

Nucleation Effect of Inclusion Complexes with Different Polyolefin as Guest Molecules on the Crystallization of Polypropylene

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Received 17 May 2009; accepted 28 July 2009

DOI 10.1002/app.31195

Published online 15 September 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The γ -cyclodextrin (γ -CD) inclusion complexes (ICs) with four kinds of polyolefin (PO) as guest molecules were prepared. The crystallization behavior of isotactic polypropylene (iPP) blended with the γ -CD and γ -CD-PO ICs was investigated by differential scanning calorimetry, polarized optical microscopy, and light scattering. The iPP blended with the ICs was found to exhibit higher crystallization temperature (T_C), smaller spherulites, and faster crystallization rate than those of neat iPP, indicating that the ICs play a role of nucleating agent on the crystallization of iPP and induce

accelerated crystallization. The IC with PO having higher T_C as guest molecules showed higher nucleation effect than the IC with PO having lower T_C as guest molecules. The results suggest that the nucleation effect of these ICs was affected by the kinds of the guest molecules. The higher T_C guest molecules could result in higher nucleation effect. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1098–1104, 2010

Key words: cyclodextrin; inclusion complex; polypropylene; crystallization; nucleation

INTRODUCTION

Isotactic polypropylene (iPP) is a thermoplastic polymer investigated for years because of its commercial and scientific importance. In industrial application, nucleating agents are commonly added to iPP to accelerate the crystallization rate, reduce processing cycle time, and improve physicochemical characteristics, such as optical, mechanical, and heat resistance properties.^{1–3} Commonly used nucleating agents are organic and inorganic small molecules, that is, metallic salts of aliphatic or aromatic carboxylic acids, metallic salts of aromatic phosphorus compounds, quinacridones, pigments, and minerals such as clay or talc.^{3–5}

Cyclodextrins (CDs) are a series of cyclic oligosaccharides consisting of six, seven, and eight glucopyranose units, named α -CD, β -CD, and γ -CD, respectively. The molecules of CDs with doughnut shape have a hydrophobic cavity and hydrophilic rims made of hydroxyl group. In the hydrophobic cavity of CD, both small molecules and polymer can be threaded and inclusion complexes (ICs) can be formed.⁶ Since Harada and Kamachi found that

α -CD could form a crystalline IC with poly(ethylene glycol) (PEG) in aqueous solution,⁷ ICs formed by CDs and polymer have attracted much attention in polymer science, because of their unique supramolecular structure, such as polyrotaxane and hydrogel, as well as good effect on macromolecular recognition in biological systems.⁸ The formation and properties of CD ICs with various polymers have been studied extensively by Tonelli and coworkers to improve miscibility, biodegradability, and crystallization of polymers.^{9–11} It can also be found that the crystallization temperature of polymers coalesced from their CD ICs is generally higher than that of neat polymer. Inoue and coworkers^{12–15} studied the formation of the ICs between α -CD and some biodegradable polymers, such as poly(3-hydroxybutyrate), poly(butylene succinate), poly(butylenes adipate), poly(ϵ -caprolactone), and PEG, and found that these CD ICs could greatly improve the crystallization of polymers as the biodegradable and biocompatible additives.

Recently, we investigated the characterization of β -CD ICs and γ -CD ICs with iPP as guest molecules and found the nucleation effect of them on the crystallization of iPP.¹⁶ These ICs showed good nucleation effect and could accelerated the crystallization of iPP remarkably. Previously, we used the same guest molecules (iPP) and different host molecules (β -CD and γ -CD) to study the nucleation effect of ICs. In this article, we will use the same host molecules γ -CD and different kinds of guest molecules to investigate the

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Contract grant sponsor: Japan Science Society (Sasakawa ScientificResearch Grant).

influence of guest molecules on the nucleation effect on iPP. To investigate the nucleation effect of γ -CD and γ -CD ICs on the crystallization of iPP, the crystallization behavior of iPP blended with the γ -CD and γ -CD ICs is studied by differential scanning calorimetry (DSC), a polarized optical microscopy (POM), and light scattering apparatus.

