

# Kinetics of Polycondensation and Copolycondensation of Bis(3-hydroxypropyl Terephthalate) and Bis(2-hydroxyethyl Terephthalate)

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**ABSTRACT:** The kinetics of polycondensation and copolycondensation reactions of bis(3-hydroxypropyl) terephthalate (BHPT) and bis(2-hydroxyethyl) terephthalate (BHET) as monomers were investigated at 270°C, in the presence of titanium tetrabutoxide (TBT) as a catalyst. BHPT was prepared by ester interchange reaction of dimethyl terephthalate (DMT) and 1,3-propanediol (PD). Applying second-order kinetics for polycondensation, the rate constants of polycondensation of BHPT and BHET,  $k_{11}$  and  $k_{22}$ , were calculated as 3.975 and 2.055  $\text{min}^{-1}$ , respectively. The rate constants of cross-reactions in the copolycondensation of BHPT and BHET,  $k_{12}$  and  $k_{21}$ , were obtained by using the results obtained from a proton nuclear magnetic resonance spectroscopy. The rate constants during the copolycondensation of BHPT and BHET at 270°C decreased in the order  $k_{11} > k_{12} > k_{22} > k_{21}$ , indicating the block nature of the copolycondensation. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 693–698, 2000

**Key words:** polycondensation; copolycondensation; BHPT; BHET

## INTRODUCTION

Poly(ethylene terephthalate) (PET) and poly(trimethylene terephthalate) (PTT) have been known as industrially important polyesters, which are widely used as commercial fibers, polymeric films, and engineering plastics.<sup>1–7</sup> To enhance the processibility and crystallization rate of PET and to improve the mechanical and thermal properties of PTT, their copolymerization using both oligomeric and monomeric forms as reactants or usage of them as polymer blend are actively studied.<sup>8–17</sup>

Many methods were known to calculate the monomer reactivity in addition copolymerization system. The method using kinetic equation derived by Dostal and Alfrey<sup>18</sup> is exemplified as one

of the well-known theoretical techniques. Compared with the active research on the relative reactivity of vinyl type monomers in the addition copolymerization system, a few comparative studies of the monomer reactivity were carried out in the copolycondensation system. Han<sup>19</sup> synthesized PET, PTT, and PET–PPT copolyester. He calculated the monomer reactivity ratio of bis(2-hydroxyethyl) terephthalate (BHET) and bis(2-hydroxypropyl) terephthalate in their copolymerization applying the copolymerization kinetic equation and using gas chromatography to obtain the rate constants of cross-reactions. However, because those polymerizations had been conducted at a much lower temperature than general industrial polycondensation and the copolycondensation temperatures of BHET and bis(2-hydroxypropyl) terephthalate, such as 260, 270, or 280°C, it was difficult to apply the monomer reactivity ratio calculated by Han with processible

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**Table I Feed Ratios of Monomer and Catalyst for Copolycondensation**

No.	BHPT		BHET		TBT Catalyst	
	g	mol	g	mol	g	mol
1	10	0.0354	0	0	0.004	$1.18 \times 10^{-5}$
2	8	0.0284	2	0.0079	0.004	$1.18 \times 10^{-5}$
3	7	0.0248	3	0.0118	0.004	$1.18 \times 10^{-5}$
4	6	0.0213	4	0.0157	0.004	$1.18 \times 10^{-5}$
5	5.261	0.0187	4.739	0.0187	0.004	$1.18 \times 10^{-5}$
6	4	0.0142	6	0.0236	0.004	$1.18 \times 10^{-5}$
7	3	0.0106	7	0.0276	0.004	$1.18 \times 10^{-5}$
8	2	0.0071	8	0.0315	0.004	$1.18 \times 10^{-5}$
9	0	0	10	0.0394	0.004	$1.18 \times 10^{-5}$

copolymerization conditions in order to control various molecular parameters of copolyesters, such as blockiness and randomness.

In this study, bis(3-hydroxypropyl) terephthalate (BHPT) and BHET were homopolymerized and copolymerized in presence of titanium tetrabutoxide (TBT) as a catalyst at 270°C, respectively, and the rate constants of the cross-reactions for BHPT and BHET were calculated by using the results obtained from a proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) spectroscopy.

