Regulation of Polymorphic Behavior of Poly(butylene adipate) upon Complexation with α-Cyclodextrin

Tungalag Dong, Weihua Kai, and Yoshio Inoue*

Department of Biomolecular Engineering, Tokyo Institute of Technology, Nagatsuta 4259-B-55, Midori-ku, Yokohama 226-8501, Japan

Received August 7, 2007; Revised Manuscript Received September 11, 2007

ABSTRACT: The effects of α-cyclodextrin (α-CD) on the crystallization of poly(butylenes adipate) (PBA) were studied in this work. Depending on the rate of cooling from the melting state, pure PBA shows a polymorphic crystallization behavior. That is, when the cooling rate is slow, PBA forms dominantly the α-form crystal and the peak crystallization temperature is above 33 °C. In contrast, when the cooling is rapid, it forms dominantly the β-form crystal and the peak crystallization temperature is below 33 °C. The crystallization behavior of PBA is almost not affected by the introduction of pure α-CD. However, the inclusion complex between PBA and α-CD (PBAIC) can effectively enhance the crystallization of PBA. By introduction of PBAIC, the crystallization rate of PBA is greatly accelerated and full α-form crystal of PBA is preferentially formed at temperature higher than 28 °C.

Introduction

Polymorphism is a well-known phenomenon found for a variety of crystalline polymers. Such polymers exhibit several polymorphs according to the crystallization conditions, mechanical stress, plastic deformation, and so on.[1] A precise knowledge of the physical properties of different polymorphic forms for a given polymeric material can be advantageously used for its possible applications.

Poly(butylene adipate) (PBA) is a biodegradable polymorphic material and it has two types of crystal forms, that is, α- and β-forms.[2] The α-form crystal is characterized as monoclinic unit cell with dimensions of $a = 6.73$ Å, $b = 7.94$ Å, $c = 14.20$ Å, and $\beta = 45.58°$, whereas in the β form, the PBA chains are packed in an orthorhombic unit cell with dimensions of $a = 5.06$ Å, $b = 7.35$ Å, and $c = 14.67$ Å. Of these two, the α-form crystal is thermodynamically favorable while the β-form crystal is kinetically favorable.[2] The β-form crystal can transform to α-form crystal by annealing at 52 °C, indicating that the α-form of PBA is a stable crystalline form. To keep the shape and function of the PBA products, the efficient formation of the α-form crystal in the products is necessary. The modulation of polymer crystallization by nucleating agents is a common method used to improve the physical properties of materials.

The cyclodextrins (CDs) comprise a family of cyclic oligosaccharides, and several members of this family are used industrially in pharmaceutical and related applications.[3] These biocompatible cyclic oligosaccharides do not elicit immune responses and have low toxicities in animals and humans. α-CD, β-CD, and γ-CD are typical CDs consisting of six, seven, and eight glucopyranose units linked by α-1,4-glycosidic bonds, respectively. Their shapes are like a hollow truncated cone without hydroxyl groups inside the cavity. Therefore, the hydrophobicity of their cavities gives them an ability to include a variety of guest molecules. The guest molecules encapsulated by CDs can change their physical, chemical, and biological properties. It has been found that CDs form water-insoluble crystalline host-gust inclusion complexes (ICs) with various biodegradable polymers, such as poly(ethylene glycol) (PEG),[4] PBA,[5] poly(ϵ-caprolactone) (PCL)[6] and so on.

Recently, Tonelli et al. found that coalescence of guest polymers from their ICs with CDs can result in a significant improvement of their physical properties caused by modification of the structures, morphologies, and even conformations that are observed for their coalesced bulk samples.[7] He et al. reported that the rates of nucleation and crystallization of poly(hydroxybutyric acid) were greatly enhanced by coalescence from its α-CD inclusion compound.[8] This acceleration was attributed to a small amount of α-CD molecules in complexed state remaining on the polymer chain, which increased the glass transition temperature of the polymer chains. In this study, we will investigate the formation of IC of PBA with α-CD (PBAIC) and the effects of α-CD on crystallization and polymorphic behavior of PBA. The IC of PBA with α-CD (PBAIC) is prepared by simply mixing PBA/acetone solution with α-CD powder. The α-CD molecules can undergo a transformation of solid-state crystalline structure from the cage to the channel structure. The formation of PBAIC will be characterized by the wide-angle X-ray diffraction (WAXD) and Fourier transform infrared spectrum (FTIR). The crystallization and polymorphic behavior of PBA containing pure α-CD and PBAIC will be investigated using the differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The PBAIC is expected to enhance the nucleation and crystallization of PBA and to induce the preferential formation of one of two crystalline forms.

