

# Bis(4-hydroxybutyl) terephthalate와 bis(2-hydroxyethyl) terephthalate의 반응성에 미치는 축합공중합 온도의 영향

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## Effect of Copolycondensation Temperature on the Reactivities of Bis(4-hydroxybutyl) Terephthalate and Bis(2-hydroxyethyl) Terephthalate

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### 1. 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]. 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 [3] 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 [4] synthesized PET, poly(propylene terephthalate) (PPT) and PET-PPT copolymers. He calculated the monomer reactivity ratios of BHET and bis(2-hydroxy-n-propyl) 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. The rate constants and the monomer reactivity ratios for BHBT and BHET were calculated by using the results obtained from a proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopy and a high performance liquid chromatography (HPLC).

## 2. Experimental

### 2.1 Materials

### 2.2 Homopolycondensation and Copolycondensation

### 2.3 Characterization [5]

## 3. Result and Discussion

In this study, because polycondensation of BHET is for the chain growth reaction without thermal decomposition reaction, it can be thought that 2nd [16] order reaction kinetics of Cefelin and Malek [6] like eq. (5) is more proper.

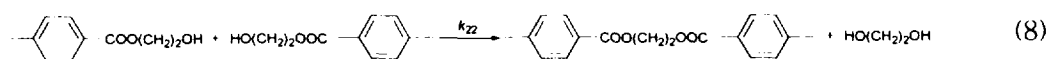
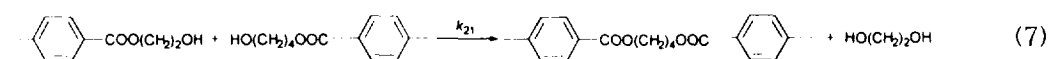
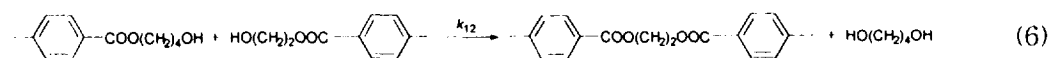
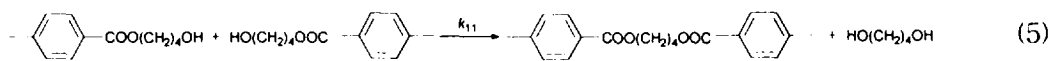
$$-(dN/dt) = k_{22}N^2 \quad (0 < t < t_c) \quad (1)$$

$$(1/N) = k_{22}t + (1/N_0) \quad (2)$$

$$P_n = k_{22}t + 1 \quad (3)$$

$$P_n = k_{11}t + 1 \quad (4)$$

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



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

$$ak_{11} - (b/a)k_{22} = bk_{12} - k_{21} \quad (9)$$

$$ak_{11} - (c/a)k_{22} = ck_{21} - k_{12} \quad (10)$$

where  $a$  is the ratio of monomers in the copolycondensation ( $[BHBT]/[BHET]$ ) and  $b$  is the ratio of diols in the copolyester ( $d[-O(CH_2)_4O-]/d[-O(CH_2)_2O-]$ ). From eq. (9), if  $b$  is determined experimentally,  $k_{12}$  and  $k_{21}$  can be easily obtained. To get the value of  $b$  in eq. (9),  $^1H$ -NMR spectroscopy was applied. In order to obtain the rate constants of the cross reactions, the left terms of eq. (9) were calculated by introducing the diol unit ratio of the copolyester which was determined by obtaining the area ratio of the  $-O(CH_2)_4O-$  peak integration to the  $-O(CH_2)_2O-$  peak integration. Fig. 2 presents these calculated values plotted against  $b$  according to eq. (9). The plot gives a straight line. Therefore,  $k_{12}$  and  $k_{21}$  were calculated, as shown in Table 2. Also the monomer reactivity ratios of BHBT and BHET were calculated. To get the value of  $c$  in eq. (10), the diols formed during the polycondensation were analyzed by HPLC. The plot shown in Fig. 2 gives a straight line. From Fig. 2,  $k_{12}$ ,  $k_{21}$ ,  $r_1$  and  $r_2$  were calculated.

