# 폴리(트리메틸렌/부틸렌 테레프탈레이트) 공중합체의
# 축합중합 속도와 특성해석

박준호, 김준호, 류원석

영남대학교 섬유패션학부

# Polycondensation Kinetics and Characterization of Poly(trimethylene/butylene terephthalate) Copolyesters

## Jun Ho Park, Joon Ho Kim, and Won Seok Lyoo

*School of Textiles, Yeungnam University, Kyongsan, Korea*

## 1. Introduction

The family of linear aromatic polyesters, poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT), and poly(butylene terephthalate) (PBT), have been known as industrially important polyesters, which are widely used as commercial fibers, polymeric films, and engineering plastics[1-3]. PET was the first aromatic polyester commercialized and became one of the most important synthetic textile polymer. In fact, PET becomes synonymous with polyester because it is used to commonly in textiles. It took more than twenty years for the next aromatic polyester, PBT, to appear in the market. PBT is now used primarily as an engineering thermoplastic. Only a small volume of PBT is used in fiber applications. Recently, PTT is used commercially for the textile and carpet.

In copolymerization, initial reactivity has important meaning. So many methods were known to calculate the monomer reactivity in addition copolymerization system. The method using kinetic equation derived by Dostal and Alfrey[4] is examplified as one of the well-known theoretical techniques. Comparing 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.

In this study, bis(3-hydroxypropyl) terephthalate (BHPT) and bis(4-hydroxybutyl) terephthalate (BHBT) were homopolymerized and copolymerized in the presence of titanium tetrabutoxide (TBT) as a catalyst at 270 ℃, respectively, and the rate constants of the crossreactions for BHPT and BHBT were calculated by using the results obtained from a proton nuclear magnetic resonance ($^1$H-NMR) spectroscopy. Properties of copolymers were analyzed using differential scanning calorimeter (DSC) and X-ray diffractometer (XRD).

## 2. Experimental

### 2.1 Materials
### 2.2 Homopolycondensation and Copolycondensation
### 2.3 Analysis

## 3. Results and Discussion

### 3.1 Kinetics and the Rate Contant of Polycondensation

Because polycondensation of BHPT is for the chain growth reaction without thermal decomposition reaction in this study, it can be thought that second-order reaction kinetics of Cefelin and Malek[5] like eq. (1) is more proper (*Figure 1*).

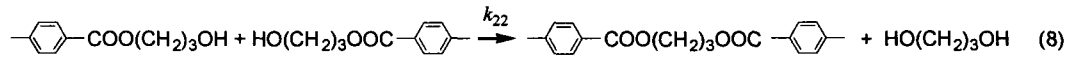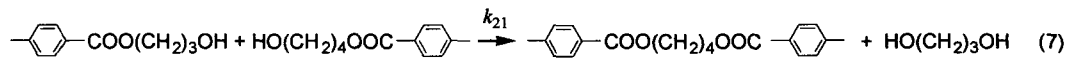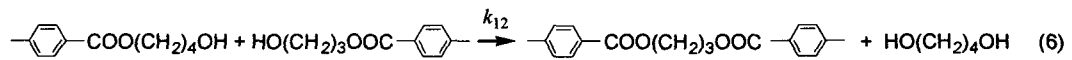$$- ( dN \,/\, dt ) \;=\; k_{22} N^2 \quad ( 0 < t < t_c ) \tag{1}$$

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

$$P_n \;=\; k_{22} t \;+\; 1 \tag{3}$$

$$P_n \;=\; k_{11} t \;+\; 1 \tag{4}$$

### 3.2 Kinetics and the Rate Contant of Copolycondensation

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



$$-\!\langle\rangle\!-COO(CH_2)_4OH + HO(CH_2)_4OOC-\!\langle\rangle\!- \xrightarrow{k_{11}} -\!\langle\rangle\!-COO(CH_2)_4OOC-\!\langle\rangle\!- + HO(CH_2)_4OH \tag{5}$$

$$-\!\langle\rangle\!-COO(CH_2)_4OH + HO(CH_2)_3OOC-\!\langle\rangle\!- \xrightarrow{k_{12}} -\!\langle\rangle\!-COO(CH_2)_3OOC-\!\langle\rangle\!- + HO(CH_2)_4OH \tag{6}$$

