Effects of Host−Guest Stoichiometry of α-Cyclodextrin−Aliphatic Polyester Inclusion Complexes and Molecular Weight of Guest Polymer on the Crystallization Behavior of Aliphatic Polyesters

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ABSTRACT: The nucleation effect of the α-cyclodextrin (α-CD)−polyester inclusion complex (IC) on the crystallization of semicrystalline aliphatic polyesters has been studied in the previous work, in which it was revealed that the effectiveness of α-CD ICs as a nucleating agent of aliphatic polyesters is mainly governed by the kinds of polyesters and the host−guest stoichiometry of α-CD−polyester ICs [Dong et al., *Macromolecules* **2005**, *38*, 7736; **2006**, *39*, 2427]. In this work, the effects of host−guest stoichiometry of α-CD−polymer ICs and molecular weight of guest polyesters on the crystallization behavior of polyesters were further studied by differential scanning calorimetry and polarized optical microscopy. As the guest polymers, two kinds of linear aliphatic polyesters, poly(ϵ-caprolactone) (PCL) and poly(butylene succinate) (PBS) with high and low molecular weight, were used. The ICs with various host−guest stoichiometry between α-CD and polyesters were successfully prepared, and they used as the nucleating agents for crystallization of PCL and PBS. It was found that the host−guest stoichiometry of ICs affects their nucleation ability on the crystallization of polyesters, and these ICs with about 30−70% uncovered parts showed most effective. Furthermore, the molecular weight of guest polymers also favorably affected their IC's nucleation ability on crystallization of polyesters. This research will be give us the route of making an effective green nucleating agent for bio-based polymer.

Introduction

In recent years, biodegradable polymers have attracted much attention as environment-friendly materials. Because of their biocompatibility and biodegradability, as well as their broad range of mechanical properties, biodegradable polymers, such as poly(hydroxyalkanoate)s (PHAs), polylactide (PLLA), and their copolymers have emerged as promising materials for various tissue engineering applications, including cardiovascular system, nerve, bone, and cartilage repair applications.[1] However, compared with the traditional engineering polymers, they are inferior with respect to physical properties and processability. The nucleating agents as additives are used not only because they can significantly increase the crystallization rate of molten polymers, and therefore increase the rate of production of molded articles, but also because they would dramatically and selectively alter the solid-state morphology of sheared polymers and, therewith, improve physical, mechanical, and optical properties.[2] Generally, some inorganic particles, such as talc[3−5] and boron nitride,[3,4] are used as nucleating agents for aliphatic polyesters. Unfortunately, the addition of talc and boron nitride restricts the tissue engineering applications of polyesters because of their nonbiodegradability and nonbiocompatibility. So, there is an urgent need for searching alternative nucleating agents for the biodegradable polymers.

The cyclodextrins (CDs) are well-known for being biocompatible, biodegradable, and soluble in water.[6] Furthermore, CDs originate from a renewable natural material, starch, and their inclusion complexes (ICs) with biodegradable polymers have potential for acting as the biodegradable and biocompatible additives. Since Harada et al. have found that CDs form ICs with linear polymers,[7] the CD ICs with polymers have attracted much attention due to their unique supramolecular architectures, such as polyrotaxane and hydrogel, as well as good models for macromolecular recognition in biological systems. Extensive studies have been carried out by Tonelli et al. to improve miscibility,[8] biodegradability,[9] and crystallizability[10] of polymers through the coalescence of guest polymers from their CD ICs. The IC complexation with CDs is considered to be one of the effective approaches for the improvement of properties of biodegradable polymers.

Our recent interest has focused on the accelerated crystallization of polymers induced by CDs. The rates of nucleation and crystallization of poly(3-hydroxybutyrae) (PHB) were greatly enhanced by introduction of α-CD−PHB IC.[11] Vogel et al. have successfully prepared the high tensile strength PHB fibers using α-CD−PHB IC as the nucleating agent.[12] This is a major advantage regarding further processing of PHB fibers for tissue engineering strategies using textile technologies. However, the preparation process is comparatively difficult to control, and the nucleation mechanism remains unclear. In the previous study, the nucleation mechanism of α-CD-enhanced crystallization of semicrystalline polymers,[13] such as poly(ϵ-caprolactone) (PCL), poly(ethylene glycol) (PEG), and poly(butylene succinate) (PBS), has been studied. It was preliminarily found that (1) the uncomplexed α-CD is less effective to enhance the crystallization of polymer, regardless of its crystalline structure, (2) the α-CD−polymer IC enhances the nucleation of the polymer more effectively when the guest polymer of IC is the same as the matrix polymer, and (3) the host−guest stoichiometry of α-CD−polymer IC also affects the extent of the nucleating effect of IC on the crystallization of polymer.

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Table 1. Concentration and Mixing Ratio of α-CD and Polymers for Preparation of ICs and Host−Guest Stoichiometry of ICs (Monomeric Unit of PCL/α-CD Molar Ratio; ST)[a]

sample	PCL/acetone	α-CD/water	ST value
PCLIC-1.1	0.06 g/100 mL	1 g/10 mL	1.1:1
PCLIC-1.4	0.1 g/100 mL	1 g/10 mL	1.4:1
PCLIC-1.6	0.2 g/100 mL	1 g/10 mL	1.6:1
PCLIC-1.9	0.5 g/100 mL	1 g/10 mL	1.9:1
PCLIC-2.2	0.85 g/100 mL	1 g/10 mL	2.2:1
PCLIC-3.1	1 g/100 mL	1 g/10 mL	3.1:1
PCLIC-3.6	2 g/100 mL	1 g/10 mL	3.6:1
PCLIC-4.4	1 g/60 mL	1 g/10 mL	4.4:1
PCLIC-6.1	1 g/40 mL	1 g/10 mL	6.1:1
PCLHIC-4.1	1 g/100 mL	1 g/10 mL	4.1:1
sample	PBS/DMSO	α-CD/DMSO	ST value
PBSIC-0.8	0.2 g/4 mL	3 g/2 mL	0.8:1
PBSIC-1.2	0.3 g/4 mL	3 g/2 mL	1.2:1
PBSIC-1.6	0.3 g/4 mL	2 g/2 mL	1.6:1
PBSIC-1.9	0.4 g/4 mL	2 g/2 mL	1.9:1
PBSIC-2.8	0.5 g/4 mL	1 g/2 mL	2.8:1
PBSHIC-2.0	0.5 g/10 mL	2 g/2 mL	2.0:1

[a] In the sample name, the numeral denotes the ST values calculated by ^{1}H NMR.