Experimental Section

Materials. PBA ($M_n = 1.2 \times 10^4$, $M_w/M_n = 1.8$) was purchased from Kanto Kagaku Co., Ltd., Japan. Before use, PBA was purified by precipitation into ethanol from chloroform solution. α-CD was supplied by Nihon Shokuhin Kako Co., Ltd., Japan. Acetone and chloroform were purchased from Nacalai Tesque, Inc, Kyoto, Japan. Before use, α-CD was dried under the vacuum at 100 °C for 10 h.

Preparation of IC Samples. PBAICW and PBAICS. PBA (0.2 g) and α-CD (1.0 g) were dissolved in acetone (100 mL) and distilled water (10 mL), respectively. The α-CD aqueous solution was slowly added into the PBA solution under vigorous stirring at 60 °C for 3 h. Subsequently, the solution was cooled to 25 °C, and

---

* To whom correspondence should be addressed. Telephone: +81-45-924-5794. Fax: +81-45-924-5827. E-mail: inoue.y.af@m.titech.ac.jp

10.1021/ma071776o CCC: $37.00

continuously stirred for further 24 h. As-produced white powder was collected by filtration and then washed with acetone and water to remove the free PBA and uncomplexed α-CD, respectively. The product was coded as **PBAICW**. The **PBAICS** was prepared by the same method as the PBAICW, except for PBA/acetone concentration, that is, 2 g of PBA was dissolved in 60 mL of acetone. According to the ^{1}H NMR analyses, the molar ratios of the PBA monomeric repeating unit to α-CD molecule of PBAICW and PBAICS were estimated to be 1.0:1 and 2.4:1, respectively, indicating that the PBA chains were partially covered by α-CD molecules.

PBAICA. PBA (0.2 g) was dissolved in acetone (40 mL) and heated to 60 °C. The α-CD powder (1.0 g: the average particle size of α-CD powder is about 5 ± 3 μm) was simply added into the PBA solution under vigorously stirring at 60 °C for 3 h. Subsequently, the solution was cooled to 25 °C, and continuously stirred for further 24 h. As-produced white powder was collected by filtration and then washed with acetone and water to remove free PBA and uncomplexed α-CD, respectively. This sample was coded as **PBAICA**. On the basis of ^{1}H NMR analysis, the molar ratio of the PBA monomeric repeating unit to α-CD molecule of PBAICA was calculated to be 1.1:1.

PBA1.2 and PBA8.6. The samples coded as PBA1.2 and PBA8.6, where the numerals denote the weight percentages of remaining α-CDs in the samples calculated by the ^{1}H NMR, were prepared from the PBA/α-CD (95/5, wt/wt) and PBA/α-CD (90/10, wt/wt) blends, respectively, as shown in below. PBA and α-CD powders with an appropriate ratio were simply added into acetone (40 mL), and then the solution was stirred at 25 °C for 24 h. With the addition of excess amount of ethanol (200 mL) into the solution, the precipitation took place immediately. The precipitate was washed by excess water to remove the uncomplexed α-CD.

PBA/PBAICW and PBA/PBAICS Blends. The PBAICW and PBAICS samples were used as the nucleating agents for crystallization of PBA. Considering the effect of particle size of the nucleating agents on their abilities to nucleate crystallization of PBA, the particle sizes of nucleating agents were diminished through shattering the particles by ultrasonic treatment (BRANSON−B3200 water bath, at 47 kHz and 120 W) in the suspension with chloroform (for 5 min at 25 °C). The PBA/nucleating agent blends (99/1; wt/wt) were prepared by dispersing the nucleating agents into a concentrated chloroform solution of PBA (0.1 g/mL), and then the solvent was allowed to evaporate during rigorous stirring.

Then, the final products were dried under vacuum at 40 °C for 1 week.

Measurements. The host−guest stoichiometry (ST) of PBAICs was estimated by solution ^{1}H NMR spectra recorded on a JEOL GSX270 NMR spectrometer in DMSO-d_6. The chemical shifts were referenced to the DMSO residual proton resonance as $\delta = 2.5$ ppm from that of tetramethylsilane: δ 5.48−5.39 (m, O(2)H and O(3)H of α-CD), 4.81−4.75 (d, C(1)H of α-CD), 4.48 (t, O(6)H of α-CD), 3.99 (t, $-\mathrm{O}-\mathrm{CH_2}-$ of PBA), 3.81−3.52 (m, C(3)H, C(5)H and C(6)H of α-CD), 3.43−3.20 (m, C(2)H and C(4)H of α-CD), 2.28 (t, $-\mathrm{C}(=\mathrm{O})-\mathrm{CH_2}-$ of PBA), 1.63−1.55 (m, $-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_2}-$ of PBA), 1.55−1.469 (m, $-\mathrm{C}(=\mathrm{O})-\mathrm{CH_2}-\mathrm{CH_2}-$ of PBA). The molar ratios of the PBA repeat unit to α-CD molecules for PBAIC samples were calculated by comparing the integral of the peak of CH$_2$ (PBA) resonance at 3.99 ppm to that of C(1)H (α-CD) one at 4.81−4.75 ppm.

