (6):

$$(1/N) = k_{22}t + \left(\frac{1}{N_o}\right) \tag{6}$$

where $N_0$ is initial mol number of PET chains.

By supposing $N_0$ to be 1, eq. (4) can be converted to a expression that $N$ is $192/(M_n - 62)$. 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:

$$P_n = k_{11}t + 1 \tag{8}$$

where $k_{22}$ is rate constant of polycondensation of BHBT.

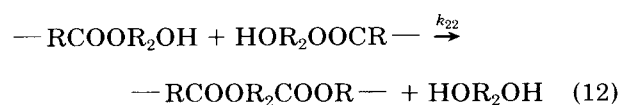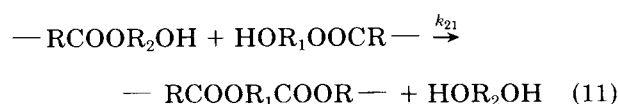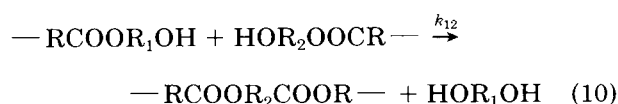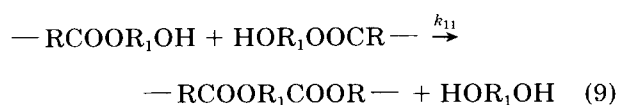## Calculation of the Rate Constant of Polycondensation

The kinetic model for PBT and PET syntheses had been studied by Pilati et al.[17-19] and Leverd et al.[20] To get polycondensation rate constants $k_{11}$ for PBT and $k_{22}$ for PET, $P_n$ of the sample polymerized for a given time was gained by the viscometry. Figures 1 and 2 show $P_n$ with respect to polycondensation time at 270°C. As we have been reported on the kinetics of polycondensation of BHET,[21] it was recognized that an initial linear region in the relation between the polycondensation time and $P_n$ exists, exhibiting second-order reaction with respect to the mol number of chains. From the slope of straight line in the region, the growth rate constants of polycondensation, $k_{11}$ and $k_{22}$, were calculated as 3.872 min$^{-1}$ and 2.238 min$^{-1}$, respectively. The linearity was lost after 45 min in Figure 1 and after 75 min in Figure 2. The reason of this was supposed that midterm ester interchange reaction[22] and decomposition reaction occurred.
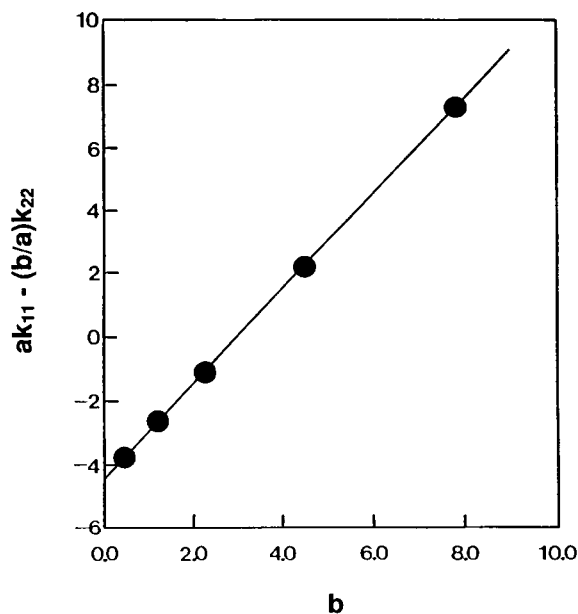
**Figure 4** Plot of $ak_{11} - (b/a)k_{22}$ vs. $b$ from P(BT/ET) copolymers obtained by copolycondensation for 10 min.