As the CDs are natural products and they are safety- and environment-friendly,[14] and furthermore their nucleation ability on the crystallization of aliphatic polyesters is comparable to those of conventional nucleation agents,[6,9] the CDs are expected to be ideal candidates as the green nucleation agents for the crystallization of biodegradable polymers. Therefore, detailed characterization of the structure and dynamics of CD−polymer ICs is very important for better understanding their nucleation mechanisms as well as designing of effective nucleating agents. In this study, the effects of host−guest stoichiometry of α-CD−polymer ICs and molecular weight of guest polymer on the crystallization of the PCL and PBS will be investigated in detail using the differential scanning calorimetry and polarized optical microscopy.

Experimental Section

Materials. α-CD was supplied by Nihon Shokuhin Kako Co., Ltd., Japan. Low ($M_n = 1.2 \times 10^4$, $M_w/M_n = 1.8$) and high molecular weight PCL (PCLH; $M_n = 1.9 \times 10^5$, $M_w/M_n = 1.7$) were purchased from Daicel Chemical Co. Low molecular weight PBS ($M_n = 1.6 \times 10^4$, $M_w/M_n = 1.7$) was purchased from Showa Highpolymer Co., Ltd., and high molecular weight PBS (PBSH; $M_n = 5.2 \times 10^4$, $M_w/M_n = 1.7$) was generously provided by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The polymer samples were purified by the precipitation from chloroform solution into ethanol.

Preparation of IC Sample. All the IC samples were prepared by solution mixing. The concentrations of polymer and α-CD solutions are listed in Table 1. For the preparation of α-CD−PCL ICs (PCLIC or PCLHIC), the α-CD aqueous solution was added slowly into the PCL solution in acetone under vigorous stirring at 60 °C for 3 h. Subsequently, the mixed solution was cooled to 25 °C and continuously stirred for another 24 h. As-produced white powder was collected by filtration and then washed with acetone and water to remove the free PCL and uncomplexed α-CD, respectively. Then, the final IC product was dried under vacuum at 60 °C for 1 week.

For the preparation of α-CD−PBS ICs (PBSIC or PBSHIC), both the solutions of PBS in dimethyl sulfoxide (DMSO) and α-CD in DMSO were heated to 80 °C in order to obtain the clear solutions, and then they were mixed together and stirred at 60 °C for 1 day. Especially, the mixture was further stirred at 60 °C for 1 day, for the preparation of PBSIC-0.8. Upon adding excess amount of chloroform into the mixture, the solution immediately became turbid. The precipitated products were filtrated and then washed by chloroform to remove the free PBS. The remaining powder was dried under a vacuum at 90 °C for 1 day, then washed with water to remove the free α-CD, and again dried under the vacuum at 60 °C for an additional 1 week.

Preparation of Polymer/IC Blends. The IC samples were used as the nucleating agents of crystallization of polymers. Considering the effect of particle size of the nucleating agents on their abilities to nucleate crystallization of polymer, the particle size of nucleating agents was 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 blends of polymer and nucleating agents were prepared by dispersing the nucleating agents into a concentrated chloroform solution of polymer (0.1 g/mL), and then the solvent was allowed to evaporate during rigorous stirring. The resultant films were dried at 25 °C under vacuum for 1 week before analysis. Here, the content of α-CD in the blends was kept to be constant, 2 wt %. The blend sample was named as, for example, $PCL_{PCLIC-1.1}$, indicating PCL sample including PCLIC-1.1.

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

The host−guest stoichiometry (ST) of ICs is estimated by solution ^{1}H NMR spectra recorded on a JEOL GSX270 NMR spectrometer in DMSO-d_6 at 80 °C. The chemical shifts were referenced to the DMSO residual proton resonance as $\delta = 2.5$ ppm from that of tetramethylsilane. The resultant molar ratios of monomeric PCL unit to α-CD molecules (ST values) are summarized in Table 1.

The DSC was employed to detect the thermal transitions and also to monitor the rate of heat flow during nonisothermal/isothermal crystallization of the sample from the molten state. In the nonisothermal crystallization, the sample was heated to the molten state at 90 °C for PCLs and 140 °C for PBSs, holding for 5 min at these temperatures, and then cooled at a rate of 10 °C/min to induce the nonisothermal crystallization. In the isothermal crystallization, after heated to the molten state and holding for 5 min, the sample was quenched to the desired crystallization temperature at 42 °C for PCLs and 92 °C for PBSs.

The polarized optical microscopic observation was performed on an Olympus BX90 polarized optical microscope equipped with a digital camera. The polymer sample was placed between a slide glass and a coverslip and was heated on a Mettler FP82HT hot stage. The samples (about 0.2 mg) were first heated to the molten state and held for 5 min and then quenched to the desired crystallization temperature at 42 °C for PCLs and 90 °C for PBSs.

Results

Preparation of ICs with Different Stoichiometries. The guest molecules encapsulated by CDs may change their physical, chemical, and biological properties, and these changes must be depend on host−guest stoichiometry of their ICs. The IC with different host−guest stoichiometries between PCL and α-CD is greatly affected by the molecular weight of the guest molecule.[15−17] Here, the PCLICs and PBSICs with different host−guest stoichiometries are prepared from the same guest polymer, that is, with the same molecular weight. For the experiment, the molar ratio of monomeric PCL unit to α-CD was varied in the mixing stage to make the ICs with different host−guest stoichiometry. Moreover, in order to avoid a wide range of compositional variation during the mixing process, the α-CD aqueous solution is slowly added into the PCL/acetone solution. If the PCL/acetone solution is added into the α-CD/water solution, the precipitating PCL molecules can more easily form complexes with high α-CD content at an earlier stage of mixing. These methods are also applied to prepare PBSICs.