The wide-angle X-ray diffraction (WAXD) pattern of the sample was recorded on a RU-200 Rigaku Co. Japan using nickel-filtered Cu Kα radiation (40KV, 200 mA) with the 2θ values ranging from 10 to 35° at a scanning rate of 1°/min.

The Fourier transform infrared (FT-IR) spectrum was measured at 30 °C on a Spectra 2000 single-beam IR spectrometer (Perkin-Elmer Co. Japan). The PBA for FT-IR measurement were prepared by casting 1.5 wt % chloroform solution on the surface of a silicon wafer. The solvent was completely evaporated under vacuum. The samples of α-CD and PBAIC samples were pressed into KBr pellets, and the spectra were recorded at 30 °C with an accumulation of 16 scans.

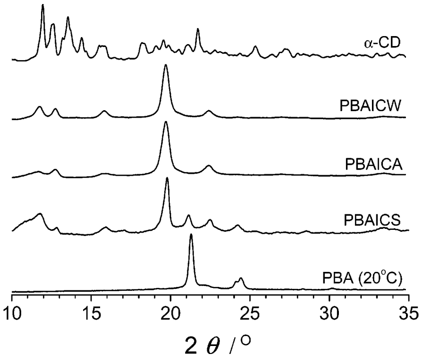

Figure 1. WAXD patterns of α-CD, PBA (crystallized at 20 °C) and their ICs.

The differential scanning calorimetry (Perkin-Elmer Pyris Diamond DSC) was employed to detect the thermal transitions and also to investigate the nonisothermal and isothermal crystallization behavior of the samples. In the nonisothermal crystallization experiment, the sample was first melted at 80 °C for 5 min, and then it was cooled to 0 °C at a desired cooling rate. Subsequently, it was kept at this temperature for 3 min, followed by heating to 80 °C at a rate of 10 °C/min. In the isothermal crystallization experiment, after melting at 80 °C for 5 min, the sample was quenched to the desired crystallization temperature and then kept at this temperature, and after isothermal crystallization for enough time, it was heated to 80 °C at a rate of 10 °C/min.

Polarized optical microscopic observation was performed on an Olympus BX90 polarizing optical microscopy (POM) equipped with a digital camera. The PBA sample was placed between a microscope glass slide and a coverslip and heated on a Mettler FP82HT hot stage. The samples (about 0.2 mg) were first heated to 80 °C and kept for 5 min and then quenched to 45 °C.

Results and Discussion

Formation of PBAICs. The formation of PBAIC has been reported by Harada et al.[5] According to their procedure, the PBA was put into a test tube with heating above the melting temperature, and then the saturated aqueous solution of α-CD was added. After the ultrasonically agitation and washing processes, the PBA complex was obtained. The preparation of PBAICW and PBAICS can be achieved by common method,[6] that is by mixing the α-CD and PBA solutions. The PBAICA could be prepared by suspending the α-CD powder in the PBA/acetone solution.

As shown in Figure 1, the WAXD patterns of PBAICW, PBAICA and PBAICS are quite different from those of pure PBA and α-CD, strongly suggesting the IC formation between α-CD and PBA. The PBA crystallized at 20 °C shows two prominent diffraction peaks at 21.3 and 24.5°, while two prominent peaks are present at ca. 20 and ca. 22.5° in the WAXD patterns of PBAICW, PBAICA and PBAICS, which are well-known to be the characteristics of α-CD-based IC crystals adopting the channel structure.[9] However, it is notable that the characteristic peaks of PBA were also observed in the WAXD patterns of PBAICS.

