Cocrystallization of Poly(1,4-cyclohexylenedimethylene terephthalate-*co*-hexamethylene terephthalate) Copolymers

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Abstract: We have synthesized poly(1,4-cyclohexylenedimethylene terephthalate-*co*-hexamethylene terephthalate) [P(CT-*co*-HT)] random copolymers having various comonomer contents, from 0 to 100 mol% HT, by melt-condensation and have investigated their crystallization behavior by using differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). We observed that P(CT-*co*-HT)s exhibit clear melting and crystallization peaks in their DSC thermograms and sharp diffraction peaks in their WAXD patterns for all of their copolymer compositions as a result of cocrystallization of the CT and HT units, even though the copolymers are statistically random copolymers. When we plotted the melting and crystallization temperatures of P(CT-*co*-HT)s and the *d*-spacings of all the reflections against the copolymer composition, we observed a eutectic point at ca. 80 mol% HT, which suggests that a crystal transition occured from a PCT-type crystal to a PHT-type crystal. Both the DSC and WAXD results support the notion that P(CT-*co*-HT) copolymers undergo an isodimorphic cocrystallization.

Keywords: poly(1,4-cyclohexylenedimethylene terephthalate-*co*-hexamethylene terephthalate), isodimorphic cocrystallization, eutectic melting point, crystal transition.

Introduction

Poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) has been commercially produced and widely used for fiber, film, a component of dental composites, etc.[1-3] Owing to incorporation of 1,4-cyclohexylenedimethyl group instead of linear alkylene groups in poly(alkylene terephthalate), PCT has high melting temperatures of 251~318 °C, depending on the *trans/cis* isomer ratio of 1,4-cyclohexylenedimethyl units.[2] It is interesting that, despite its high melting temperature, PCT exhibits ductile mechanical property as compared to poly(ethylene terephthalate).[4-6] It has recently been demonstrated by Yee *et al.*[4,5] that the ductile mechanical property of PCT originates from the cooperative secondary relaxation due to the conformation transition of cyclohexylene rings from chair, twisted boat to chair. However, the poor thermal stability above the melting temperature of PCT often makes it difficult to process in the melt for practical applications. Consequently, the synthesis of PCT-based

copolymers or reactive blending with other polyesters have been studied to improve their processability as well as thermal and mechanical properties through variation of the copolymer composition.[7-11]

It is well-known that, in most copolyesters where both *A* and *B* components are crystallizable, the degree of crystallinity decreases with increasing the composition of minor component, and as a result the copolymers often become totally amorphous even at low comonomer content. If two crystallizable components of the copolymers are compatible in their crystal lattices (i.e., cocrystallization), thermal and mechanical properties of the copolymers can be controlled without significant loss of crystalline properties.[10-15] Yoo *et al.*[9] reported that poly(1,4-cyclohexylenedimethylene terephthalate-*co*-ethylene terephthalate) copolymers, in which ethylene terephthalate (ET) units can crystallize with complete rejection of 1,4-cyclohexyleneterephthalate (CT) units from the crystal whereas CT units can cocrystallize with ET units to some extent, exhibits cocrystallization. However, copolymers with the middle range of comonomer content are completely amorphous. It has been recently reported that poly(1,4-cyclohexylenedimethylene terephtha-

late-*co*-butylene terephthalate) copolymers can cocrystallize over all the copolymer compositions.[10,11]

Since the repeat length of hexamethylene unit in poly (hexamethylene terephthalate) (PHT) matches well with that of the cyclohexylenedimethyl unit in PCT, it is likely expected that poly(1,4-cyclohexylenedimethylene terephthalate-*co*-hexamethylene terephthalate) (P(CT-*co*-HT)) copolymers may exhibit cocrystallization. In this study, therefore, we synthesized P(CT-*co*-HT) with various copolymer compositions from 0 to 100 mol% HT, characterized their chain structure using ^{1}H NMR spectroscopy, and investigated their thermal property and cocrystallization behavior by using differential scanning calorimetry and wide-angle X-ray diffraction.