EXPERIMENTAL

Materials

Three kinds of polyolefin (PO) specimens were supplied by Prime Polymer, Japan. The first was an iPP specimen, the second was a copolymer of ethylene and 1-butene, and the third was a copolymer of ethylene and 4-methyl-pentene. The fourth PO was an isotactic 1-polybutene (iPB) specimen obtained from Mitsui Chemicals. The abbreviations for these four POs were PO1, PO2, PO3, and PO4, respectively. The viscosity-average molecular weight (M_V) of the PO1, PO2, and PO3 was obtained by intrinsic viscosity measurements using a modified Ubbelohde viscometer in decalin solutions at 135°C. M_V of the PO4 was obtained in toluene at 50°C. A concentration of 0.2 g dL⁻¹ was used, and the calculated M_V of the PO1, PO2, PO3, and PO4 was 159,000, 68,000, 62,000, and 406,000, respectively. The crystallization temperature of POs was 114.1, 107.5, 102.8, and 64.3°C, respectively.

γ -CD was purchased from Kanto Chemical, Japan. The solvents such as dimethyl sulfoxide (DMSO) and 1,2,4-trichlorobenzene (TCB) were used as received from Aldrich.

Sample preparation

Formation of ICs

The preparation of γ -CD-PO1 IC was carried out according to Tonelli's report.¹⁷ A total of 0.1 g (2.38 mmol) of PO1 was dissolved in 70 mL of TCB to obtain a clear solution at 120°C with continuous vigorous stirring under nitrogen atmosphere. A total of 7 mL of hot (120°C) γ -CD solution (3.1 g, 2.38 mmol) in DMSO was added dropwise to the polymer solution, while stirring was maintained at 120°C for 3 h. The combined solution was allowed to cool to room temperature and stirred for another 24 h. The resulting white precipitate was collected by vacuum filtration, washed with hot TCB (120°C), water, and acetone, respectively, to remove uncomplexed PO1 and γ -CD. The resulting product was vacuum dried at 40°C for 24 h. The structure of IC is shown in Figure 1.

The other γ -CD-PO ICs were also prepared by the same method of the formation of γ -CD-PO1 ICs. The components of ICs are listed in Table I.

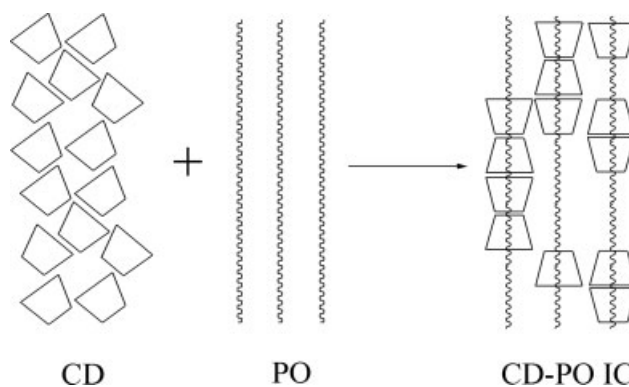


Figure 1 The synthesis process of inclusion complexes.

Blend of iPP (PO1) with ICs or γ -CD

The iPP (PO1) pellets with ICs or γ -CD (0.2 wt %, the ICs or γ -CD were passed through a boult with size of 74 μ m for the same particle size) were put into a QM-2-A miniature injection molding machine (Custom Scientific Instruments) at 185°C to melt, and mixed with screw for 5 min to disperse the ICs into the iPP matrix. After melt mixing, the specimens were extruded and dried.

Measurements

DSC

The DSC experiments were performed with a Perkin-Elmer Pyris1 DSC under nitrogen atmosphere. Indium was used as a standard for calibration. In the nonisothermal crystallization, all ICs and iPP/ICs blend specimens of about 3 mg were heated from 50 to 200°C at a heating rate of 20°C/min and maintained at 200°C for 5 min to erase their thermal history. Then, the specimens were cooled to 50°C at a cooling rate of 10°C/min to record the crystallization behavior of specimens.

POM

Structure development during the isothermal crystallization was observed under an Olympus BX-50 polarized optical microscope equipped with a sensitive tint plate. The thin-film specimens were put on a cover glass, melted at 200°C for 5 min to erase any trace of the crystals, and then quenched to the desired crystallization temperature at 130°C. The image data were recorded by an Olympus DP71 digital camera in an interval of 30 s and stored in a personal computer.