## Kinectics of Copolycondensation

Han[2] applied the expressions for addition copolymerization system were driven by Dostal and Alfrey[1] to the copolycondensation of polyesters. Now, applying this to the copolycondensation of BHBT and BHET gave following reactions:
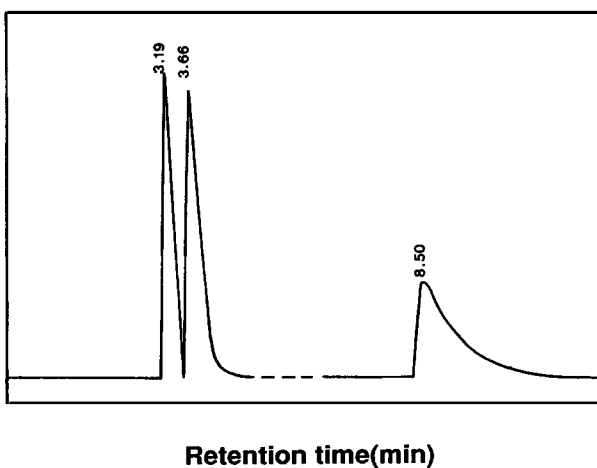
$$-RCOOR_1OH + HOR_1OOCR - \xrightarrow{k_{11}}$$

$$-RCOOR_1COOR - + HOR_1OH \quad (9)$$

$$-RCOOR_1OH + HOR_2OOCR - \xrightarrow{k_{12}}$$

$$-RCOOR_2COOR - + HOR_1OH \quad (10)$$

$$-RCOOR_2OH + HOR_1OOCR - \xrightarrow{k_{21}}$$

$$- RCOOR_1COOR - + HOR_2OH \quad (11)$$

$$-RCOOR_2OH + HOR_2OOCR - \xrightarrow{k_{22}}$$

$$-RCOOR_2COOR - + HOR_2OH \quad (12)$$

where $R_1$ is $-(CH_2)_4-$, $R_2$ is $-(CH_2)_2-$, and R is $-C_6H_4-$, respectively. Reactions (10) and (11) are crossreactions, whereas reactions (9) and (12) are homoreactions in general terms.

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) or (14),[2]
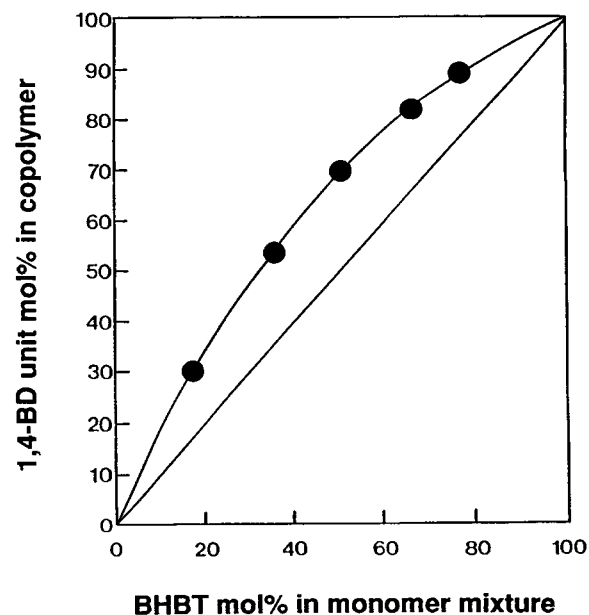


**BHBT mol% in monomer mixture**

**Figure 5** Composition in P(BT/ET) copolymer as a function of the monomer ratio: the copolymer was obtained by copolycondensation for 10 min and 1,4-BD unit mol % was calculated from $^1$H-NMR spectroscopy data.

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

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

where $a$ is the ratio of monomers in the copolycondensation ([BHBT]/[BHET]), $b$ is the ratio of diol units in the copolyester $(d[-OR_1O-]/$