Experimental

Synthesis and Characterization of Materials. PCT, PHT, and P(CT-*co*-HT)s with various copolymer compositions were synthesized from 1,4-cyclohexanedimethanol (CHDM), 1,6-hexanediol (HD), and dimethyl terephthalate (DMT) using titanium isopropoxide catalyst *via* melt-condensation. Commercially available CHDM monomer, a mixture of *trans/cis* (70/30) isomers, was used without further purification. The relative isomer composition of *trans/cis*-CHDM was identified by a gas chromatograph with mass selective detector. Two-step reaction was carried out on a laboratory-scale polymerisation reactor. The first-step reaction was the transesterification of CHDM and/or HD with DMT at 170~280°C under nitrogen atmosphere, and the second-step was the polycondensation reaction at 260~320°C under high vacuum condition. Finally, the product in the melt was quenched into cold water and then dried in a vacuum oven for several days.

^{1}H NMR spectroscopy was used for characterizing the chain structure of copolymer such as the copolymer composition, the number-average sequence length, and the degree of randomness. ^{1}H NMR spectra of the samples in $CDCl_3$/ CF_3COOD (5/5, v/v) solution with tetramethylsilane (TMS) internal standard were recorded on a Bruker AMX500 FT-NMR spectrometer operating at 500 MHz. The inherent viscosities of the samples were measured in a mixed solvent of phenol and 1,1,2,2-tetrachloroethane (6/4, v/v) using an Ubbelohde viscometer at 35°C.

Differential Scanning Calorimetry (DSC). A Perkin-Elmer DSC-7 equipped with an intercooler was used to study the crystallization and melting behavior. Temperature and heat flow of the instrument were calibrated with high-purity indium. DSC measurement was carried out under nitrogen atmosphere at a heating and cooling rate of 20 and 10°C/min, respectively. Melt-quenched samples were prepared by heating the samples to the temperature 30°C higher than their respective melting temperature, holding for 3 min, quenching into cold water, and then drying for several

days under vacuum at 25°C. The peak temperature of melting and crystallization of the sample was taken as the apparent melting and crystallization temperature, respectively, and the inflection point of glass transition was determined as the glass transition temperature. In order to determine the equilibrium melting temperatures (T_m^o) of the samples, isothermal crystallization was carried out on DSC at various crystallization temperatures (T_c). The samples were heated to the temperature 30°C higher than their respective apparent melting temperature, held for 3 min in order to completely melt the crystal, rapidly cooled to the predetermined crystallization temperature (T_c) at a rate of 200°C/min, and then crystallized isothermally for 1-3 hrs. The melting temperatures (T_m) of isothermally crystallized samples were determined from the following heating thermogram. The T_m^o's for all the samples were determined from the Hoffman-Weeks plot.[16]

Wide-Angle X-ray Diffraction (WAXD). The WAXD experiments were performed on melt-crystallized films. All samples were compression-molded into 0.4 mm thick film on a hot press at the temperature 30°C higher than the apparent melting temperature of the respective sample, rapidly transferred on another hot press controlled at the temperature 30°C lower than their respective melting temperature, and then isothermally crystallized for several hours. The X-ray diffraction patterns were obtained using a diffractometer (Philips Analytical PW3040 X'Pert) with Cu-$K\alpha$ radiation at room temperature. The instrument was operated at 45 KV and 40 mA and calibrated with a standard silicon sample. The samples were scanned in the 2θ range of 5~40° at the step scan mode. The step width was 0.02° and the count time for each step was equal to 2 sec/step.