$$-\!\langle\rangle\!-COO(CH_2)_3OH + HO(CH_2)_4OOC-\!\langle\rangle\!- \xrightarrow{k_{21}} -\!\langle\rangle\!-COO(CH_2)_4OOC-\!\langle\rangle\!- + HO(CH_2)_3OH \tag{7}$$

$$-\!\langle\rangle\!-COO(CH_2)_3OH + HO(CH_2)_3OOC-\!\langle\rangle\!- \xrightarrow{k_{22}} -\!\langle\rangle\!-COO(CH_2)_3OOC-\!\langle\rangle\!- + HO(CH_2)_3OH \tag{8}$$
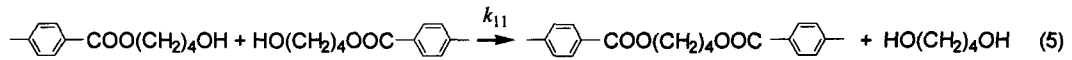
The rate constants of the crossreactions in the copolycondensation of BHBT and BHPT, $k_{12}$ and $k_{21}$, can be calculated from eq. (9) or (10) (*Table 1*).

$$a k_{11} \;-\; (b/a) k_{22} \;=\; b k_{12} \;-\; k_{21} \tag{9}$$

$$a k_{11} \;-\; (c/a) k_{22} \;=\; c k_{21} \;-\; k_{12} \tag{10}$$

## 3.3 DSC analysis[6,7]

Typical calorimetric curves of PBT, PTT and PBT-PTT copolymers obtained after cooling from the melt are reported in *Figure 2a*. An endothermal baseline shift associated with the glass transitions were observed in the temperature range between 40 and 60 ℃ in first scan, but were not found in second scan.

The DSC curves show a melting peak whose location depends on copolymer composition. It is well known that the thermal behaviour of a polymer is affected by its previous thermal history and that the amorphous and crystalline contents depend on the rate at which the sample has been cooled.

The calorimetric results indicate that an increase in the amount of the comonomer leads to a reduction of the melting temperature in samples subjected to the same thermal history. The reduction of the melting temperature in BHPT mol % of 50 and 62.8 show large difference compared to PBT and PTT melting temperature. These two values are similar, so there is further reduction of melting temperature in BHPT mol % between 50 to 62.8.

## 3.4 X-ray diffraction analysis

To find out the crystal structure of PBT/PTT copolymer, wide-angle X-ray diffraction measurement was carried out. Raw homopolymers and copolymers were used without any pre-treatment. The change of crystal structure was measured with reaction time in mole ratio of 1:1 copolymer. The size of unit cell of copolymer was increased slowly, when mol % of one monomer was increased to the other monomer, indicating that unit cell was broaden by paracrystalline defect chain. *Figure 2b* shows typical wide-angle X-ray diffraction patterns of PTT, PBT and their copolymers, respectively.

## 4. Referencees

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2) W. S. Lyoo, S. G. Lee, W. S. Ha, J. Lee, and J. H. Kim, *Polym. Bull.*, **42**, 9(1999).

3) J. H. Kim, S. Y. Lee, J. H. Park, W. S. Lyoo, and S. K. Noh, *J. Appl. Polym. Sci.*, **77**, 693(2000).

4) F. R. Billmeyer, "Textbook of Polymer Science", John Wiley & Sons, New York, 1984.

5) P. Cefelin and J. Malek, *Collect Czech Chem. Commun*, **34**, 419(1969).

6) J. M. Huang and F. C. Chang, *J. Polym. Sci. Part B*, **38**, 934(2000).