The WAXD patterns of α-CD, PCL, PBS, and respective ICs are shown in Figure 1. A series of peaks are detected for the

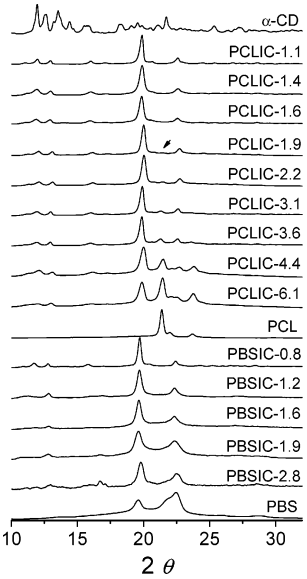

Figure 1. WAXD patterns of α-CD, PCL, PBS, and their ICs. The arrow indicates peak of PCL crystalline phase.

α-CD powder. The prominent peaks are located at around 12.5°, indicating the presence of the cage structure.[18] The characteristic peaks of crystalline phase are observed for pure PCL at 21.4°, 22.0°, and 23.7°. The WAXD patterns of PCLICs are quite different from those of pure PCL and α-CD, strongly supporting the IC formation between α-CD and PCL. Two prominent peaks at ca. 20° and 22.5° are present in the diffraction patterns of all ICs, which are well-known to be the characteristics of α-CD-based IC crystals adopting the channel structure.[19] However, it is notable that the characteristic peaks of PCL were also observed in the WAXD patterns of PCLICs, except for the PCLIC-1.1, PCLIC-1.4, and PCLIC-1.6, indicating that the crystalline region of PCL existed in its complex state. The relative intensity of the WAXD peak corresponding to the crystalline phase of PCL increases with increasing the ST value. From these results, it is shown that the crystallization of PCL was remarkably suppressed in the α-CD cavity, and the suppression is more prominent when the ST value became lower. If there is less amount of α-CD threaded onto the PCL, it is natural that more parts of polymer chain would be located outside the α-CD cavity, which can form the crystalline phase.

PBS shows two strong peaks at 19.5° and 22.4°, and these peak positions are almost close to those of the α-CD-based IC crystals. But, it clearly showed that the peak at ca. 20° is very intensive in each PBSIC, indicating that they adopt the channel structure. The peak at 22.4°, which is the characteristic peak of crystalline PBS, also appeared in the PBSIC-1.6, PBSIC-1.9, and PBSIC-2.8, indicating that the bulk PBS can be more easily crystallized in PBSIC when the numbers of threaded α-CD molecules are small.

Effect of Host−Guest Stoichiometry of ICs on Crystallization of Polymer. Figure 2 shows the DSC cooling thermograms of PCL, PBS, and their ICs with different host−guest stoichiometries obtained after holding the samples at high temperature (90 °C for PCL and 140 °C for PBS) for 5 min. The DSC cooling scan curves of these heated samples at cooling rate 10 °C/min reveal the relative nucleation abilities of the α-CD and ICs, as indicated by the peak crystallization temperature and the temperature range over which they crystallized. Usually, a higher crystallization temperature, T_c, and a narrower crystallization temperature range indicate faster crystallization. The results of cooling scan, subsequent heating scan, and crystallinity for polymers are shown in Table 2.

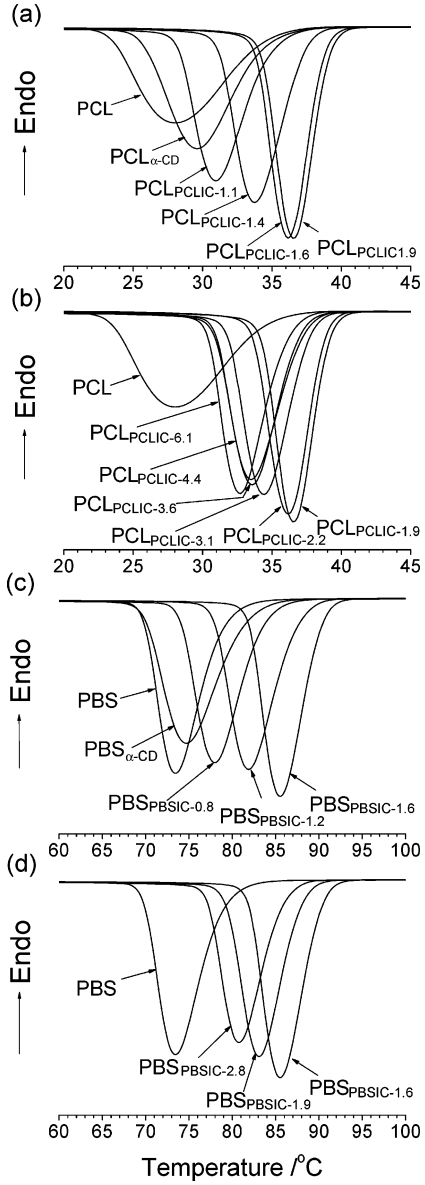

Figure 2. DSC nonisothermal crystallization behavior of (a) pure PCL and PCL containing α-CD, PCLIC-1.1, PCLIC-1.4, PCLIC-1.6, and PCLIC-1.9; (b) pure PCL and PCL containing PCLIC-1.9, PCLIC-2.2, PCLIC-3.1, PCLIC-3.6, PCLIC-4.4, and PCLIC-6.1; (c) pure PBS and PBS containing α-CD, PBSIC-0.8, PBSIC-1.2, and PBSIC-1.6; and (d) pure PBS and PBS containing PBSIC-1.6, PBSIC-1.9, and PBSIC-2.8.

As shown in Figure 2a,b, the T_c value of PCL, which is about 28.1 °C in the pure state, shifts to higher temperature range with the addition of α-CD and PCLICs. It is clearly seen that the T_c values are different from each other, and the nucleation ability of PCLIC is better than that of pure state α-CD. Concerning the nucleation effect of PCLICs on the crystallization of PCL, we can classify these PCLICs into two groups. One is the PCLIC with high content of α-CD molecules (ST ≤ 1.9). As shown in Figure 2a, the T_c value of PCL increased rapidly with the decrease of ST value. This result is different from the other group, that is, the PCLIC with lower content of threaded α-CD molecules (ST > 1.9). As shown in Figure 2b, the T_c value of PCL decreases from 36.5 °C of $PCL_{PCLIC-1.9}$ to 32.8 °C of $PCL_{PCLIC-6.1}$. Their nucleation ability decreases with the decrease of the ST value. Obviously, it is reverse to the trend observed for the former group.