Results and Discussion

Chain Structure of Copolymers. Structural information of copolymers such as the copolymer composition, the number-average sequence length, and the degree of randomness was obtained from ^{1}H NMR spectra. Figure 1 shows a ^{1}H NMR spectrum of P(CT-*co*-HT) copolymer with 44 mol% HT with peak assignment. The copolymer composition was easily calculated using the relative area of oxymethylene resonances (*b* and *c* corresponding to hydrogens of hexamethylene and cyclohexylenedimethylene uints, respectively), as listed in Table I. When the copolymer composition estimated from ^{1}H NMR was compared with the feed composition, the HT comonomer contents in all copolymers were slightly smaller than those of the feed composition. This is probably because HD is more volatile than CHDM during polycondensation performed under high vacuum condition.[14] On the other hand, depending on the alkylene unit (hexamethylene or cyclohexylenedimethylene unit) next to terephthalate unit of copolymer backbone, the hydrogen atoms in phenyl ring are separated into three peaks due to magnetically different
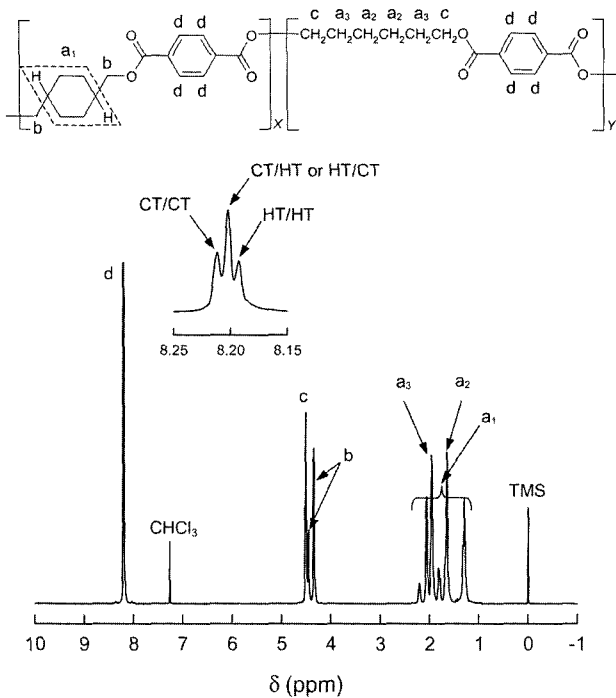
$$L_{CT} = \frac{2A_{CT/CT} + A_{HT/CT}}{A_{HT/CT}}$$

$$L_{HT} = \frac{2A_{HT/HT} + A_{CT/HT}}{A_{CT/HT}} \tag{1}$$

Figure 1. ^{1}H NMR spectrum of P(CT-co-HT) copolymer with 44 mol% HT and its peak assignment.

environment, i.e., CT/CT, CT/HT (or HT/CT) and HT/HT dyads, as can be seen in the expanded ^{1}H NMR spectrum of Figure 1. Therefore, the resonances between 8.15 and 8.25 ppm in NMR spectra were used to determine the number-average sequence length and the degree of randomness of P(CT-co-HT) copolymer. The relative concentrations of the dyads were determined using the areas of three deconvoluted peaks ($A_{CT/CT}$, $A_{CT/HT}$, and $A_{HT/HT}$), from which the number-average sequence lengths of CT and HT (L_{CT} and L_{HT}) were calculated using the following relation:[14,17]

The number-average sequence lengths are listed in Table I. Based on the sequence length, the degree of randomness, DR, of copolymer is defined as[14,17]

$$DR = 1/L_{CT} + 1/L_{HT} \tag{2}$$

By definition, $DR = 0$ is for a homopolymer mixture or for a pure block copolymer, $DR = 1$ for a random copolymer, indicating that the distribution of comonomer units obeys the Bernoullian statistics, and $DR = 2$ for an alternating copolymer, e.g., a chain consisting of only CT/HT dyads. Since the DR values of all P(CT-co-HT) copolymers are very close to unity, as can be seen in Table I, all copolymers synthesized in this study are statistically random copolymers. The inherent viscosities of all the samples are in the range of 0.60~0.79 dL/g, as listed in Table I, indicating that all the samples synthesized have high molecular weight enough to form in film.

Cocrystallization Behavior. Figure 2 shows the heating and cooling thermograms of the melt-quenched samples. It was found that all P(CT-co-HT) copolymers exhibit clear melting (T_m) and cold-crystallization (T_{cc}) peaks on heating scans as well as melt-crystallization peaks (T_{mc}) on cooling scans. This indicates that P(CT-co-HT) copolymers show cocrystallization behavior over the entire copolymer composition. When the melting and crystallization temperatures (T_m and T_{mc}) are plotted against composition, it reveals that a eutectic point is observed around 80 mol% HT, as shown in Figure 3. This suggests that the crystal transition between PCT and PHT occurs around 80 mol% HT. Cocrystallization is classified largely into two classes: isomorphic and isodi-