**Retention time(min)**

**Figure 6** High-performance liquid chromatogram of diol mixture formed by copolycondensation for 10 min: EG, 3.19 min; 1,4-BD, 3.66 min; THF, 8.50 min (amplified).
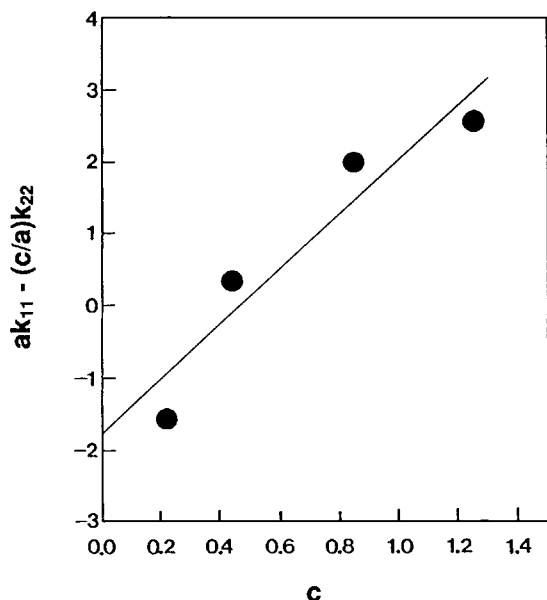
**Figure 7** Plot of $ak_{11} - (c/a)k_{22}$ vs. $c$ from P(BT/ET) copolymers obtained by copolycondensation for 10 min.

$d[-OR_2O-])$, and $c$ is the ratio of diols formed during the reaction $(d[HOR_1OH]/d[HOR_2OH])$.

## Calculation of the Rate Constant of Copolycondensation by ${}^1$H-NMR Spectroscopy

From eqs. (13) or (14), if $b$ or $c$ is determined experimentally, $k_{12}$ and $k_{21}$ can be easily obtained. To get the value of $c$ in eq. (14), HPLC was applied. On the other hand, the value of $b$ in eq. (13) was determined by ${}^1$H-NMR spectroscopy. Figure 3 shows an example of ${}^1$H-NMR spectrum of copolyester, which was copolymerized using the same mole ratio of BHBT and BHET. The diol unit ratio of the copolyester was determined by obtaining the area ratio of the $-OCH_2CH_2CH_2CH_2-$ peak integration ($\delta$ of 4.6 ppm) to the $-OCH_2CH_2O-$ peak integration ($\delta$ of 4.9 ppm).[4,23] 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 mol 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) are plotted as a function of $b$ in Figure 4. The plot gives a straight line. The rate constants of the cross reactions, $k_{12}$ and $k_{21}$, are obtained from the slope and from the intercept of the straight line in Figure 4, respectively. Thus, 1.499 and 4.422 were obtained as values of $k_{12}$

and $k_{21}$, respectively. 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 2.583 and 0.506, respectively. The $r_1$ was about five times larger than the $r_2$. Because the $r$ is relative value, it can be identified that the reactivity of BHBT is predominant when BHBT and BHET are copolymerized at 270°C.

It was found that the $k_{21}$ was the largest and $k_{12}$ was smallest in this reaction system. 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 blocky 1,4-BD units.

In this reaction system, $r_1$ ($=2.538$) was larger than 1 and $r_2$ ($=0.506$) was smaller than 1. Therefore, it was thought that the copolyester that 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 was proceeded. Composition diagram of copolyester synthesized is shown in Figure 5. The composition diagram was plotted by standardizing BHBT, which was predominant in reactivity. As shown in Figure 5, there was no azeo-
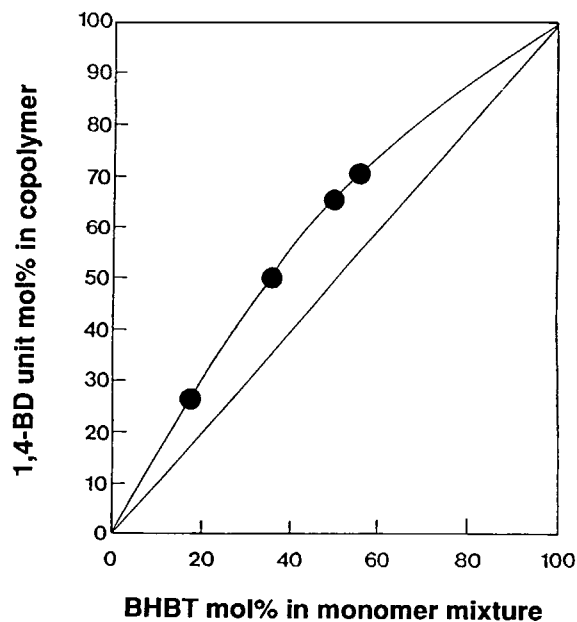


**Figure 8** Composition in P(BT/ET) copolymer as a function of the monomer ratio: the copolymer was obtained by copolycondensation for 10 min, and 1,4-BD unit mol % was calculated from HPLC data.