Table 2. Nonisothermal Crystallization Temperature (T_c), Crystallization Enthalpy (ΔH_c), Melting Temperature (T_m), Melting Enthalpy (ΔH_m), and Crystallinity (X_c) of PCL and PBS Containing Nucleating Agents[a]

	cooling scan		heating scan		
sample	T_c/°C	ΔH_c/J/g	T_m/°C	ΔH_m/J/g	X_c/%
PCL	28.1	−74.2	54.9	76.2	45.9
$PCL_{\alpha-CD}$	29.8	−72.7	54.2	75.1	45.2
$PCL_{PCLIC-1.1}$	31.1	−70.5	55.1	75.3	45.4
$PCL_{PCLIC-1.4}$	33.9	−72.2	54.6	78.7	47.4
$PCL_{PCLIC-1.6}$	36.3	−73.4	55.1	76.8	46.3
$PCL_{PCLIC-1.9}$	36.5	−73.8	55.5	75.7	45.6
$PCL_{PCLIC-2.2}$	36.2	−74.6	55.3	78.3	47.2
$PCL_{PCLIC-3.1}$	34.5	−74.7	55.3	77.2	46.5
$PCL_{PCLIC-3.6}$	33.7	−72.1	55.1	76.6	46.1
$PCL_{PCLIC-4.4}$	33.5	−73.3	54.9	77.9	46.9
$PCL_{PCLIC-6.1}$	32.8	−72.5	54.8	77.2	46.5
PBS	73.5	−72.4	114.7	71.9	36.0
$PBS_{\alpha-CD}$	74.8	−69.7	113.6	70.2	35.1
$PBS_{PBSIC-0.8}$	78.0	−72.6	113.8	74.1	37.1
$PBS_{PBSIC-1.2}$	81.8	−74.2	113.5	77.9	39.0
$PBS_{PBSIC-1.6}$	85.5	−75.1	113.8	79.7	39.9
$PBS_{PBSIC-1.9}$	83.1	−68.9	113.8	75.0	37.5
$PBS_{PBSIC-2.8}$	80.8	−73.8	113.7	74.2	37.1
PCLH	27.3	−56.9	55.4	58.9	35.5
$PCLH_{PCLIC-4.4}$	30.6	−65.7	55.0	71.1	42.8
$PCLH_{PCLHIC-4.1}$	35.2	−69.3	55.4	77.2	46.5
$PCL_{PCLHIC-4.1}$	37.8	−75.2	55.5	77.6	46.7
PBSH	73.1	−63.6	113.6	69.9	35.0
$PBSH_{PBSIC-1.9}$	80.7	−64.2	111.9	71.7	35.9
$PBSH_{PBSHIC-2.0}$	87.7	−69.5	114.4	75.7	37.9
$PBS_{PBSHIC-2.0}$	87.1	−76.2	113.4	79.7	39.9

[a] The crystallinity (X_c) of polymer was calculated from $\Delta H_m/\Delta H°$, where $\Delta H°$ is the melting enthalpy expected for polymer with 100% crystallinity. Here, assuming the heats of fusion $\Delta H°$ of PCL and PBS are 166 and 200 J/g, respectively.[24]

Similar results are also observed for the crystallization behavior in the PBS blends. With the addition of α-CD, the T_c value of PBS shifts from 73.5 to 74.8 °C. With the addition of PBSICs, the T_c values increased above 78.0 °C. As shown in Figure 2c,d, when the ST values are lower than 1.6, the T_c value of PBS increased rapidly with the decrease of the ST value, whereas when the ST values higher than 1.6, T_c value of PBS decreases with the decrease of the ST value.

As shown in Table 2, although the melting peaks of polymer are not very sensitive to the addition of the nucleating agents, it also seems that high crystallinity values are related with a high crystallization temperature. These results may be due to the increased crystallization rate and the improved perfectness of PCL and PBS crystals with addition of the nucleating agents.

The isothermal crystallization behavior of PCL and PBS is illustrated in Figure 3. The pure PCL and PBS show the broadest crystallization peaks. However, the overall crystallization time of PCL and PBS is slightly shortened by an addition of α-CD, suggesting α-CD itself has a little nucleation effect on the isothermal crystallization process of PCL and PBS. Among them, the PCLIC-1.9 and PBSIC-1.6 induce the fastest crystallization of PCL and PBS, respectively.

The crystallization kinetics was determined from the isothermal DSC measurements. The isothermal heat flow curve was integrated to determine the degree of crystallinity of the sample as a function of crystallization time. The relative crystallinity X_t at any given time was calculated from the integrated area of the DSC curve recorded from $t = 0$ to $t = \infty$ and divided by the integrated area of the whole heat flow curve. The isothermal bulk crystallization kinetics was analyzed with the Avrami equation:[20]

$$X_t = 1 - \exp(-kt^n) \tag{1}$$

where n is an index related to the dimensional growth and the way of formation of primary nuclei and k is the overall rate

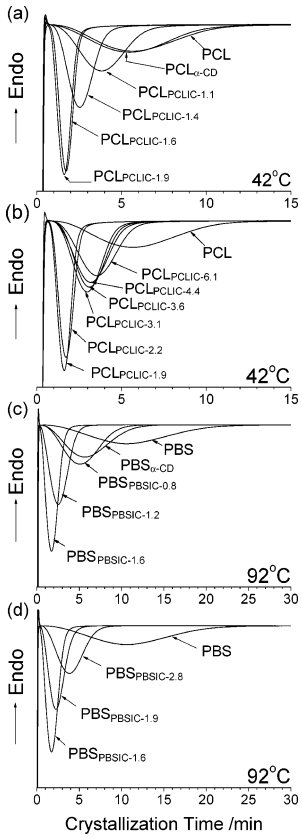

Figure 3. DSC isothermal crystallization behavior of (a) pure PCL and PCL containing α-CD, PCLIC-1.1, PCLIC-1.4, PCLIC-1.6, and PCLIC-1.9; (b) pure PCL and PCL containing PCLIC-1.9, PCLIC-2.2, PCLIC-3.1, PCLIC-3.6, PCLIC-4.4, and PCLIC-6.1; (c) pure PBS and PBS containing α-CD, PBSIC-0.8, PBSIC-1.2, and PBSIC-1.6; and (d) pure PBS and PBS containing PBSIC-1.6, PBSIC-1.9, and PBSIC-2.8.