Table I. Composition, Sequence Lengths, Degree of Randomness, and Inherent Viscosity of P(CT-co-HT) Copolymers

| Sample Code	Feed Composition (HT, mol%)	Composition by ^{1}H NMR (HT, mol%)	L_{CT}	L_{HT}	Degree of Randomness (DR)	Inherent Viscosity (dL/g)
PCT	0.0	0.0				0.60
P(CT-co-8 HT)	10.0	7.5	11.48	1.28	0.89	0.62
P(CT-co-16 HT)	20.0	16.2	5.73	1.30	0.95	0.65
P(CT-co-29 HT)	35.0	29.2	3.16	1.53	0.97	0.64
P(CT-co-44 HT)	50.0	43.5	2.17	1.91	0.99	0.70
P(CT-co-59 HT)	65.0	59.2	1.68	2.52	0.99	0.75
P(CT-co-70 HT)	75.0	69.8	1.46	3.35	0.98	0.79
P(CT-co-87 HT)	90.0	87.4	1.24	7.91	0.93	0.76
PHT	100.0	100.0				0.72
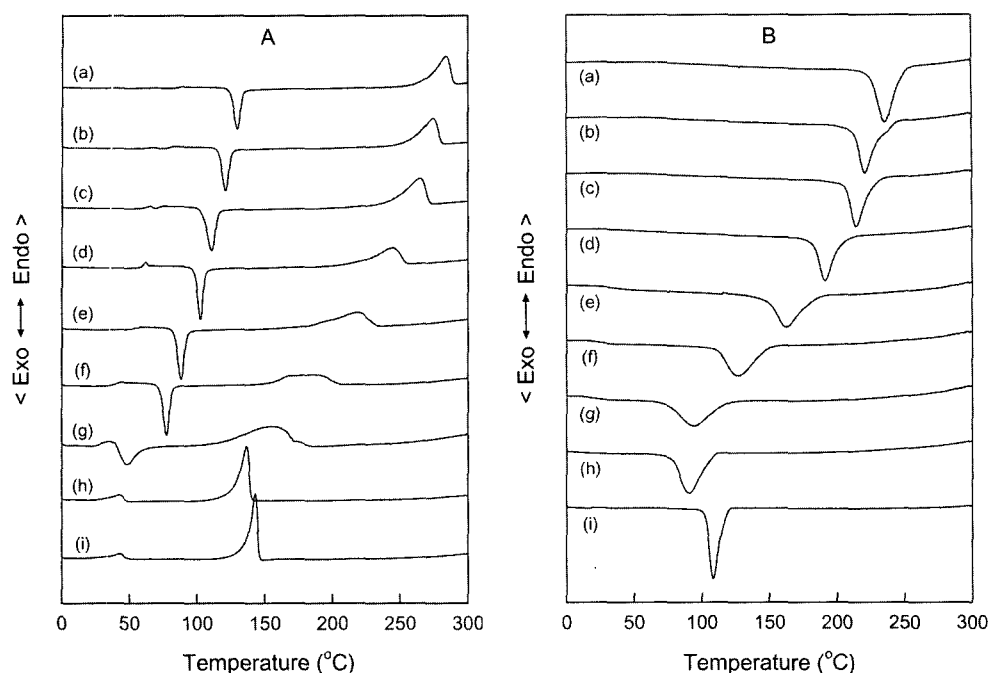
Figure 2. DSC heating (A) and cooling (B) thermograms of the melt-quenched samples: (a) PCT; (b) P(CT-*co*-8 HT); (c) P(CT-*co*-16 HT); (d) P(CT-*co*-29 HT); (e) P(CT-*co*-44 HT); (f) P(CT-*co*-59 HT); (g) P(CT-*co*-70 HT); (h) P(CT-*co*-87 HT); (i) PHT.
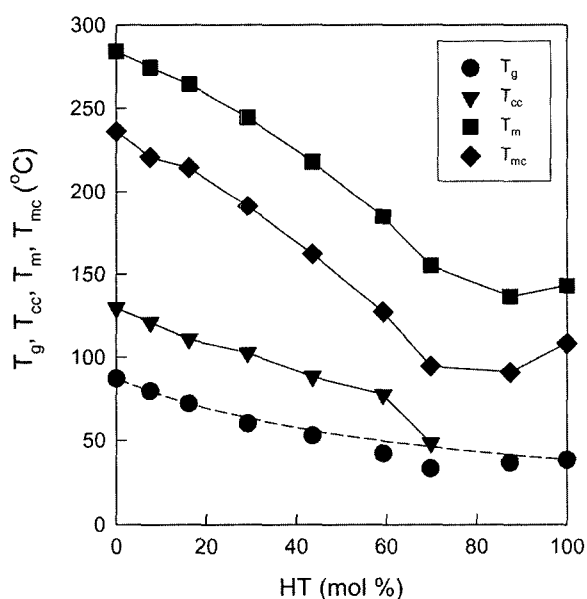

