

Poly(*m*-methylene 2,6-naphthalate-co-1,4-cyclohexanedimethylene 2,6-naphthalate) 공중합체의 공결정화 거동

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Cocrystallization Behavior of Poly(*m*-methylene 2,6-naphthalate-co-1,4-cyclohexanedimethylene 2,6-naphthalate) Random Copolymers

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1. Introduction

Since the family of poly(*m*-methylene 2,6-naphthalate) (P*m*N) with the chemical structure as shown in Figure 1(a) was first reported in 1969, the polymers belonging to this family have attracted considerable interests in the commercial and academic points of view due to realization of large-quantity production of 2,6-naphthalenedicarboxylic acid. The commercially available polymers among this family are poly(ethylene 2,6-naphthalate) (PEN, *m*=2) and poly(butylene 2,6-naphthalate) (PBN, *m*=4). The crystal structures, thermal properties, and mechanical properties of PEN and PBN have been intensively studied. Recently, the crystal structures of poly(hexamethylene 2,6-naphthalate) (PHN, *m*=6) were firstly identified by ours. On the other hand, we have reported the crystal structure and thermal property of poly(1,4-cyclohexanedimethylene 2,6-naphthalate) (PCN, Figure 1(b)) which has cyclic aliphatic group instead of linear *m*-methyl one in its backbone. It was characterized that PCN has a high melting point, rapid crystallization rate, and brittle properties. When CN unit was copolymerized with EN, BN and HN units for the purpose to modify thermal and mechanical properties of PCN, it was observed that melting and crystallization peaks in DSC thermogram and X-ray diffraction patterns were obviously observed for all copolymer compositions in the cases of P(BN-co-CN) and P(HN-co-CN) copolymers, which provides a strong evidence for cocrystallization. However, such

evidences were not observed in the case of P(EN-co-CN) copolymers. Cocrystallization behavior in random copolymers whose component homopolymers are both crystalline is a rare phenomenon. In the present study, a series of P(*m*N-co-CN) random copolymers (*m*=2, 4, and 6) were prepared and their cocrystallization behavior was systematically investigated using differential scanning calorimetry, wide angle X-ray diffraction and thermodynamic theory.

2. Experimental Section

All the samples used in this study were synthesized in our laboratory. Two-step polymerization was performed on a laboratory-scale polymerization reactor in the melt state. Monomers such as dimethyl-2,6-naphthalate, 1,4-cyclohexanedimethandiol, ethylene glycol, 1,4-butanediol, and 1,6-hexanediol were commercial grade and were used without further purification. It is known that 1,4-cyclohexanedimethandiol (a product of SK NJC Inc.) consists of a mixture of *trans/cis* (70/30) isomers.

The copolymer composition and the dyad sequence distribution of the copolymers were determined using $^1\text{H-NMR}$ spectroscopy operated at 500 MHz.

Melting and crystallization behavior of the samples were measured with a Perkin Elmer DSC-7 equipped with intercooler system. The heating and cooling rates were 20 °C/min. The amorphous films for DSC measurements were prepared by compression-molding on hot plate at 30°C higher than respective melting points followed by quenching into cooling water at 0°C.

The wide angle X-ray diffraction patterns of the samples melt-crystallized were obtained using a M18XHF diffractometer (MAC Science Co.) with Ni-filtered Cu-K α radiation at a scanning rate of 2°/min. The samples for WAXD were prepared in film forms by using a hot press at the temperature 20 °C higher than their respective melting temperature, cooled to the temperature 20 °C lower than their apparent melting temperatures, and then annealed for an hour.

3. Results & Discussion

Figures 2(A) and (B) show the heating thermograms for the melt-quenched P(EN-co-CN) films and the WAXD patterns of the melt-crystallized ones, respectively. Melting and crystallization peaks in DSC thermogram and diffraction patterns are not observed in the middle of copolymer composition. This means that P(EN-co-CN) copolymer is not able to cocrystallize. In the case of P(BN-co-CN) and P(HN-co-CN) copolymers, a clear melting and crystallization peak in DSC thermogram and distinct X-ray diffraction pattern are observed for

all copolymer compositions, indicating that both copolymer systems do cocrystallize. As can be seen in Figures 3 and 4, there is a minimum of the melting temperature at middle range of copolymer composition, and the diffraction patterns are divided into two groups, PBN- and PCN-types for P(BN-*co*-CN) and PHN- and PCN-types for P(HN-*co*-CN), respectively. These results support the isodimorphic cocrystallization of P(BN-*co*-CN) and P(HN-*co*-CN) copolymer systems. The reason why BN or HN units except EN are cocrystallized with CN units is that the repeating lengths and volumes of BN and HN units in the crystal lattice are comparable to those of CN unit.