constant associated with both nucleation and growth contributions. The linear form of eq 1 is given as eq 2:

$$\log[-\ln(1 - X_t)] = \log k + n \log t \tag{2}$$

n and k are obtained by plotting $\log[-\ln(1 - X_t)]$ against $\log t$. Meanwhile, the crystallization half-time $t_{1/2}$, which is defined as the time when the crystallinity arrives at 50%, can be determined from the kinetics parameters measured by using the following equation:

$$t_{1/2} = \left(\frac{\ln 2}{k}\right)^{1/n} \tag{3}$$

The calculated n values range from 2 to 3, which are almost insensitive to the addition of nucleating agents. The kinetic constants k and $t_{1/2}$ show a strong dependence on the crystallization temperature. With increasing the crystallization temperature, the value of k decreases, while that of $t_{1/2}$ increases. These results indicate that with increasing the crystallization temperature, the crystallization rate decreases.

Figure 4 shows the $t_{1/2}$ values of bulk polymer plotted against the percentage of the monomeric units of polymer uncovered by α-CD molecules in ICs for PCL and PBS. The percentage of uncovered segment of polymer in ICs was approximately calculated with following equation:

$$\text{percentage of uncovered segment (\%)} = \frac{ST \times L - H}{ST \times L} \times 100\%$$

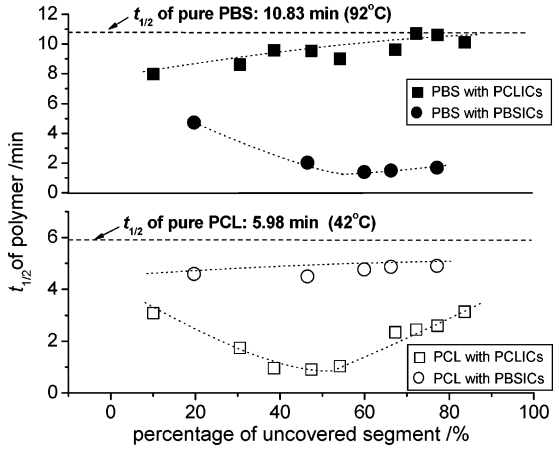

Figure 4. $t_{1/2}$ values plotted against the percentage of uncovered segment of polymer in the ICs.

Here, *ST*, *L*, and *H* denote the stoichiometry of IC, unit length of polymer chain, and depth of the α-CD cavity, respectively. The *L* value for PBS is about 1.09 nm.[21] The *H* for the α-CD is 0.78 nm.[22] The *L* for PCL is almost identical to the height of α-CD cavity.[23]

As shown in Figure 4, the $t_{1/2}$ values plotted against the percentage of uncovered segment for PCL nucleated with PBSICs and for PBS with PCLICs are very close to those of pure PCL and PBS, respectively, regardless of the ST values. The plots of $t_{1/2}$ for PCL with PCLICs and PBS with PBSICs are distantly separated from those of the pure PCL and PBS. It is indicated that the IC of a given polymer can greatly enhance the nucleation and the crystallization of the same polymer itself. However, the plot of $t_{1/2}$ shows the presence of the minimum $t_{1/2}$ value at around 30−70% uncovered segment of polymer in ICs, indicating that the IC of a given polymer with appropriate host−guest stoichiometry optimizes the acceleration of polymer crystallization.

The developments of crystalline morphologies within the PCL and PBS samples are followed using polarized optical microscopy. Figure 5 shows the spherulitic morphologies of PCL and PBS containing nucleating agents crystallized at 42 and 90 °C after quenched directly from 90 and 140 °C, respectively. As shown in panels a1−a7 of Figure 5, the diameter of the spherulites for pure PCL reaches up to 200 μm before they impinge with each other. However, with the addition of α-CD or PCLICs, the number of nuclei increases and the average diameter of spherulites decreases. The PCLIC-2.2 is the most effective in nucleation for PCL. As shown in panels b1−b5 of Figure 5, the number of nuclei of PCL increases a little with the addition of PBSICs; the size of spherulite is almost the same as that of pure PCL, indicating the PBSICs are less effective to nucleate the crystallization of PCL. Panels c1−c7 and d1−d5 of Figure 5 show the spherulitic morphologies of PBS with PBSICs and PCLICs, respectively. Although the PCLIC-2.2 is the most effective to nucleate the crystallization of PCL, their nucleation ability is declined when it is added into PBS. Although the PBSICs are ineffective to nucleate crystallization of PCL, they can greatly enhance the nucleation in PBS, and the PBSIC-1.6 is the most effective. These observations agree well with those of the DSC analysis.