Figure 3. Copolymer composition dependence of glass transition (T_g), cold-crystallization (T_{cc}), melting (T_m), and melt-crystallization temperatures (T_{mc}) of PCT, PHT, and P(CT-*co*-HT) copolymers. The dashed line is based on the Fox equation for glass transition temperatures of P(CT-*co*-HT) copolymers.

morphic cocrystallization, depending on the existence of a eutectic point at which the crystal structure changes from *A*-type to *B*-type.[9,12-15] Therefore, the existence of a eutectic point for P(CT-*co*-HT) copolymers indicates that the copoly-

mers exhibit isodimorphic cocrystallization.

Several theories have been proposed for melting point depression of copolymers, and are classified largely into two types, i.e., the comonomer exclusion model[18-20] and the comonomer inclusion model.[21-23] In this study, a new model proposed by Wendling and Suter,[23] which combines the Sanchez-Eby model (a comonomer inclusion model) with the Baur model (a comonomer exclusion model), was adopted to predict melting point depression of P(CT-*co*-HT) random copolymers. The Wendling-Suter equilibrium inclusion model is given by[23]

$$\frac{1}{T_m^o} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^o}[\ln(1-X_B+X_Be^{-\varepsilon/RT})-\langle\tilde{\xi}\rangle^{-1}] \qquad (3)$$

$$\langle\tilde{\xi}\rangle^{-1} = 2(X_B-X_Be^{-\varepsilon/RT})(1-X_B+X_Be^{-\varepsilon/RT}) \qquad (4)$$

where T_m^o and ΔH_m^o denote the equilibrium melting temperature and the heat of fusion of homopolymer, respectively, R the gas constant, X_B the bulk composition of B units in the copolymer, X_{CB} the concentration of comonomer B units in the cocrystal, ε the average defect Gibbs free energy, and $\langle\tilde{\xi}\rangle$ the average length of the crystallizable copolymer sequences. When the melting temperatures predicted by the equilibrium inclusion model of eq. (3) are compared with equilibrium melting temperatures of PCT, PHT and P(CT-*co*-HT) determined experimentally, the ε value is used as an adjustable parameter, as shown in Figure 4. In such fitting works, the values of 27.75 kJ/mol[9] and 41 kJ/mol[24] are used
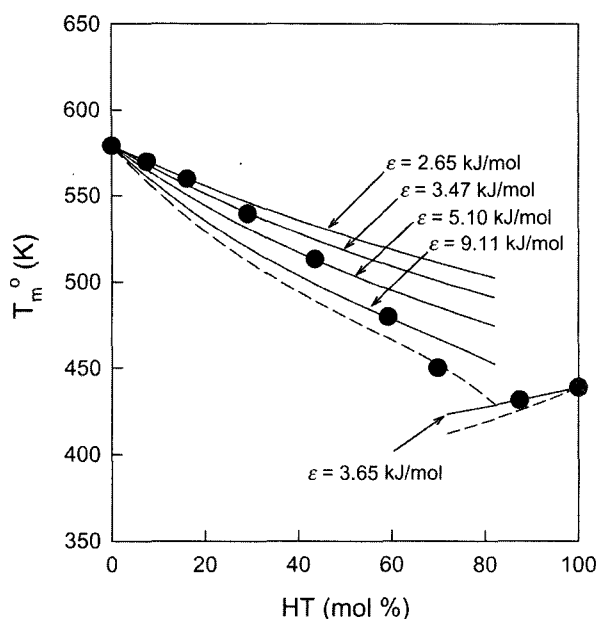
Figure 4. Comparison of the equilibrium melting temperatures (solid circles) of PCT, PHT, and P(CT-*co*-HT) copolymers with the theoretical melting temperature curves predicted by the Baur (dashed lines) and Wendling-Suter (solid lines) models.