Light scattering apparatus

The real time analysis on the isothermal crystallization was carried out by the light scattering

TABLE I
List of ICs

	IC1	IC2	IC3	IC4
CD	γ -CD	γ -CD	γ -CD	γ -CD
PO	PO1	PO2	PO3	PO4

apparatus.¹⁸ The specimen on a cover glass was melted at 200°C for 5 min in a hot stage. Then, the film specimen was rapidly transferred to another hot stage set on the light scattering stage and annealed at 130°C for crystallization. A polarized He-Ne laser of 632.8 nm wavelength was applied vertically to the film specimen. The scattered light was passed through an analyzer and then reached a highly sensitive CCD camera with 512 × 512 pixels in a sensor of dimensions 13.3 mm × 8.8 mm (Princeton Instruments, TE/CDD-512-TKM-1). Hv geometry in which the optical axis of the analyzer was set perpendicularly to that of the polarizer was used. This realized the time-resolved measurement of a two-dimensional angular distribution of scattered light with 512 × 512 data points in a time scale of 5 s and that of a one-dimensional one with 512 data points in a time scale of 0.2 s. The input data from the CCD camera were digitized by the ST-13X controller.

RESULTS AND DISCUSSION

Formation of ICs

Tonelli and coworkers have studied the formation of γ -CD-PO ICs with iPP or iPB as guest molecules and found that PO with high molecular weight as guest molecules was partially covered by CD and PO with low molecular weight as guest molecules was fully covered by CD.¹⁷ Figure 2 shows the DSC thermograms of four kinds of POs and four kinds of ICs during the cooling scan. ICs of PO1, PO2, PO3, and PO4 show small exothermic peaks due to the crystallization of POs at around 123, 115, 109, and 72°C, respectively. Because ICs were washed with hot TCB (120°C) to remove the free POs, the exothermic peaks are attributed to the melting of the uncovered portion of the crystalline PO chains. This indicates that the ICs are partially covered by γ -CD and there are free parts of molecular chains not included in the cavity of γ -CD. Furthermore, it can also be found that although the crystallization peaks of ICs are smaller than those of neat POs, the ICs have higher crystallization temperature (T_c) than the respective neat POs used as guest molecules of ICs. This phenomenon is also observed in other CD-polymer ICs^{13,14,19} and is attributed to the faster crystallization of polymer chains of ICs not included into the

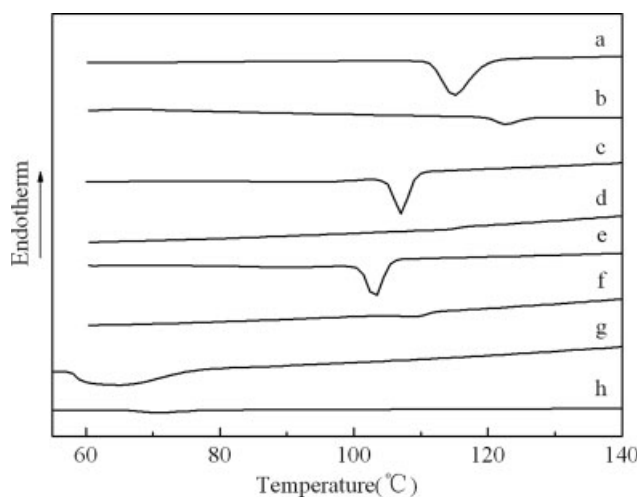


Figure 2 DSC thermograms of PO1 (a), IC1 (b), PO2 (c), IC2 (d), PO3 (e), IC3 (f), PO4 (g), and IC4 (h) crystallization behavior at a cooling rate of 10°C/min.

CD cavity.¹³ Thus, the results in Figure 2 are also an evidence of the formation of ICs.

Nonisothermal crystallization behavior of iPP and the blends

The crystallization of iPP blended with γ -CD and γ -CD-PO ICs was investigated by nonisothermal measurement of DSC. Here, 0.2 wt % of the γ -CD or ICs were blended with iPP. As shown in Figure 3, exothermic peak appeared during the cooling scan due to the crystallization of iPP. The crystallization temperature (T_c) is obtained from the peak position in Figure 3 and is shown in Table II. By blending γ -CD, IC1, IC2, IC3, and IC4, the T_c of iPP increases from 114.2°C to 117.9, 121.8, 119.9, 119.5, and