The FT-IR spectra of α-CD, PBA and PBAICs are shown in Figure 2. The peak wavenumber of the carbonyl band for the pure PBA is 1729.7 cm^{-1}, whereas it shifts to 1737.7, 1737.5, and 1734.7 cm^{-1} for PBAICW, PBAICA and PBAICS, respectively. The carbonyl band of PBA shifted from the lower wavenumber crystalline region[10] toward the higher wavenumber amorphous region.[5] The DSC thermograms of PBAICA and PBAICA do not show any detectable thermal transition in the heating scan. However, the small melting peaks with lower melting enthalpy are apparent in the DSC heating thermograms

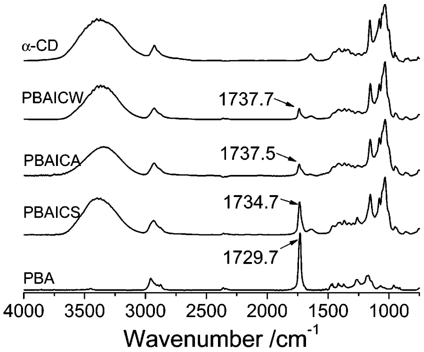

Figure 2. FT-IR spectra of α-CD, PBA and their ICs.

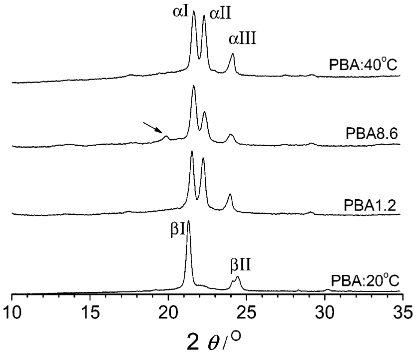

Figure 3. WAXD patterns of pure PBA crystallized from 80 °C at 20 and 40 °C, PBA8.6 and PBA1.2 samples.

of PBAICS. These results indicated that the crystallization of PBA is greatly restricted by complexation with α-CD.

These results also indicated that the PBA chain can penetrate into the α-CD cavities even in the solid state to give the α-CD complex. Similar results have been observed by Peet et al.[11] and Harada et al.,[12] independently. The α-CD spontaneously forms the IC upon mixing with neat liquid PEG and concurrently undergoes a solid-state crystalline phase transformation from the cage to the channel structure upon complexation. We also carried out the similar procedures to investigate the formation of IC between α-CD particles and other polymers (data not shown here). When PCL was used instead of PBA in acetone or in dioxane, the products with higher yield were obtained. However, when the α-CD particles were added into the PCL/chloroform solution, no detectable IC was found. In the PEG/chloroform solution, the PEG did not form the IC with α-CD yet. These results indicate that the solvents for polymers greatly affect the formation of ICs. Similar results have been previously reported by Tonelli et al., which indicated that the electrostatic, van der Waals, and hydrogen-bonding interactions and relief of conformational strain in CDs are not important, while hydrophobic interactions, exclusion of high energy, cavity-bound water, and crystalline packing of host CDs are important in the formation of ICs.[13] It is known that, although the penetration of a long polymer chain into host CD cavities should lead to a significant lowering of its conformational entropy, the water molecules that are released to the external environment during the threading process may largely compensate this entropic loss.[13] Since water is immiscible with chloroform, the release of water from α-CD cavities may be very slow, result in that the polymer chain cannot replace the water molecules. If the solvents, such as acetone and dioxane, are miscible with water, the polymer chains are more favorable for replacement with water molecules, leading the formation of ICs.

In Figure 3 are shown the WAXD patterns of the pure PBA films isothermally melt-crystallized at 40 and 20 °C. For the sample crystallized at 40 °C, three diffraction peaks appear. Two of them are strong, and the other one is relatively weak. These peaks correspond to the α-form crystal and are labeled αI, αII, and αIII, respectively.[14] When the crystallization temperature is decreased to 20 °C, the strong (βI) and weak (βII) diffraction peaks, corresponding to the β-form crystal,[14] appear at completely different positions from those observed for the sample crystallized at 40 °C. This indicates that the sample crystallized at 20 °C has a different crystalline structure from that crystallized at 40 °C. In Figure 3 are also shown the WAXD patterns of PBA8.6 and PBA1.2 films quenched from the melt and isothermally crystallized at 40 °C, which are very similar to that of the pure PBA crystallized at 40 °C, indicating that the α-form crystal is produced. Here, it is notable that the characteristic peak at ca. 20 °C is observed in the WAXD patterns of PBA8.6, indicating that the channel structure of α-CD existed in its complexed state. Because the amounts of α-CD are very small, the characteristic peaks for the channel structure cannot be detected in PBA1.2.