## EXPERIMENTAL

### Synthesis and Purification of BHET<sup>20</sup>

The transesterification of dimethyl terephthalate (DMT) (97 g; 0.5 mol) with ethylene glycol (EG) (83 mL; 1.5 mol) in the presence of zinc acetate (0.55 g;  $2.5 \times 10^{-3}$  mol) as a catalyst was charged into a four-necked, round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a distillation column. The mixture of DMT, EG, 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 has been completed, the product was washed and dissolved in hot water. A white needle-shaped crystal (melting point: 109.5°C) was obtained by recrystallizing the above crystallized BHET from 1,1,2,2-tetrachloroethane.

### Synthesis and Purification of BHPT<sup>16,21</sup>

The transesterification of DMT (97 g; 0.5 mol) with 1,3-propanediol (PD) (83.6 mL; 1.1 mol) in

the presence of zinc acetate (0.054 g;  $2.97 \times 10^{-4}$  mol) as a catalyst was also performed under the same conditions adopted in the case of BHET.

### Homopolycondensation of BHPT and BHET<sup>21</sup>

Purified BHET (10 g; 0.039 mol) were melted under nitrogen flow in polycondensation tube, equipped with a mechanical stirrer and a silicone sealing apparatus. Molten BHET was stirred at 50 rpm. At 200°C, nitrogen flow stopped, and TBT (0.004 g;  $1.18 \times 10^{-5}$  mol) catalyst was added in a polycondensation tube. A pressure was decompressed about 20 mm Hg by a vacuum pump, and then it was slowly decompressed so that highly reduced pressure of 0.3 mm Hg reached. The pressure was maintained during a given polycondensation time (10, 20, 35, 50, 65, and 80 min). The reaction temperature was increased with decompression to 270°C and maintained. 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; 0.035 mol) was also polymerized under same conditions (TBT:  $1.05 \times 10^{-5}$  mol).

### Copolycondensation of BHET and BHPT

The copolycondensation was conducted for 10 min under the same conditions as used in homopolycondensation. The feed ratios of monomer and catalyst are listed in Table I.

### Characterization

The  $P_n$  of polymerized sample was determined by the viscosity method. For PET, a phenol–TCE (40/60 wt) mixture solution was used as a solvent. The intrinsic viscosity  $[\eta]$  at 25°C was obtained by

the usual method. From equation (1),<sup>22</sup> the number-average molecular weight ( $M_n$ ) was calculated by using  $[\eta]$ . The  $P_n$  was calculated by substituting  $M_n$  for equation (2), as follows:

$$[\eta] = 1.40 \times 10^{-3} [M_n]^{0.64} \quad (1)$$

$$P_n = (M_n - 62)/192 \quad (2)$$

In contrast, in the case of PTT, the phenol-TCE (50/50 wt) mixture solution was used as a solvent.  $[\eta]$  at 25°C was obtained by the usual method. From equation (3),<sup>21</sup>  $[\eta]$  at 25°C and equation (4),  $M_n$  and  $P_n$  of PTT were obtained.

$$[\eta] = 8.2 \times 10^{-2} [M_n]^{0.63} \quad (3)$$

$$P_n = (M_n - 77)/206 \quad (4)$$

<sup>1</sup>H-NMR spectra of PET, PTT, and the copolyester formed through polycondensation and copolycondensation were obtained by nuclear magnetic resonance (NMR) spectrophotometers (DPX-300 NMR spectrophotometers, Bruker). Trifluoroacetic acid was used as a solvent of the samples.

## RESULTS AND DISCUSSION

### Kinetics of Polycondensation

Polycondensation of BHET has been known as a first-order<sup>23</sup> or second-order<sup>24</sup> reaction to the mol number of chains. Because this study is for the chain growth reaction without the thermal decomposition reaction, it can be thought that the second-order reaction kinetics of Cefelin and Malek,<sup>24</sup> like equation (5), as follows, is more proper:

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

where  $N$  is the mol 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 the PET chains occurs, respectively.