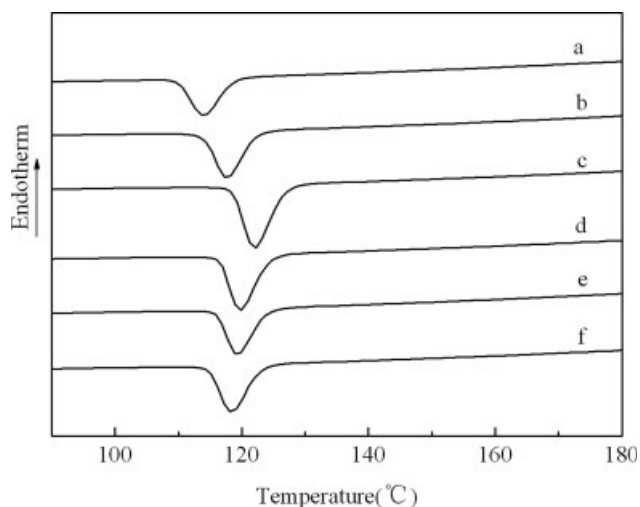


Figure 3 DSC thermograms during the nonisothermal crystallization of neat iPP (a), iPP/ γ -CD (b), iPP/IC1 (c), iPP/IC2 (d), iPP/IC3 (e), and iPP/IC4 (f) blends at a cooling rate of 10°C/min.

TABLE II
Crystallization Parameters of iPP and the Blends

Specimen	Onset T_C (°C)	T_C (°C)	ΔT_C (°C)
iPP	120.1	114.2	0
iPP/ γ -CD	123.5	117.9	3.7
iPP/IC1	128.5	121.8	7.6
iPP/IC2	126.2	119.9	5.7
iPP/IC3	125.6	119.5	5.3
iPP/IC4	125.0	118.3	4.1

118.3°C, respectively. The T_C shifts to higher temperature as the crystallization rate increases. Thus, the increase of the T_C by blending the ICs indicates the increase of the crystallization rate. This means that

the nucleation effect is found in the crystallization of iPP blended with the γ -CD and ICs. As the T_C of the iPP/IC1 blend is much higher than that of iPP/ γ -CD blend, the nucleation ability of IC1 is much higher than that of γ -CD. However, the T_C of iPP blended with the other three ICs is not so high as that of iPP blended with IC1, suggesting that the nucleation effect of IC2, IC3, and IC4 on the crystallization of iPP is smaller than that of IC1.

By blending γ -CD and ICs, the onset crystallization temperature (onset T_C) of iPP increases. This means that iPP can start to crystallize at higher temperature because of the acceleration of the crystallization by blending γ -CD and ICs. As the onset T_C of