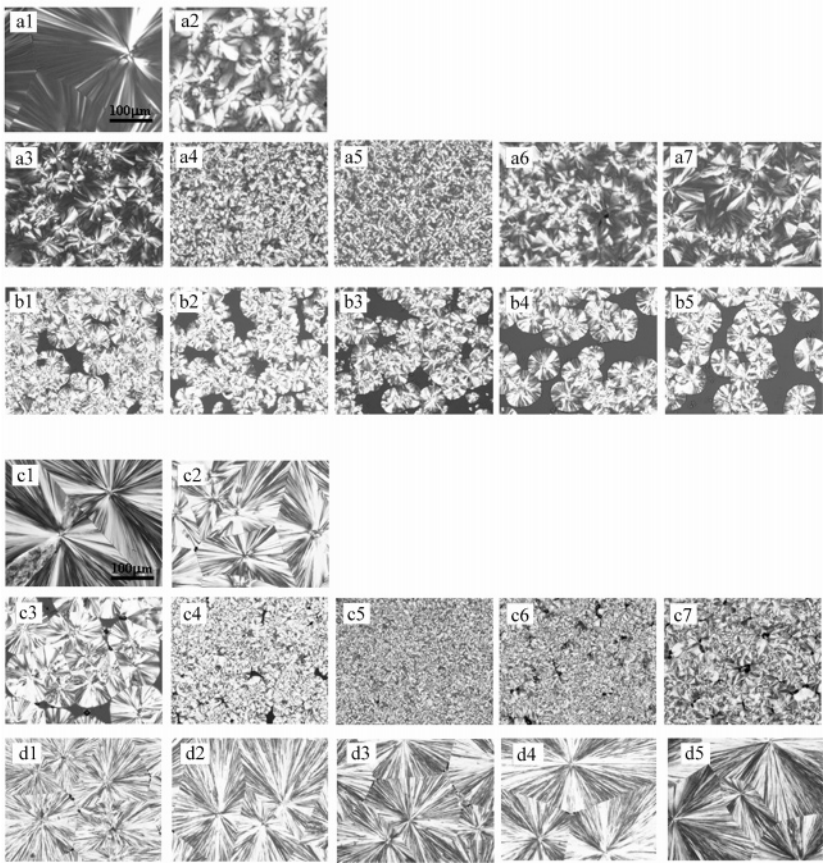

Figure 5. Polarized optical micrographs of pure PCL (a1) and PCL with α-CD (a2), PCLIC-1.1 (a3), PCLIC-1.6 (a4), PCLIC-2.2 (a5), PCLIC-3.6 (a6), PCLIC-6.1 (a7), PBSIC-0.8 (b1), PBSIC-1.2 (b2), PBSIC-1.6 (b3), PBSIC-1.9 (b4) and PBSIC-2.8 (b5); those of pure PBS (c1) and PBS with α-CD (c2), PBSIC-0.8 (c3), PBSIC-1.2 (c4), PBSIC-1.6 (c5), PBSIC-1.9 (c6), and PBSIC-2.8 (c7), PCLIC-1.1 (d1), PCLIC-1.6 (d2), PCLIC-2.2 (d3), PCLIC-3.6 (d4), and PCLIC-6.1 (b5).

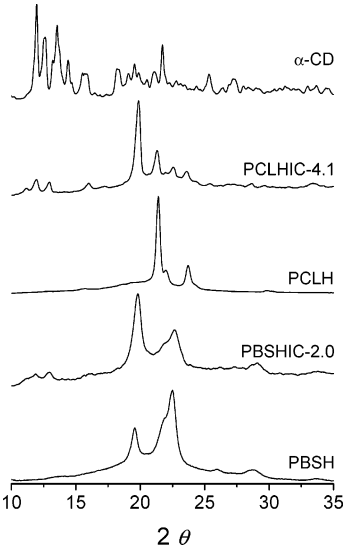

Figure 6. WAXD patterns of α-CD, PCLH, PBSH, and their ICs.

Effect of Molecular Weight of Polymer ICs on Crystallization of Polymer. The formations of PCLHIC-4.1 and PBSHIC-2.0 are confirmed by WAXD. As shown in Figure 6, a prominent peak can be observed at about 20° for the PCLHIC-4.1 and PBSHIC-2.0, indicating that the PCLHIC-4.1 and PBSHIC-2.0 adopt the channel structures. The host−guest stoichiometry of each IC is estimated on the basis of the ^{1}H NMR analysis. The molar ratios of the polymer monomeric repeat unit to α-CD are about 4.1:1 and 2.0:1 for PCLHIC-4.1 and PBSHIC-2.0; these values are close to the ST values of PCLIC-4.4 and PBSIC-1.9, respectively. It is indicated that the concentrations of α-CD molecules in the PCLHIC-4.1 and PBSHIC-2.0 are almost the same as those in the PCLIC-4.4 and PBSIC-1.9, respectively. Thus, it will be possible to investigate the effect of the molecular weight of threading chains in the ICs on the crystallization behavior of polymer.

In Figure 7 are shown the DSC nonisothermal crystallization curves for the PCL and PBS samples. Under the cooling, the T_c for pure PCL, PCLH, PBS, and PBSH were 28.1, 27.3, 73.5, and 73.1 °C, respectively. As shown in Figure 7a,b, after an addition of PCLHIC-4.1, the T_c values of PCL and PCLH increase to 37.8 and 35.2 °C, respectively. An increase of 9.7 °C in the T_c value of PCL and 7.9 °C in that of PCLH suggest that PCLHIC-4.1 is the most effective to enhance the crystallization of PCLs. The same result is observed for PBS sample, as shown in Figure 7c,d. The T_c of PBS and PBSH with PBSHIC-2.0 increases from 73.5 and 73.1 °C to 87.1 and 87.7 °C, respectively, and these increments of T_c value are much higher than those induced by an addition of PBSIC-1.9 into PBS and PBSH. These results suggest that higher the molecular weight of polymer in IC is more effective in enhancing the crystallization of polymer. The values of crystallinity of PCLH and PBSH are not very sensitive to the addition of the nucleation agents, as shown in Table 2. However, it also seems that high crystallinity is related to a high T_c value measured during cooling.

In Figure 8 are shown the photomicrographs of spherulites of PCL and PBS samples, grown in the absence and presence of nucleating agents. All of the spherulites grow under the same conditions. Panels a1, b1, c1, and d1 of Figure 8 indicate the presence of larger spherulites and fewer nuclei for PCL, PCLH, PBS, and PBSH without any nucleating agents, respectively. It is clearly shown that the nuclear density in the PCLs including PCLHIC-4.1 (Figure 8, a3 and b3) is much larger than that in