for the ΔH_m^o s of PCT and PHT crystals, respectively, and the T_m^o s of PCT and PCN are, respectively, 579 and 439 K, which are determined by the Hoffman-Weeks plots. As a result, it was found that, when the HT comonomer units are incorporated into PCT crystals, the defect free energy (ε) increases from 2.65 to 9.11 kJ/mol with increasing the HT comonomer content from 7.5 to 59 mol%. This indicates that the inclusion of the HT comonomer units into PCT crystals becomes difficult with increasing the HT comonomer con-

tent. This result is unusual compared to the previous reports for isodimorphic cocrystallization of other copolymers, in which the defect free energy is constant regardless of the comonomer content or decreases with increasing the comonomer content.[12-15,21] The reason for this unusual behavior is not clearly understood. However, one possible explanation is as follows: Considering that the equilibrium melting point of PCT (579 K) is much higher than that of PHT (439 K), we may conjecture that the interaction energy between CT units in PCT crystal is much lower (negatively larger) than the energy between HT units in PHT crystal. In other words, the PCT crystal is thermodynamically more stable than the PHT crystal. When a larger amount of HT units is incorporated into the PCT crystal, the probability to find the HT-HT contacts in the PCT crystal becomes greater. As a result, the defect free energy in the crystal becomes larger than expected, as the HT content in PCT crystal increases.

When the glass transition temperatures (T_g) of P(CT-*co*-HT) random copolymers are plotted against the HT comonomer content and compared with the ones predicted by the Fox equation (the dashed line), as shown in Figure 3, the glass transition temperature of P(CT-*co*-HT) copolymers decreases with increasing the HT comonomer content due to flexible HT units, and the glass transition temperatures predicted by the Fox equation agree well with the experimental ones within an experimental error.

In order to investigate the change of crystalline structures of the copolymers due to cocrystallization, we obtained the WAXD patterns for PCT, PHT, and P(CT-*co*-HT)s melt-crystallized isothermally. Figure 5 shows that sharp diffraction peaks are observed over the entire copolymer composition. This also supports cocrystallization of P(CT-*co*-HT)s. It has been reported that PCT has a triclinic crystal structure[25,26] while PHT has three different crystal structures of α-, β-,

Table II. Crystallographic Data for PCT and PHT

		PCT[a]	PHT[b]		
			α-form	β-form	γ-form
Crystal System		Triclinic	Monoclinic	Triclinic	Triclinic
Unit Cell Parameters	a (nm)	0.646	0.91	0.48	0.53
	b (nm)	0.665	1.72	0.57	1.39
	c (nm)	1.422	1.55	1.57	1.55
	α (°)	89.45	127.3	104.4	123.6
	β (°)	47.03	90.0	116.0	129.6
	γ (°)	114.95	90.0	107.8	88.0
Repeating Unit(s)/Unit Cell		1	6	1	2
Unit Cell Density (g cm⁻³)		1.259	1.282	1.254	1.295
Unit Cell Volume (nm³)		0.362	1.930	0.329	0.637

[a]The crystallographic data are of poly(1,4-*trans*-cyclohexylenedimethylene terephthalate) from ref 26. [b]From ref 27.

and γ-forms,[27] as listed in Table II. According to Boye,[25] the unit cell of PCT with above 68% *trans*-CHDM isomer is nearly the same as that of poly(1,4-*trans*-cyclohexylene-dimethylene terephthalate) (P*t*CT). Hall and Ibrahim[27] reported that the PHT crystal has monoclinic α-form under stress, triclinic β-form under relaxed annealing at high temperature, and triclinic γ-form when crystallized from solution. Therefore, the diffraction peaks of PCT and PHT homopolymers in Figure 5 are assigned as P*t*CT and PHT β-form crystal lattices, respectively, since all the samples are melt-crystallized isothermally. Close examination of WAXD patterns in Figure 5 reveals that the patterns are separated into two types, i.e., PCT-type and PHT-type diffraction patterns. The PCT-type crystal is developed below 80 mol% HT, while the PHT-type crystal is developed above 80 mol% HT.