Integrating equation (5) gives equation (6), as follows:

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

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

By supposing  $N_0$  to be 1, equation (4) can be converted to an expression that  $N$  is  $192/(M_n - 62)$ . Thus, equation (6) can be expressed as follows in equation (7):

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

By applying equation (6) to the case of BHPT and by converting equation (2) that  $N$  is  $206/(M_n - 77)$ , equation (8) can be derived, as follows:

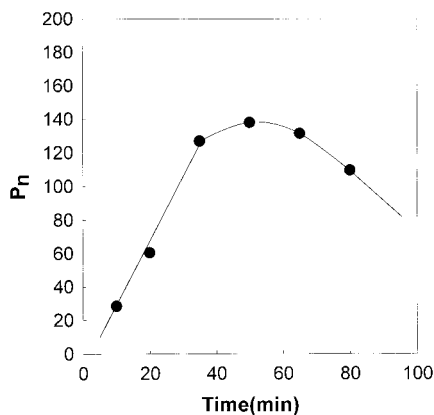
$$P_n = k_{11}t + 1 \quad (8)$$

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

### Calculation of the Rate Constant of Polycondensation

The kinetic model for bis(2-hydroxy-*n*-propyl) terephthalate and BHET syntheses had been studied by Han.<sup>19</sup> Han obtained the monomer reactivity ratio of bis(2-hydroxy-*n*-propyl) terephthalate and BHET in their copolymerization applying the copolymerization kinetic equation and using a gas chromatography to obtain the rate constants of cross-reactions at a polycondensation temperature of 160°C. But it was difficult to apply these monomer reactivity ratios with processible copolymerization conditions (industrial polycondensation temperatures of 260, 270, or 280°C) in order to control various molecular parameters of copolyesters. So, in this study, we tried to obtain copolycondensation rate constants at 270°C.

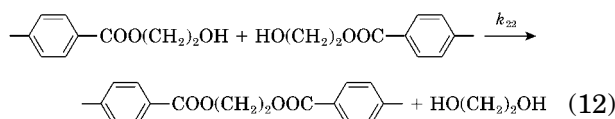
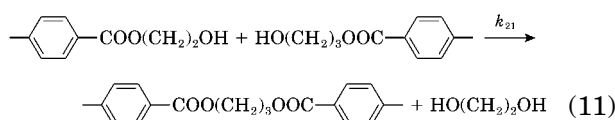
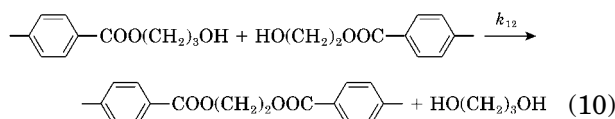
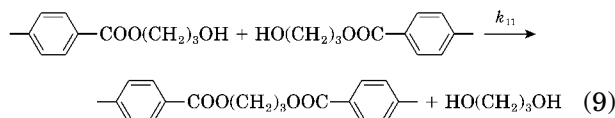
To get the polycondensation rate constants  $k_{11}$  for PTT and  $k_{22}$  for PET,  $P_n$  of the sample polymerized for a given time was gained by viscometry. Figures 1 and 2 show  $P_n$  with respect to the polycondensation time at 270°C. As we have reported on the kinetics of polycondensation of BHET,<sup>25</sup> it was recognized that an initial linear region in the relation between the polycondensation time and  $P_n$  exists, exhibiting a second-order reaction with respect to the mol number of chains. From the slope of the straight line in the region, the growth rate constants of polycondensation,  $k_{11}$  and  $k_{22}$ , were calculated as 3.975 and 2.055  $\text{min}^{-1}$ , respectively. The linearity was lost after 45 min in Figure 1. The reason of this was supposed that a midterm ester interchange reaction<sup>26</sup> and a decomposition reaction occurred.



**Figure 1**  $P_n$  of PTT obtained by polycondensation of BHPT at 270°C using TBT catalyst with polycondensation time.

### Kinetics of Copolycondensation

Han<sup>19</sup> applied the expressions for an addition copolymerization system driven by Dostal and Alfrey<sup>18</sup> to the copolycondensation of polyesters. Applying this to the copolycondensation of BHPT and BHET gave the following reactions.



Reactions (10) and (11) are cross-reactions, whereas reactions (9) and (12) are homoreactions in general terms.