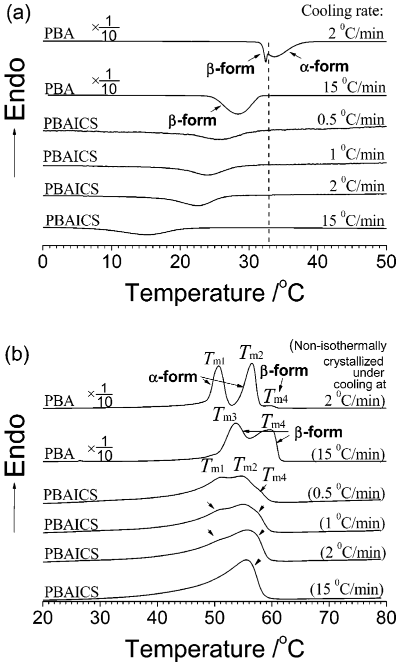

Figure 4. (a) Nonisothermal crystallization and (b) melting behavior of pure PBA and PBAICS, observed by cooling and heating scan DSC measurements.

Crystallization Behavior of Uncovered Segments of PBA in the PBAICS. Figure 4 shows the cooling and heating DSC thermograms of PBA and PBAICS. As shown in Figure 4a, when the cooling is slow, that is, cooling rate is −2 °C/min, pure PBA shows two-stages crystallization behavior. The peak crystallization temperatures of the first and second stage are 33.8 and 32.4 °C, respectively, and a point of intersection for two crystallization curves is about 33 °C. A subsequent heating scan at heating rate 10 °C/min is shown for PBA in Figure 4b. The relationship between melting peaks and WAXD patterns for pure PBA has been studied in the literature.[2,14] Here, three endothermic peaks appeared, resulted by the fusion of both the α- and β-form crystals. The melting peaks at T_{m1} and T_{m2} correspond to the fusion of the α-form crystals, whereas that at T_{m4} to the β-form crystals.[2,14] Thus, the two-stages crystallization found in the cooling DSC thermograms correspond to the α- and β-form crystallization at higher and lower temperature region, respectively. When the cooling rate is increased to 15 °C/min, the whole crystallization peak shifts to the lower

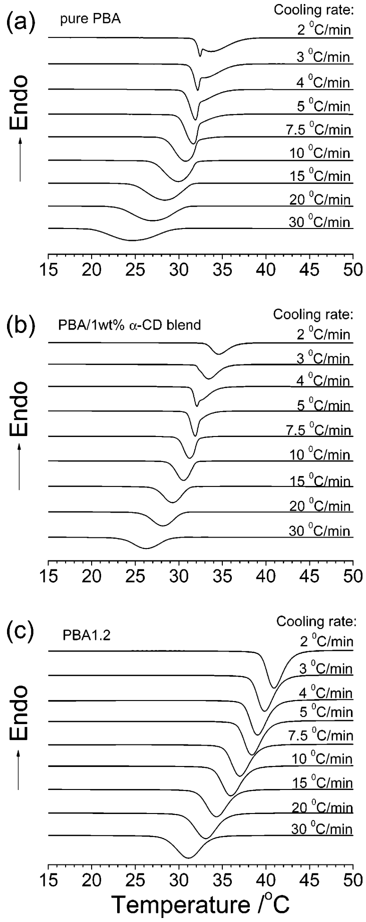

Figure 5. Nonisothermal crystallization behavior of (a) pure PBA, (b) PBA/1 wt % α-CD blend, and (c) PBA1.2 samples observed by DSC under different cooling rate.

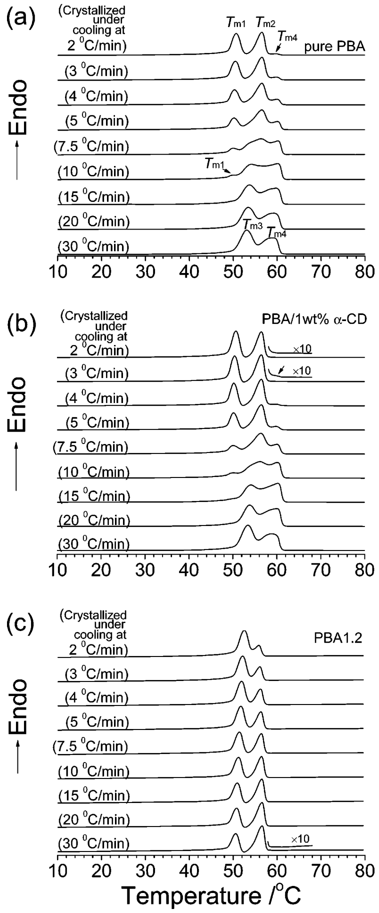

Figure 6. Melting behavior of pure (a) PBA, (b) PBA/1 wt % α-CD blend, and (c) PBA1.2 after nonisothermally crystallized under different cooling rate (see also Figure 5).

temperature region below 33 °C as seen in Figure 4a, a typical melting behavior of the *β*-form crystal (melting points T_{m3} and T_{m4}) appears in its corresponding heating scan as seen in Figure 4b. So, the *β*-form crystal of PBA is formed at lower crystallization temperature, below 33 °C, than the α-form.