When the *d*-spacings of all the reflections are plotted against the HT comonomer content, it is observed that there is a discontinuity around 80 mol% of HT, as can be seen in Figure 6. This indicates that the transition of crystal lattice from PCT to PHT occurs at about 80 mol% HT. It is also noteworthy that the *d*-spacings of PCT-type crystals remain unchanged up to 60 mol% HT, whereas those of PHT-type crystals vary significantly even at small CT comonomer content. This is because the unit cell volume (0.362 nm³) of PCT is larger than that (0.329 nm³) of PHT β-form, as listed in
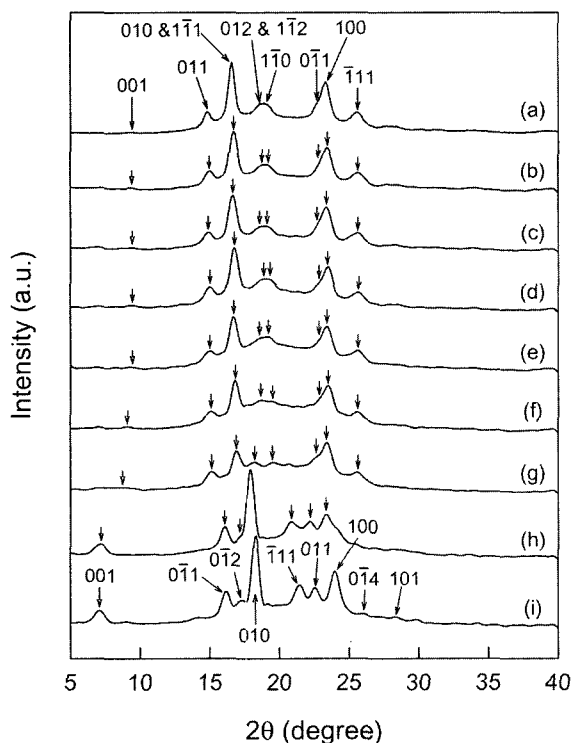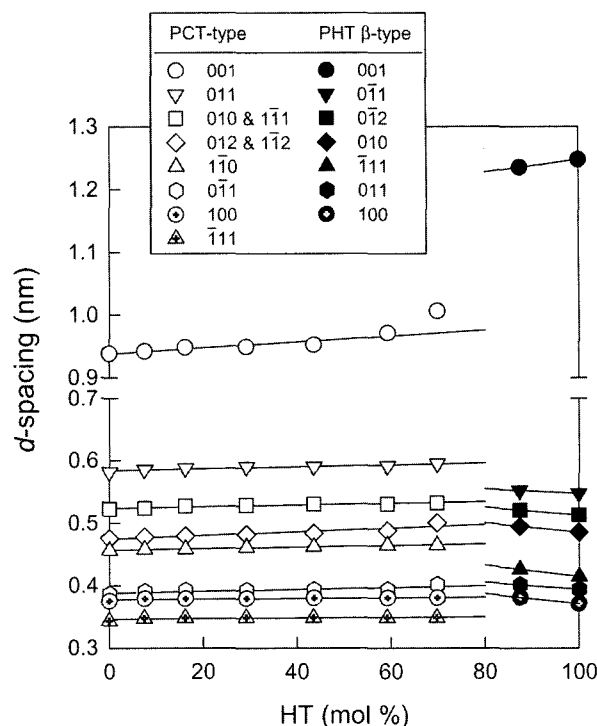

Figure 6. Changes of *d*-spacings for the melt-crystallized P(CT-*co*-HT) copolymers with copolymer composition.

Table II, although the unit cell densities (1.266 and 1.262 nm) and crystallographic repeat lengths (1.422 and 1.57 nm) of PCT and PHT β-form crystals are close to each other. In other words, the PCT crystal lattice accommodates easily HT comonomer units without significant distortion of its unit cell, while PHT β-form crystal lattice is distorted significantly even at small CT comonomer content due to the incorporation of CT units with larger volume into its lattice. This WAXD result also supports that the copolymers show an isodimorphic cocrystallization, which is consistent with the DSC result.

Conclusions

P(CT-*co*-HT) copolymers synthesized in our laboratory are statistically random copolymers. Nevertheless, they show clear melting and crystallization peaks in DSC thermograms and sharp diffraction peaks in WAXD patterns for all copolymer compositions. This indicates that P(CT-*co*-HT)s show cocrystallization. In addition, when the melting and crystallization temperatures of P(CT-*co*-HT)s as well as the *d*-spacings of all the reflections are plotted against the copolymer composition, it is observed that there exists a eutectic point at about 80 mol% HT, where the crystal transition from PCT to PHT occurs. Both DSC and WAXD results support that the copolymers exhibit isodimorphic cocrystallization.

Figure 5. WAXD patterns of the melt-crystallized samples: (a) PCT; (b) P(CT-*co*-8 HT); (c) P(CT-*co*-16 HT); (d) P(CT-*co*-29 HT); (e) P(CT-*co*-44 HT); (f) P(CT-*co*-59 HT); (g) P(CT-*co*-70 HT); (h) P(CT-*co*-87 HT); (i) PHT.

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