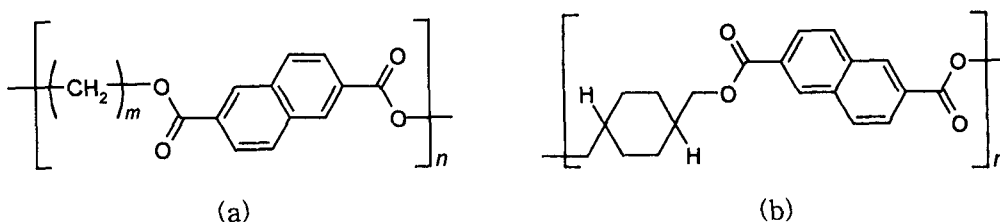


Figure 1. Chemical structures of (a) poly(*m*-methylene 2,6-naphthalate) and (b) poly(1,4-cyclohexanedimethylene 2,6-naphthalate).

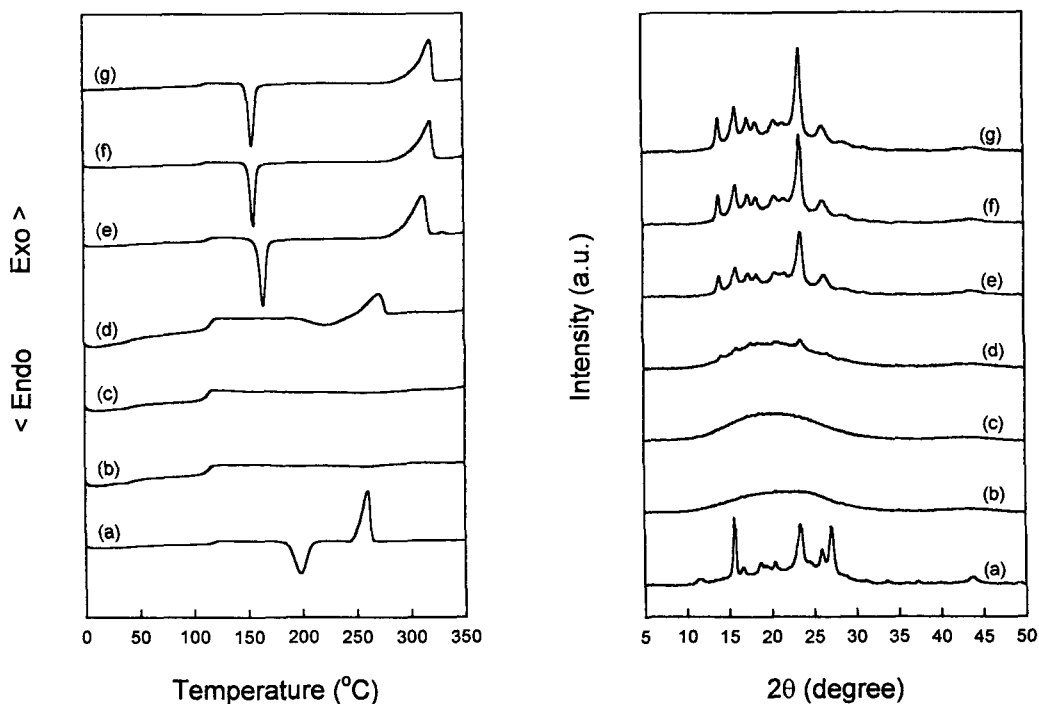


Figure 3. Heating thermograms (A) and WAXD patterns (B) of P(EN-*co*-CN).