It should be noted that PBA in PBAICS shows the peculiar crystallization behavior. The parts of PBA polymer chains uncovered by α-CD cavities are also crystallizable, as indicated by WAXD and DSC results. In Figure 4a, the crystallization peak of PBA in the PBAICS is detected at temperature only below 33 °C even under slow cooling. As mentioned just above, the PBA chains uncovered by α-CD should form only the *β*-form crystal. However, both characteristic melting peaks for the α-form (at T_{m1} and T_{m2}) and those for the *β*-form (at T_{m4}) are observed and the former seems to be predominant in the heating scan thermograms for PBAICS. These results suggest that the α-form crystal of PBA is readily formed in its complexed state from the melt. As shown in Figure 4, parts a and b, the fraction of the α-form crystals decreased with increase of cooling rate, indicating that the range of crystallization temperature of the α-form crystals for PBA is greatly decreased upon formation of ICs.

Crystallization Behavior of PBA Containing α-CD and PBAIC. Figure 5 shows the DSC curves of pure PBA, PBA/1 wt % α-CD blend, and PBA1.2 samples nonisothermally crystallized at the various cooling rates. The corresponding melting DSC curves are shown in Figure 6. As for the pure PBA, with the increase of the cooling rate, the intensities of the melting peaks corresponding to the melting of the *β*-form crystal increase. Finally, when the cooling rate reaches 15 °C/min, only a typical melting behavior of the *β*-form crystal was observed.

As shown in Figures 5b and 6b, the crystallization temperature of PBA/1 wt % α-CD blend is slightly higher than that of pure PBA, and the *β*-form crystal is formed as the cooling rate is faster than 3 °C/min. The crystallization and melting behavior of PBA is almost not affected by the introduction of pure α-CD. However, as seen in Figures 5c and 6c, when the cooling rate ranges from 2 to 30 °C/min for PBA1.2, only the α-form crystal is formed.

Here, we can compare the crystallization and melting behavior of pure PBA and PBA1.2. As shown in Figure 5, the peak crystallization temperature of the α-form crystal for pure PBA, which is about 33.8 °C, shifts to higher temperature, 41.0 °C with the introduction of PBAIC, under cooling rate 2 °C/min. However, the peak crystallization temperature of PBA/1 wt % α-CD blend increases from 33.8 to 34.6 °C, the increment of crystallization temperature is only 0.8 °C. It is indicated that the α-CD in the complex state is more effective for promoting the crystallization of PBA than for the free state α-CD.

On other hand, pure PBA formed the *β*-form crystal at the crystallization temperature below 33 °C. As shown in Figures 5c and 6c, when the cooling rate is 30 °C/min, the crystallization peak temperature of PBA1.2 detected at about 31 °C, the whole range of crystallization temperature spans the ranges of the α- as well as *β*-form crystal formation for pure PBA. However, the PBA1.2 sample only contains α-form crystals. It is suggested that the α-CD complex effectively induced the α-form crystallization of PBA.

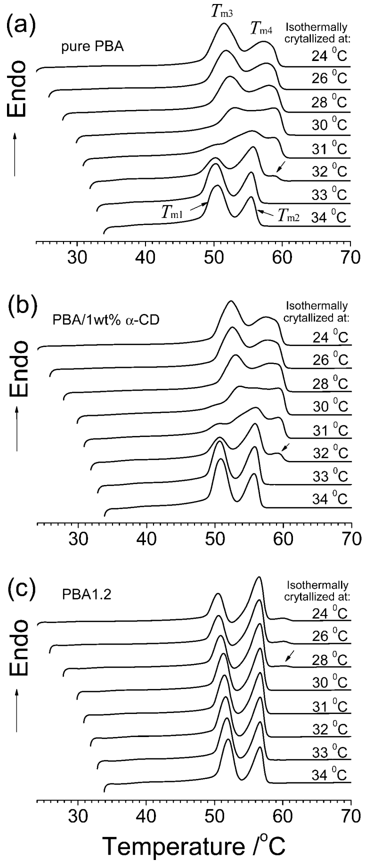

Figure 7. Melting behavior of (a) pure PBA, (b) PBA/1 wt % α-CD blend, and (c) PBA1.2 after isothermally crystallized at temperature ranging from 24 to 34 °C.