#### 4. Conclusions

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 each temperature decreased in the order  $k_{21} > k_{11} > k_{22} > k_{12}$  and the monomer reactivity ratios of BHBT was larger than those of BHET. So the molecular type of the precondensate synthesized might be supposed to be a series of block copolymer. And the  $^1H$ -NMR spectroscopic analysis was more correct tool than the HPLC analysis for the precise calculation of the crossreaction constants. The differences between monomer reactivity ratios were decreased with increasing polycondensation temperature, indicating that a probability of randomization was increased.

#### 5. References

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Table 1. Rate constants and reactivity ratios of copolycondensation of BHBT and BHET at three different copolycondensation temperatures for 10 min, calculated from <sup>1</sup>H-NMR and HPLC data

	Copolycondensation Temp. (°C)	k <sub>11</sub> (min <sup>-1</sup> )	k <sub>12</sub> (min <sup>-1</sup> )	k <sub>21</sub> (min <sup>-1</sup> )	k <sub>22</sub> (min <sup>-1</sup> )	r <sub>1</sub>	r <sub>2</sub>
The data by <sup>1</sup> H-NMR	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
The data by HPLC	260	2.58	0.79	3.83	1.30	3.27	0.34
	270	3.87	1.79	3.82	2.24	2.16	0.59
	280	5.29	3.76	5.34	4.06	1.41	0.76

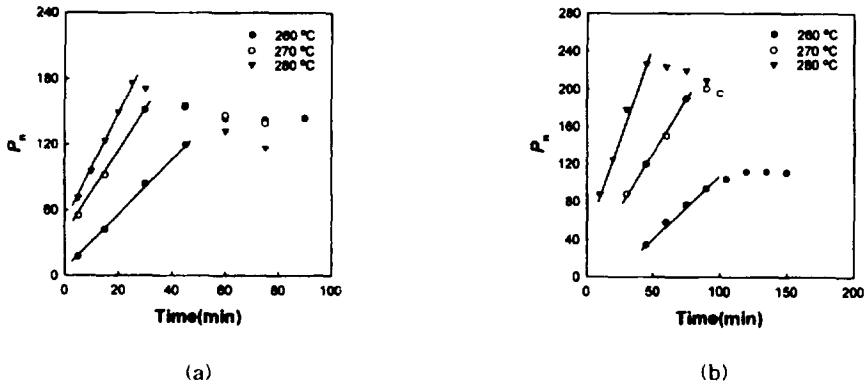


Figure 1. ( $P_n$ )s of PBT (a) and PET (b) obtained by polycondensation of BHBT and BHET, respectively, at 260, 270, and 280 °C using titanium tetrabutoxide catalyst with polycondensation times.

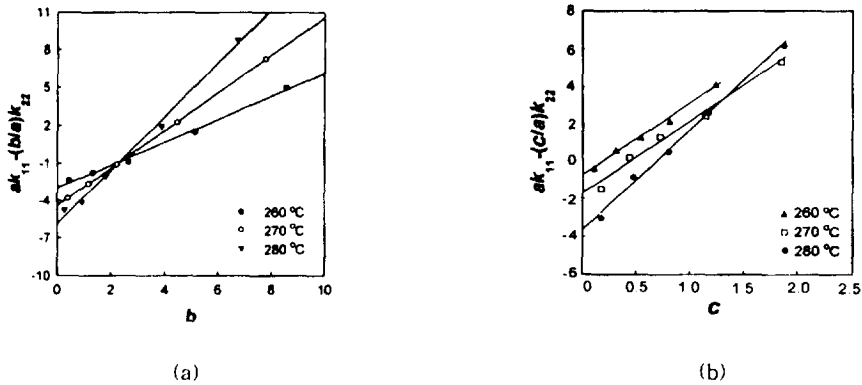


Figure 2. Plots of  $ak_{11}-(b/a)k_{22}$  vs. b (a) and  $ak_{11}-(c/a)k_{22}$  vs. c (b) from P(BT/ET) copolymers obtained by copolycondensation at 260, 270, and 280 °C for 10 min.