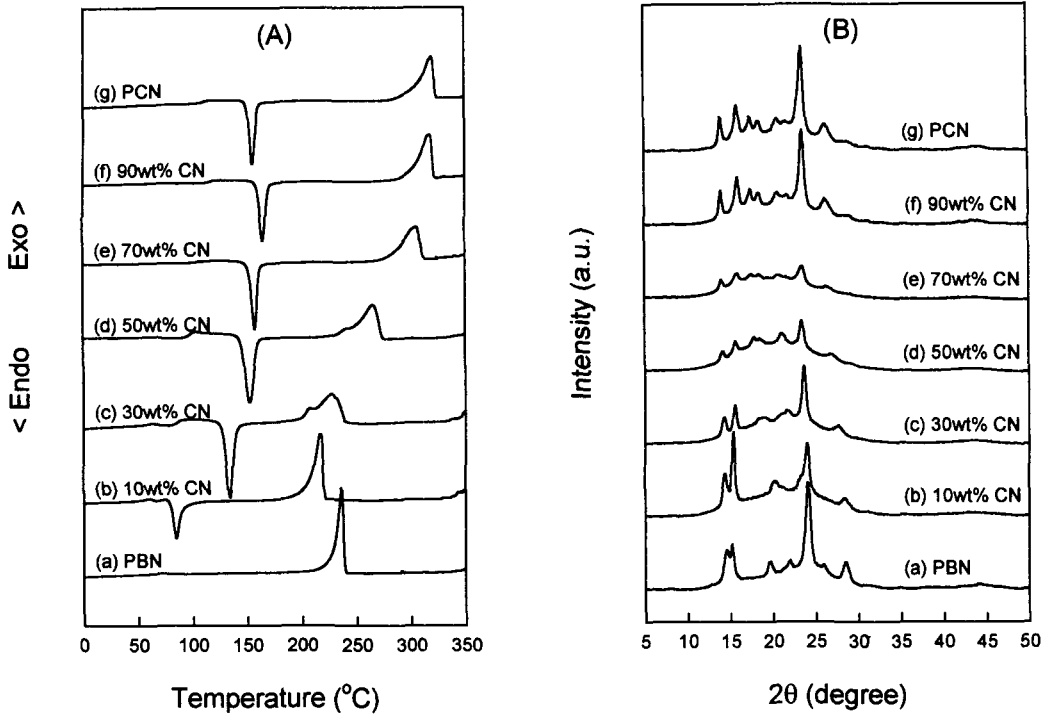


Figure 3. Heating thermograms (A) and WAXD patterns (B) of P(BN-co-CN).

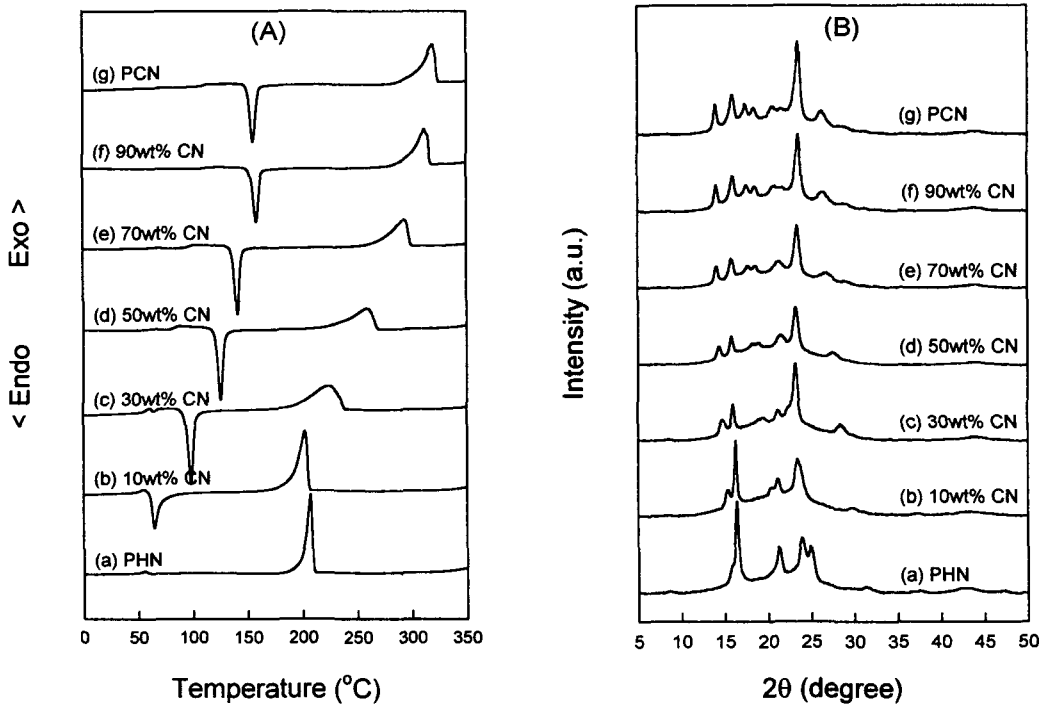


Figure 4. Heating thermograms (A) and WAXD patterns (B) of P(HN-co-CN).