Figure 7 shows the melting behavior of PBA, PBA/1 wt % α-CD blend, and PBA1.2 after being isothermally crystallized at various temperatures ranging from 24 to 34 °C. As shown in Figure 7a, PBA shows the change of the crystalline form at about 31 ± 1 °C. In the temperature range higher and lower than this temperature, the α- and *β*-form crystal were predominantly formed, respectively. In the temperature range 31 ± 1 °C, the pure PBA shows triple melting peaks; which are resulted by the fusion of combined α- and *β*-form crystal. Clearly, the *β*-form crystals formed at a temperature below 33 °C.

As shown in Figure 7b, the melting behavior of PBA/1 wt % α-CD blend is almost similar to that of pure PBA. However, the temperature range, in which PBA shows the change of the crystalline form in PBA1.2 decreases to below 28 °C, as shown in Figure 7c. Therefore, in the nonisothermal crystallization of PBA1.2 (Figure 6c), the whole range of crystallization temperature is above 28 °C, leading the formation of only the α-form crystal in PBA1.2 sample.

Spherulite Morphology. In Figure 8 are shown the spherulitic morphologies of PBA samples crystallized at 45 °C after being quenched directly from 80 °C. The diameter of the spherulites of pure PBA reaches up to 100 *μ*m before the spherulites impinge with each other. With the addition of α-CD particles (1 wt %), the number of nuclei does not change, indicating that the pure α-CD has a smaller effect on the nucleation of PBA. However, with the additions of PBAICW and PBAICS particles, the number of nuclei increases and the average diameter of spherulites reduces, indicating that α-CD in the complex state can effectively enhance the nucleation of the α-form crystals in PBA. It is also shown that the nucleation ability of PBAICS is much higher than that of PBAICW, due to the difference of host−guest stoichiometry of ICs. Higher nuclear densities of PBA can be observed for the PBA1.2 and PBA8.6 samples, and the nuclear densities increased with increasing of PBAIC component. It is attributable to good distribution for PBAICs in PBA1.2 and PBA8.6 samples compared with PBA/PBAICW 1 wt % and PBA/PBAICS 1 wt % blend.

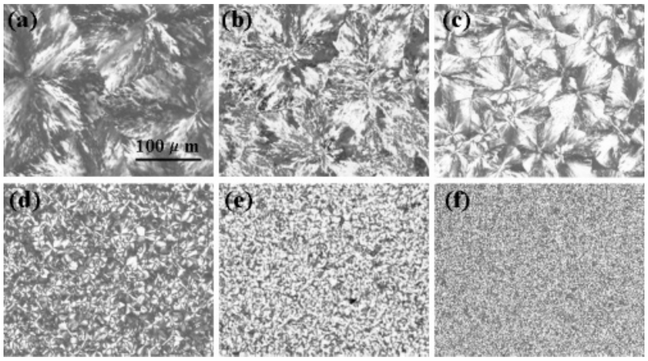

Figure 8. Spherulite morphologies of (a) pure PBA, (b) PBA/1 wt % α-CD blend, (c) PBA/PBAICW 1 wt %, (d) PBA/PBAICS 1 wt %, (e) PBA1.2, and (f) PBA8.6.

The DSC and POM results demonstrated that α-CD alone cannot effectively enhance the crystallization of PBA. However, the PBAIC with small amount of α-CD can greatly accelerate the crystallization of PBA. Therefore, it is thought that not the α-CD itself, but the PBA segments not covered by α-CD induce the enhanced crystallization of PBA. We can see that the PBAICS with a small amount of threading α-CD molecules also shows the remarkable crystallization behavior; that is, the uncovered parts of PBA by α-CD cavities readily form the α-form crystal from the melt. Therefore, it is thought that the α-form crystallization of bulk PBA starts as the ordering of the uncovered PBA segments on the surface of PBAIC particles, accompanied by the ordering of the adjacent bulk PBA segments.

Conclusion

The effects of α-CD on the crystallization and polymorphic behavior of PBA were studied by nonisothermal and isothermal crystallization process. The α-CD in the complex state is more effective for promoting the crystallization of the α-form crystal for PBA than for the free state α-CD, and small amount of α-CD in the complex state can greatly decrease range of crystallization temperature of the α-form crystal for PBA. It is suggested that PBA in PBAIC preferentially forms the α-form crystal from the melt.

