Isodimorphism in poly(butylene terephthalate-*co*-butylene-2,6-naphthalate) random copolymers

정영규, 조원호, 이상철*

서울대학교 섬유고분자공학과, *금오공과대학교 고분자공학과

Introduction

Random copolymers are widely used as materials since they afford a convenient possibility of adjusting properties through the compositions of the copolymers. In the case of semicrystalline polymers, the degree of crystallinity generally decreases as the content of the minor component increases, leading often to fully amorphous materials even at low concentrations of the comonomer. Only a few systems have been found where some crystallinity can be observed over the entire range of composition. The cocrystallization phenomena are divided into three classes: isomorphism, isodimorphism, and isopolymorphism. When the A and B comonomers have much structural similarity and the excess free energy of cocrystallization is very small, only one type of crystalline lattice is formed. This is the case of isomorphism in a strict sense. Such isomorphic melting behavior has been reported for a few copolymer systems.[1,2] On the other hand, a cocrystallization in either the crystal structure of the one or the other comonomer is observed. These copolymer systems have a statistically random distribution of comonomer units and approximately the same degree of crystallinity, while exhibiting a minimum (eutectic point) in their melting point vs. composition curve. This phenomenon is called isodimorphism, i.e., inclusion of B units in the A crystalline lattice and of A units in the B lattice. The existence of varied crystal structures as a results of cocrystallization of two comonomers was termed isopolymorphism, in analogy to the equilibrium effects of isomorphism and polymorphism.

Recently, there are some reports on the cocrystallization and the eutectic behavior for copolyesters.[3~5] In the present study, the isodimorphism and the cocrystallization behavior of poly(butylene terephthalate-*co*-butylene-2,6-naphthalate) [(P(BT-*co*-BN)] random copolymers are investigated using wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC).

Experimental

A series of P(BT-co-BN) random copolymers used in this study was synthesized from dimethyl terephthalate, dimethyl-2,6-naphthalate and 1,4-butanediol using titanium tetrabutoxide as a catalyst by molten state condensation. The samples were dissolved in the mixture of phenol/1,1,2,2-tetrachloroethane (6/4, v/v), and subsequently precipitated in excess acetone, It was then washed with acetone several times and dried in a vacuum oven at 40℃ for several days. The intrinsic viscosities of all samples in the mixture of phenol/1,1,2,2-tetrachloroethane (6/4, v/v) were measured on Ubbelohde viscometer at 35℃. ^{1}H-NMR spectra were measured on the P(BT-co-BN) copolymers to determine the real composition and sequence distribution. It reveals that the samples used in the study are almost statistically random. The P(BT-co-BN) copolymers were compression-molded into thin films in a hot press at 260℃ for 5min, and then quenched in liquid nitrogen. The thermal properties of copolymer samples were investigated with a Perkin-Elmer DSC 7 differential scanning calorimeter. All samples were first heated from -50℃ to 280℃ at a rate of 20℃/min, maintained at this temperature for 5min, and cooled to -50℃ at a rate of 10℃/min. All scans were performed in a nitrogen atmosphere to minimize the oxidative degradation. The quenched copolymer samples were annealed in annealing oven at the lower temperature than respective melting temperature by 40℃. For annealed samples, WAXD patterns were obtained on a diffractometer (MAC M18XHF[22] SRA) using Ni-filtered CuKα radiation at a scanning rate of 5 °/min.