**Table III  Rate Constants and Reactivity Ratios of Copolycondensation of BHBT and BHET at 270°C for 10 Min**

| | $k_{11}$ (min$^{-1}$) | $k_{12}$ (min$^{-1}$) | $k_{21}$ (min$^{-1}$) | $k_{22}$ (min$^{-1}$) | $r_1$ | $r_2$ |
|---|---|---|---|---|---|---|
| The data by $^1$H-NMR spectroscopy | 3.872 | 1.499 | 4.422 | 2.238 | 2.583 | 0.506 |
| The data by HPLC | 3.872 | 1.797 | 3.822 | 2.238 | 2.155 | 0.586 |

tropic composition presented in eq. (15) in this reaction system:

$$a = c = (k_{21} - k_{22})/(k_{12} - k_{11}) \qquad (15)$$

## Calculation of the Rate Constant of Copolycondensation by HPLC

To compare the results obtained by $^1$H-NMR spectroscopy, the diols formed during the polycondensation were analyzed by HPLC. The THF and water were in the diol mixture found during the copolycondensation of BHBT and BHET were formed by the dehydration of 1,4-BD. Sivaram et al.[12] and Chang and Tsai[24] studied the formation mechanism of THF during PBT synthesis.

In order for correct determining the relative amounts of EG, 1,4-BD, and THF in the diol mixture found during the copolycondensation, calibration curves of those were drawn, respectively. Figure 6 shows the high-performance liquid chromatogram of the diol mixture formed during the copolycondensation using the same mol ratio of monomers. The peaks at retention times (($R_t$)s) of 3.19, 3.66, and 8.50 min were those of EG, 1,4-BD, and THF, respectively. The dotted line around the $R_t$ of about 5 min represented that the sensitivity of HPLC was amplified to 16 times after 5 min. The reason for amplifying peak was because there was minimal amount of THF in the diol mixture. From the HPLC results, it was identified that THF was produced to the extent of 7% (mol/mol) of 1,4-BD.

The left terms of eq. (14) were calculated by introducing the ratio of diols formed during the copolycondensation. Figure 7 shows these calculated values plotted against $c$ according to eq. (14). From the slope and the intercept of the straight line in Figure 7, $k_{12}$ and $k_{21}$ were calculated to be 3.822 and 1.797, respectively. As a result, the monomer reativity ratio of BHBT, $r_1$ and that of BHET, $r_2$, were found to be 2.155 and 0.586, respectively. As shown in Table III, these values are approximately compatible with those obtained by the $^1$H-NMR spectroscopy. However, considering that the relation be-

tween the left terms of eq. (14) and the ratio of diols formed during the copolycondensation shows poor linearity as presented in Figure 7. The poor linearity might be reasoned by the following several experimental errors: an inflow of diol formed into the vacuum pump due to its hypervacuum state during the copolycondensation and errors, which would occur in HPLC analysis, etc. Because the correlation coefficient ($C_r$) of straight line in Figure 4 ($C_r$ of 0.9998) was better than that in Figure 7 ($C_r$ of 0.9857), it is thought that the method by $^1$H-NMR spectroscopy is more effective tool than that by HPLC to obtain the monomer reactivity ratios of BHBT and BHET during the copolycondensation. Figure 8 shows composition diagram of copolyester plotted with $b$ value obtained by rate constants from HPLC analysis. The shape of this diagram was consistent to the shape of the diagram in Figure 5.

## CONCLUSION

Investigating the kinetics of copolycondensation of BHBT and BHET by ester interchange reaction, we may conclude as below: the rate constants during the copolycondensation of BHBT and BHET at 270°C decreased in the order $k_{21} > k_{11} > k_{22} > k_{12}$ and the monomer reactivity ratio of BHBT was four or five times larger than that of BHET. The $^1$H-NMR spectroscopic analysis was more correct tool than the high-performance liquid chromatographic analysis for the precise calculation of the crossreaction constants.

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