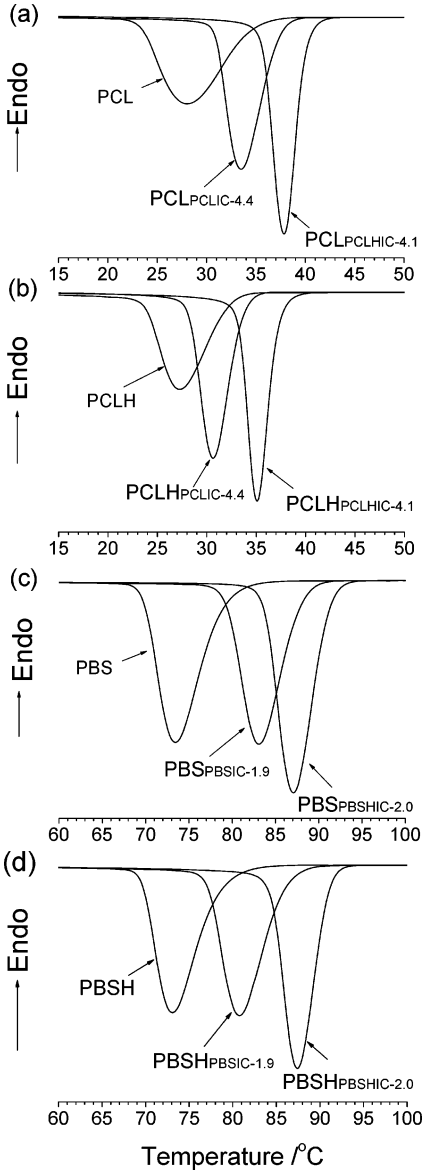

Figure 7. DSC nonisothermal crystallization behavior of (a) pure PCL and PCL containing PCLIC-4.4 and PCLHIC-4.1; (b) those of pure PCLH and PCLH containing PCLIC-4.4 and PCLHIC-4.1; (c) those of pure PBS and PBS containing PBSIC-1.9 and PBSHIC-2.0; and (d) those of pure PBSH and PBSH containing PBSIC-1.9 and PBSHIC-2.0.

PCLs including PCLIC-4.4 (Figure 8, a2 and b2). Analogously, the nuclear density in PBSs including PBSHIC-2.0 (Figure 8, c3 and d3) is much larger that in PBSs including PBSIC-1.9 (Figure 8, c2 and d2). Obviously, PCLHIC-4.1 and PBSHIC-2.0 are good nucleating agents for PCLs and PBSs, respectively. It is suggested that the nucleation ability of ICs of the high-molecular-weight polymer is better than that of ICs of the low-molecular-weight one for crystallization of given polymers.

Now, we definitely demonstrated that the guest molecules favorably affect the nucleation of polymers. The polarized optical microscopic observations directly support this result. In Figure 9 are shown the α-CD and PBSIC-1.6 particles immersed in the PBS molten state, and isothermally crystallized at 90 °C, just after quenched from the melting state at 140 °C. Parts a and c of Figure 9 show the morphologies of α-CD and PBSIC-1.9 particles, respectively. The α-CD crystals show the very regular crystalline surface, whereas those of the PBSIC-1.9 show the irregular one. As shown in Figure 9b, only one PBS spherulite grows from the α-CD particle. On the other hand, it

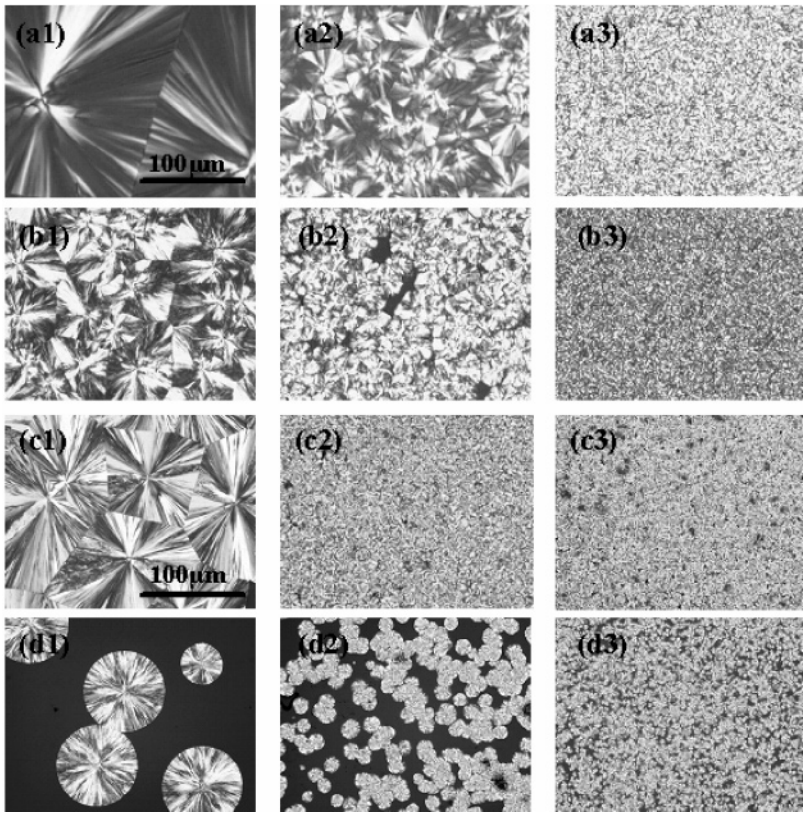

Figure 8. Polarized optical micrographs of pure PCL (a1) and PCL containing PCLIC-4.4 (a2) and PCLHIC-4.1 (a3); those of pure PCLH (b1) and PCLH containing PCLIC-4.4 (b2) and PCLHIC-4.1 (b3); those of pure PBS (c1) and PBS containing PBSIC-1.9 (c2) and PBSHIC-2.0 (c3); and those of pure PBSH (d1) and PBSH containing PBSIC-1.9 (d2) and PBSHIC-2.0 (d3).