Results and Discussion

Figure 1 shows the DSC heating curves for the quenched copolymer samples. For all compositions, single melting temperatures (T$_m$) are found during the heating process in DSC. Despiting being a statistically random copolymer, melting peak of P(BT-co-BN) copolymer containing 50wt% BN appears clear. The DSC cooling thermograms in Figure 2 also show crystallization peaks, which is the strong evidence for cocrystallization behavior. The melting temperatures and the crystallization temperatures (T$_c$) according to the composition are shown in Figure 3. The relationship between heat of fusion or heat of crystallization and copolymer composition in Figure 4 are also presented. As shown in Figures 3 and 4, this copolymer system exhibits typical eutectic behavior in the thermodynamic parameters such as melting temperature, crystallization temperature, heat of fusion and heat of crystallization, which suggests the occurrence of isodimorphism in the crystalline

phases of these copolymers. A minimum at the thermodynamic parameters vs. composition curve is a conversion point where the lattice transition occurs. The cocrystallization behavior and the lattice transition in WAXD patterns of the P(BT-co-BN) copolymers are also observed in Figure 5. It should be noted that the P(BT-co-BN) copolymer containing 50wt% BN, which is close to the eutectic composition, displays transition between PBT and PBN crystal lattices.

References

1. (a) A. J. Yu and R. D. Evans, *J. Am. Chem. Soc.*, **81**, 5361 (1959). (b) A. J. Yu and R. D. Evans, *J. Polym. Sci.*, **42**, 249 (1960).
2. R. W. Campbell and H. Wayne Hill, Jr., *Macromolecules*, **8**, 238 (1975).
3. H. Y. Yoo, S. Umenoto, T. Kikutani and N. Okui, *Polymer*, **35**, 117 (1994).
4. X. Lu and A. H. Windle, *Polymer*, **36**, 451 (1995).
5. (a) M. Scandola, G. Ceccorulli, M. Pizzoli and M. Gazzano, *Macromolecules*, **25**, 1405 (1992). (b) N. Yoshie, M. Sakurai, Y. Inoue and R. Chujo, *Macromolecules*, **25**, 2046 (1992)
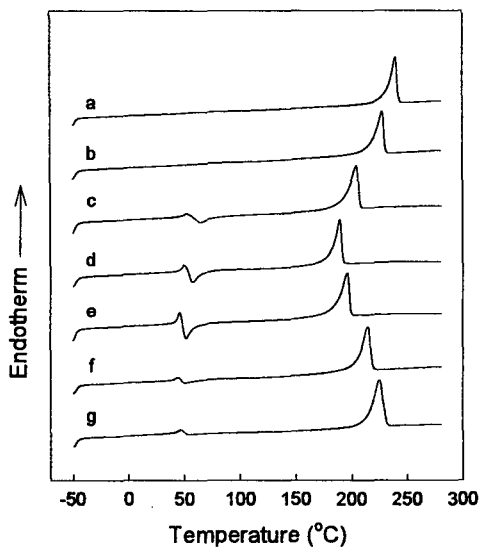
Figure 1. DSC heating curves for the copolymers :
(a) PBN; (b) P(BT-*co*-BN) 1/9; (c) P(BT-*co*-BN) 3/7;
(d) P(BT-*co*-BN) 5/5; (e) P(BT-*co*-BN) 7/3;
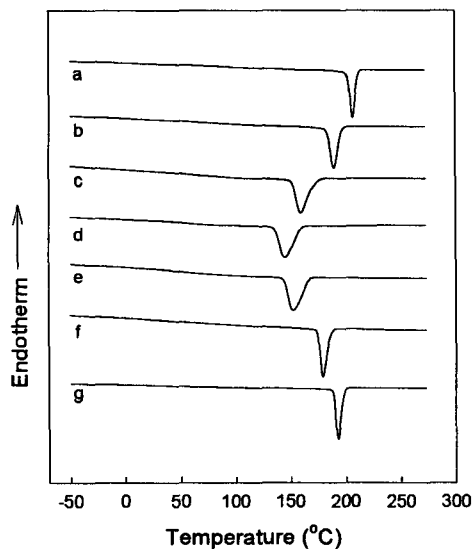(f) P(BT-*co*-BN) 9/1; (g) PBT.