References and Notes

(1) (a) Yee, W.; Kotaki, M.; Liu, Y.; Lu, X. *Polymer* **2007**, *48*, 512. (b) Li, Y.; Kaito, Macromol, A. *Rapid Commun.* **2003**, *24*, 255. (c) Garbarczyk, J.; Paukszta, D.; Borysiak, S. *J. Macromol. Sci. B* **2002**, *41*, 1267. (d) Bruckner, S.; Meille, S. V.; Petraccone, V.; Pirozzi, B. *Prog. Polym. Sci.* **1991**, *16*. 361.

(2) (a) Gan, Z.; Abe, H.; Doi, Y. *Macromol. Chem. Phys.* **2002**, *203*, 2369. (b) Gan, Z.; Kuwabara, K.; Abe, Iwata, H.; T.; Doi, Y. *Biomacromolecules* **2004**, *5*, 371.

(3) (a) Wenz, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 803. (b) Bender, M. L. Komiyama, M. *Cyclodextrin Chemistry*; Springer-Verlag: Berlin, 1978. (c) Szejtli, J. *Cyclodextrins and Their Inclusion Complexes*; Akademiai Kiado: Budapest, 1982. (d) Inoue, Y. *Annu. Rep. NMR Spectrosc.* **1993**, *27*, 59. (e) Davis, M. E.; Brewster, M. E. *Nature Rev.* **2004**, *3*, 1023.

(4) (a) Harada, A.; Kamach, M. *Macromolecules* **1990**, *23*, 2821. (b) Harada, A.; Li, J.; Kamachi, M. *Nature (London)* **1992**, *356*, 325.

(5) Harada, A.: Nishiyama, T.; Kawaguchi, Y.; Okada, M.; Kamachi, M. *Macromolecules* **1997**, *30*, 7115.

(6) (a) Dong, T.; He, Y.; Zhu. B.; Shin, K.; Inoue, Y. *Macromolecules* **2005**, *38*, 7736. (b) Dong, T.; Shin, K.; Zhu, B.; Inoue, Y. *Macromolecules* **2006**, *39*, 2427. (c) Huang, L.; Allen, E.; Tonelli, A. E. *Polymer* **1998**, *39*, 4857. (d) Shin, K.; Dong, T.; He, Y.; Inoue, Y. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 1433.

(7) (a) Wei, M.; Shuai, X.; Tonelli, A. E. *Biomacromolecules* **2003**, *4*, 783. (b) Shuai, X.; Porbeni, F. E.; Wei, M.; Bullions, T.; Tonelli, A. E. *Macromolecules* **2002**, *35*, 2401. (c) Wei, M.; Davis, W.; Urban, B.; Song, Y.; Porbeni, F. E.; Wang, X.; White, J. L.; Balik, C. M.; Rusa, C. C.; Fox, J.; Tonelli, A. E. *Macromolecules* **2002**, *35*, 8039. (d) Rusa, C. C.; Wei, M.; Bullions, T. A.; Rusa, M.; Gomez, M. A.; Porbeni, F. E.; Wang, X.; Shin, I. D.; Balik, C. M.; White, J. L.; Tonelli, A. E. *Cryst. Growth Des.* **2004**; *4*, 1431.

(8) (a) He, Y.; Inoue, Y. *Biomacromolecules* **2003**, *4*, 1865. (b) He, Y.; Inoue, Y. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 3461.

(9) (a) McMullan, R. K.; Saenger, W.; Fayos, J.; Mootz, D. *Carbhydr. Res.* **1973**, *31*, 37. (b) Takeo, K.; Kuge, T. *Agric. Biol. Chem.* **1970**, *34*, 1787.

(10) He, Y.; Inoue, Y. *Polym. Int.* **2000**, *49*, 623.

(11) Peet, J.; Rusa, C. C.; Hunt, M. A.; Tonelli, A. E.; Balik, C. M. *Macromolecules* **2005**, *38*, 537.

(12) Harada, A.; Okada, M.; Kawaguchi, Y. *Chem. Let.* **2005**, *34*, 542.

(13) (a) Rusa, C. C.; Bullions, T. A.; Fox, J.; Porbeni, F. E.; Wang, X.; Tonelli, A. E. *Langmuir* **2002**, *18*, 10016. (b) Rusa, M.; Wang, X.; Tonelli, A. E. *Macromolecules* **2004**, *37*, 6898. (c) Rusa, C. C.; Rusa, M.; Peet, J.; Uyar, T.; Fox, J.; Hunt, M. A.; Wang, X.; Balik, C. M.; Tonelli, A. E. *J. Inclus. Phenom., Macrocycl. Chem.* **2006**, *55*, 185.

(14) Kai, W.; Zhu, B.; He, Y.; Inoue, Y. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 2340.

MA071776O