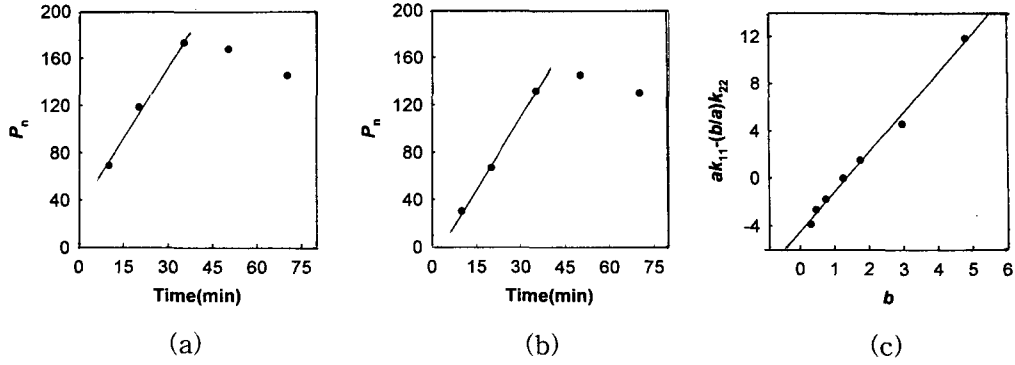7) M. Pyda, and B. Wunderlich, *J. Polym. Sci. Part B*, **38**, 622(2000).

Figure 1. $(P_n)$s of PBT (a) and PTT (b) with polycondensation times, and plots of $ak_{11}-(b/a)k_{22}$ vs. b from P(BT/TT) copolymers (c).

Table 1. Rate contants and reactivity ratios of polycondensation and copolycondensation of BHBT and BHPT from $^1$H-NMR data

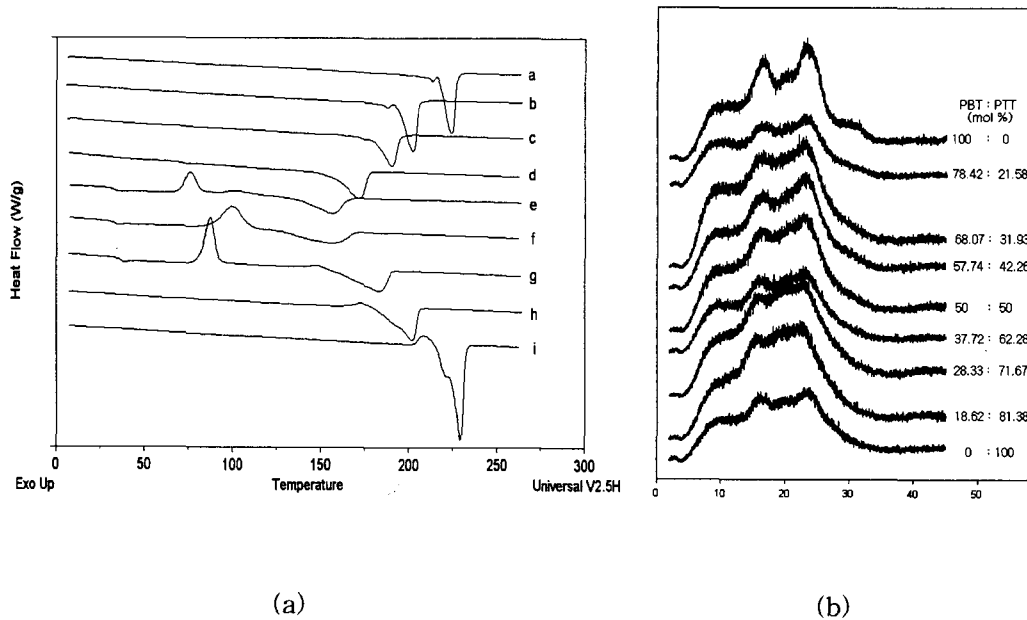| $k_{11}$ | $k_{12}$ | $k_{21}$ | $k_{22}$ | $r_1$ | $r_2$ |
|----------|----------|----------|----------|-------|-------|
| 4.183 | 3.345 | 4.475 | 4.075 | 1.25 | 0.91 |



Figure 2. Calorimetric curves (a) and X-ray diffraction patterns (b) of PBT, PTT, and copolymers (a: 100/0 (PBT/PTT mol %), b: 78.42/21.58, c: 68.07/31.93, d:57.74/42.26, e: 50/50, f: 37.72/62.28, g: 28.33/71.67, h: 18.62/81.38, I: 0/100).