Figure 2. DSC cooling curves for the copolymers :
(a) PBN; (B) P(BT-*co*-BN) 1/9; (c) P(BT-*co*-BN) 3/7;
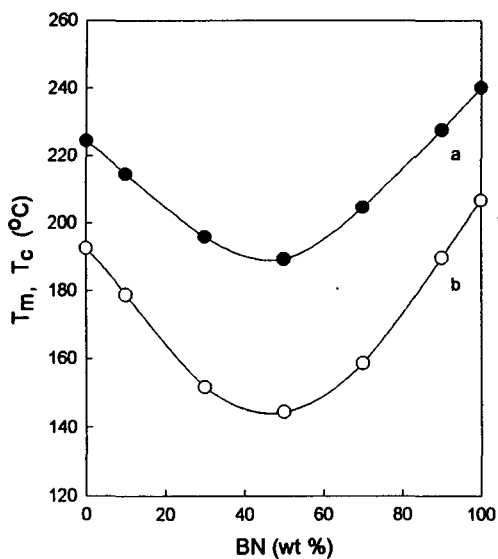(d) P(BT-*co*-BN) 5/5; (e) P(BT-*co*-BN) 7/3;
(f) P(BT-*co*-BN) 9/1; (g) PBT.

Figure 3. Melting temperature (a) and crystallization temperature (b) versus compostion curves for P(BT-*co*-BN) copolymers.
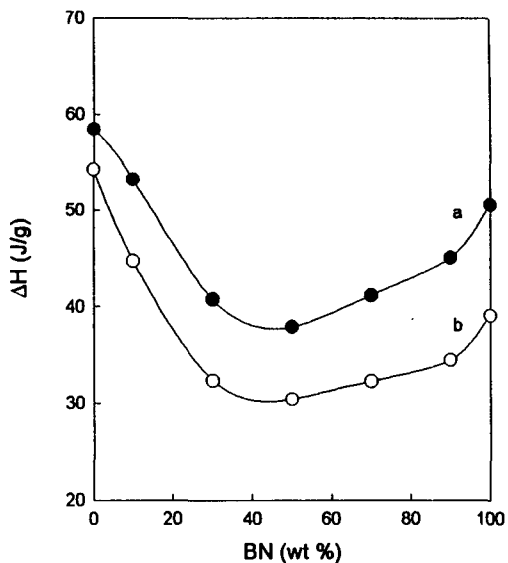
Figure 4. Heat of fusion (a) and heat of crystallization (b) versus composition curves for P(BT-*co*-BN) copolymers.
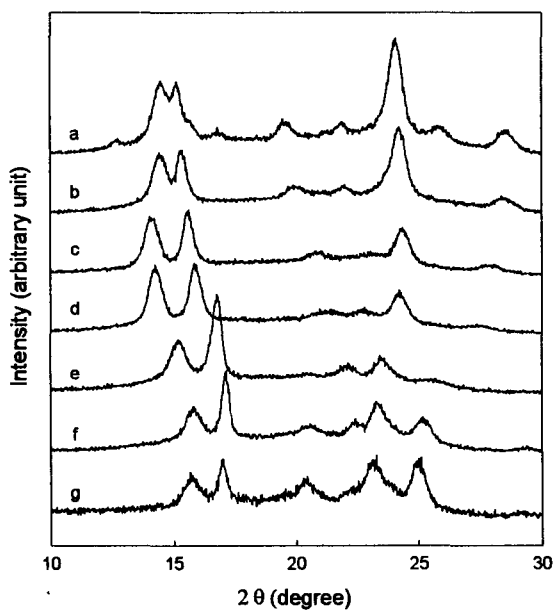
Figure 5. X-ray diffraction patterns for the copolymers : (a) PBN; (b) P(BT-*co*-BN) 1/9; (c) P(BT-*co*-BN) 3/7; (d) P(BT-*co*-BN) 5/5; (e) P(BT-*co*-BN) 7/3; (f) P(BT-*co*-BN) 9/1; (10) PBT.