The rate constants of the crossreactions in the copolycondensation of BHPT and BHET,  $k_{12}$  and  $k_{21}$ , can be calculated from equations (13) or (14).<sup>19</sup>

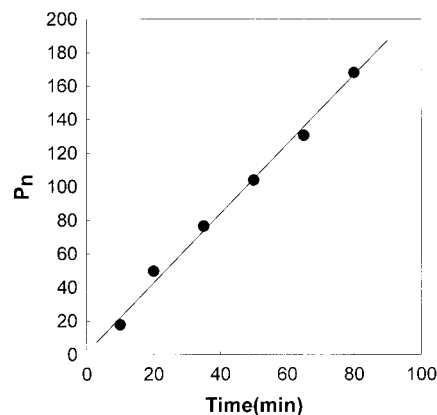
$$ak_{11} - \frac{b}{a}k_{22} = bk_{12} - k_{21} \quad (13)$$

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

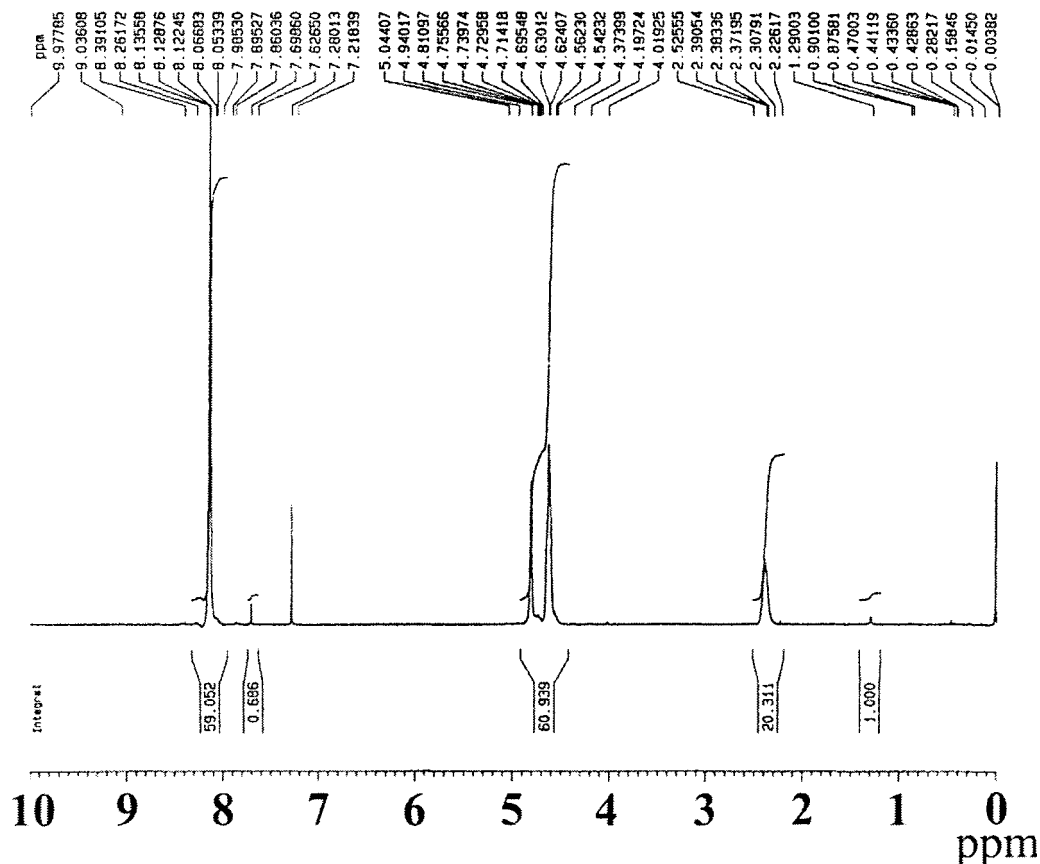
where  $a$  is the ratio of monomers in the copolycondensation ( $[\text{BHPT}]/[\text{BHET}]$ ),  $b$  is the ratio of diol units in the copolyester ( $d[-\text{OR}_1\text{O-}]/d[-\text{OR}_2\text{O-}]$ ), and  $c$  is the ratio of diols formed during the reaction ( $d[\text{HOR}_1\text{OH}]/d[\text{HOR}_2\text{OH}]$ ).

### Calculation of the Rate Constant of Copolycondensation

From equations (13) or (14), if  $b$  or  $c$  is determined experimentally,  $k_{12}$  and  $k_{21}$  can be easily obtained. To get the value of  $b$  in equation (13) was determined by <sup>1</sup>H-NMR spectroscopy. Figure 3 shows an example of <sup>1</sup>H-NMR spectrum of copolyester, which was copolymerized using the same mole ratio of BHPT and BHET. The diol unit ratio of the copolyester was determined by obtaining the area ratio of the  $-\text{OCH}_2\text{CH}_2\text{CH}_2-$  peak integration ( $\delta$  of 4.6 ppm) to the  $-\text{OCH}_2\text{CH}_2\text{O}-$  peak integration ( $\delta$  of 4.8 ppm). Figure 3 apparently showed that the peak area of the 1,3-PD units was larger than that of the EG units, regardless of the <sup>1</sup>H-NMR spectrum of the copolyester copolymerized using the same mole ratio of BHPT and BHET. This fact had the important meaning in the calculation of the reactivity ratios of BHPT and BHET. Table II shows composition in P(TT/ET) as a function of the monomer ratio.