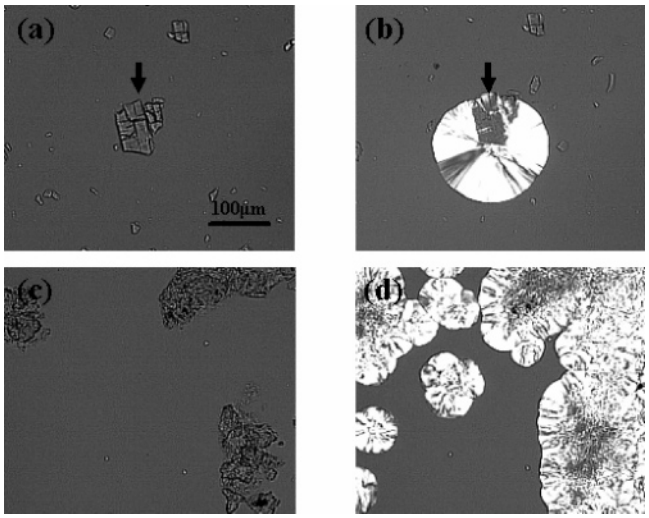

Figure 9. Polarized optical micrographs of PBS containing α-CD at 140 °C (a) and 90 °C (b) and PBSIC3 at 140 °C (c) and 90 °C (d).

is obvious that dense populations of spherulites cluster around the PBSIC-1.9 particles, while the average size of spherulites is greatly reduced by the presence of PBSIC-1.9 particles (as shown in Figure 9d). This is a direct consequence of the increase in the density of nucleating sites in the vicinity of PBSIC-1.9 particles. These results mean that the complex state of α-CD with polymer is more effective for promoting the crystallization of polymer than the free state α-CD. Therefore, it is thought that not α-CD itself but the PBS segments not covered by α-CD induce the enhanced crystallization of PBS.

Discussion

In the present study, the ICs were used as the nucleating agents for the crystallization of crystalline polymers, PCL and PBS. The ICs show different nucleation abilities on these two different polymers. Moreover, the stoichiometry between the host α-CD and the guest polymer in the IC greatly affects the nucleating extent. It is thought that this phenomenon may be caused by a combination of two effects. One is α-CD itself that is less effective to enhance the crystallization of polymers, regardless of its crystalline structure.[13] Therefore, if there are too many threaded α-CD, they would lose the effective nucleation ability of IC. The other is the segment of polymer uncovered by α-CD, which is considered to be the main factor for the enhancement of nucleation of the bulk polymer containing its own ICs. The nucleation of polymer crystallization may be attributable to the limited mobility of uncovered part of the polymer segments constrained by its interior part resided in the α-CD cavity. When there are too little threaded α-CD molecules, the mobility of the polymer segments protruded from the α-CD cavity in the IC should become the same as that of the bulk polymer segments, similarly losing its effective nucleation ability. Therefore, both these important causes are thought to take place in the enhancement of polymer nucleation.

Obviously, the nucleation ability of ICs with high-molecular-weight polymer is more effective. In the PCLIC series, the PCLIC-1.9 is the most effective nucleating agent for crystallization of PCL. After an addition of PCLIC-1.9, the T_c of PCL increased to 36.3 °C. The PCLHIC-4.1 increases the T_c of PCL to 37.8 °C, which is higher than the former one. On the other hand, the PBSIC-1.6 is the most effective nucleating agent for PBS in the PBSICs series. After an addition of PBSIC-1.6, the T_c of PBS increased from 73.5 to 85.5 °C, T_c increment 12.0 °C. The T_c of PBS increased to 87.1 °C by addition of PBSHIC-2.0, T_c increment 13.6 °C. These results indicate that the nucleation ability of IC with higher-molecular-weight polymer is more effective.

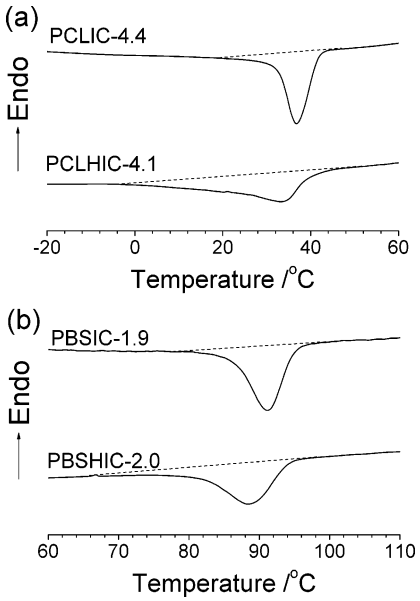

Figure 10. DSC cooling scans of (a) PCLIC-4.4 and PCLHIC-4.1 and (b) PBSIC-1.9 and PBSHIC-2.0. The arrows indicate the α-CD particles.

The uncovered parts of polymer in ICs with small amount of α-CD are still crystallizable, and the T_c values of polymer in ICs are higher than those of their pure polymers. However, as shown in Figure 10a, the T_c of PCLH in PCLHIC-4.1 is a little lower than that of PCL in PCLIC-4.4, and the temperature range of crystallization process of PCLHIC-4.1 is broader than that of PCLIC-4.4. As shown in Figure 10b, the T_c of PBSH in PBSHIC-2.0 is also little lower than that of PBS in PBSIC-4.4, and the temperature range of the crystallization process of PBSHIC-2.0 is relatively broader, indicating chain diffusion of high-molecular-weight polymer in ICs is slower than that of the low-molecular-weight one. It is suggested that the mobility of the high-molecular-weight polymer chain in IC is much limited. Therefore, the uncovered part of high-molecular-weight polymer segments in ICs can effectively induce the nucleation of polymer crystallization.

Conclusion

The inclusion complexes with different host−guest stoichiometry between α-CD and polymers (PCL and PBS) were successfully prepared by adjusting of solution concentration. The formation of these ICs was demonstrated by the WAXD and FTIR analyses. These ICs used as the nucleating agent for crystallization of polymers, PCL and PBS, show different nucleation abilities on different polymers. It was found that the host−guest stoichiometry of ICs greatly affected its nucleating extent. Furthermore, the molecular weight of threading polymer in ICs also favorably affected their nucleation abilities. The nucleation ability of the ICs with high-molecular-weight polymers was better than that with the low-molecular-weight ones. It is thought that two factors affect the nucleation ability of ICs for crystallization of polymer. One is α-CD itself that is almost not induced the polymer crystallization, regardless of its crystalline structure. When there are too many threaded α-CD molecules, the probability of contact between the uncovered parts of polymer segments in ICs and the bulk polymer chains is diminished. The other is the segment of polymer uncovered by α-CD, which is considered to be the main factor for the enhancement of nucleation of the bulk polymer containing its own ICs. The nucleation of polymer crystallization may be attributable to the limited mobility of the uncovered part of the polymer segments constrained by its interior part residing in the α-CD cavity. Therefore, both these important causes are thought to take place in the enhancement of polymer nucleation.

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