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



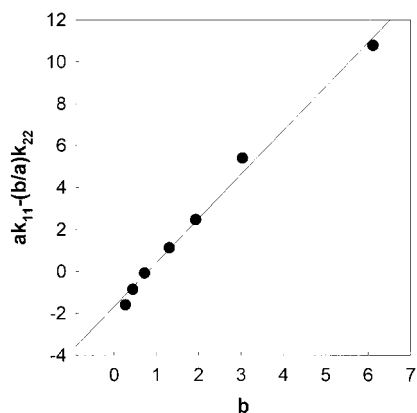
**Figure 3**  $^1\text{H-NMR}$  spectrum of  $P(\text{TT}/\text{ET})$  copolymer obtained by copolycondensation of BHPT and BHET with the mol ratio of 1.0 for 10 min at  $270^\circ\text{C}$  using a TBT catalyst.

In order to obtain the rate constants of the crossreactions, the left terms of equation (13) are plotted as  $a$  function of  $b$  in Figure 4. The plot

**Table II** Composition in the  $P(\text{TT}/\text{ET})$  Copolymer as a Function of the Monomer Ratio: The Copolymer was Obtained by Copolycondensation for 10 min and 1,3-PD Unit Mol% was Calculated from  $^1\text{H-NMR}$  Spectroscopy Data

Composition PTT/PET (Wt Ratio)	1,3-PD Unit (Mol %)	EG Unit (Mol %)
100 : 0	100	0
20 : 80	90.18	9.82
70 : 30	82.01	17.99
60 : 40	74.36	25.64
52.6 : 47.4 (mol ratio of 1)	68.17	31.83
40 : 60	52.15	47.84
30 : 70	43.30	56.70
20 : 80	29.06	70.94
0 : 100	0	100

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, 2.100 and 1.691 were obtained as values of  $k_{12}$  and  $k_{21}$ , respectively.



**Figure 4** Plot of  $ak_{11} - (b/a)k_{22}$  versus  $b$  from  $P(\text{TT}/\text{ET})$  copolymers obtained by copolycondensation for 10 min.

**Table III** Rate Constants of Copolycondensation of BHPT and BHET at 270°C

Data	$k_{11}$ ( $\text{min}^{-1}$ )	$k_{12}$ ( $\text{min}^{-1}$ )	$k_{21}$ ( $\text{min}^{-1}$ )	$k_{22}$ ( $\text{min}^{-1}$ )
The data by $^1\text{H-NMR}$ spectroscopy	3.975	2.100	1.691	2.055

It was found that the  $k_{12}$  was larger than  $k_{21}$  in this reaction system, as shown in Table III. That is, the reaction in which the 1,3-PD unit was missed during the formation of the EG unit occurred as soon as possible, and the reaction in which the EG unit was missed during the formation of the 1,3-PD 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 1,3-PD units. In addition, it was thought that the copolyester that had richer 1,3-PD units than EG units was produced in the early reaction stage, and the EG units in copolyester increased as a reaction was proceeded.

## CONCLUSION

Investigating the kinetics of copolycondensation of BHPT and BHET by ester interchange reaction at 270°C, we may conclude as below. Applying second-order kinetics for polycondensation, the rate constants of polycondensation of BHPT and BHET,  $k_{11}$  and  $k_{22}$ , were determined. In addition, the rate constants of cross-reactions in the copolycondensation of BHPT and BHET,  $k_{12}$  and  $k_{21}$ , were determined by using the results obtained from  $^1\text{H-NMR}$  spectrum. The rate constants decreased in the order  $k_{11} > k_{12} > k_{22} > k_{21}$ . Thus, the molecular type of the precondensate synthesized might be supposed to be a series of random copolymer containing BHPT miniblocks. In the near future, we will report effect of polycondensation temperature on the rate constants of BHPT and BHET.

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