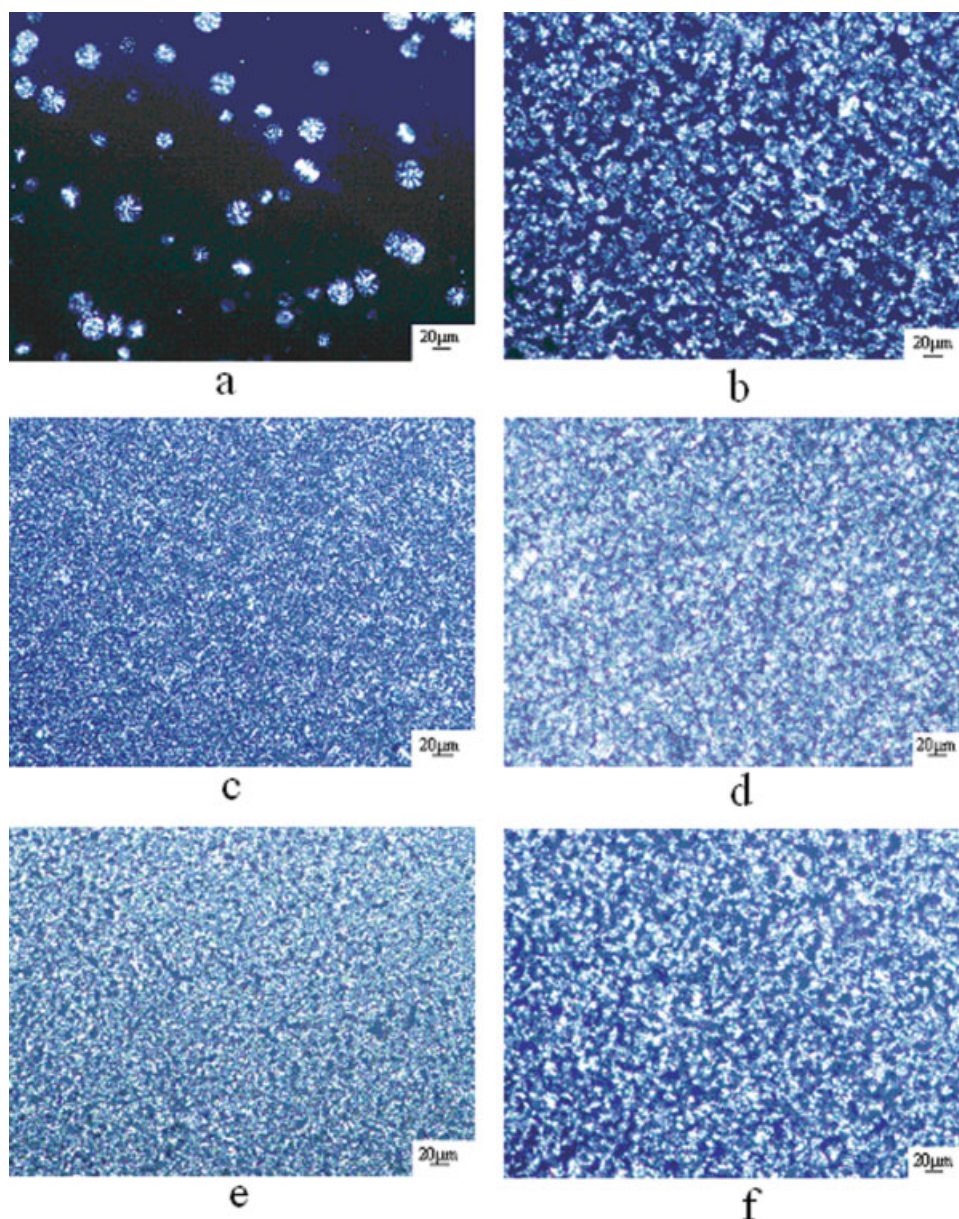


Figure 4 Polarized optical micrographs of neat iPP and the blends during the crystallization at 130°C for 30 s: neat iPP (a), iPP/ γ -CD (b), iPP/IC1 (c), iPP/IC2 (d), iPP/IC3 (e), and iPP/IC4 (f). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

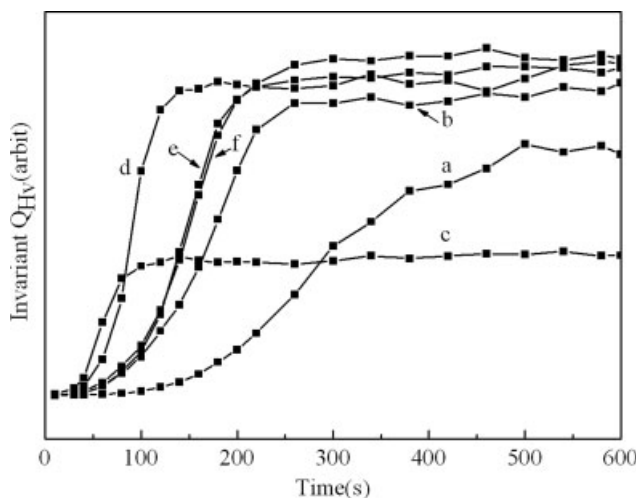


Figure 5 Time variation of invariants Q_{Hv} of neat iPP (a), iPP/ γ -CD (b), iPP/IC1 (c), iPP/IC2 (d), iPP/IC3 (e), and iPP/IC4 (f) blends during the crystallization at 130°C.

iPP/IC1 blend is higher than that of iPP/ γ -CD, iPP/IC2, iPP/IC3, and iPP/IC4 blends, the crystallization of iPP/IC1 blend is faster, that is, the order of crystallization rate by blending ICs and γ -CD is IC1 > IC2 > IC3 > IC4 \approx γ -CD. According to Rybnikar,^{20,21} the nucleation effect can be evaluated by the difference between the T_C of the nucleated polymer and that of neat polymer, ΔT_C . The nucleation effect is high when ΔT_C is higher than 6.5°C. The effect is medium when ΔT_C is between 5 and 6.5°C. The nucleation effect is low, when ΔT_C is between 3 and 5°C. The ΔT_C of iPP/IC1 blend is higher than 6.5°C, and ΔT_C of iPP/IC2 and iPP/IC3 blend is between 5 and 6.5°C, whereas ΔT_C of iPP/ γ -CD and iPP/IC4 blend is less than 5°C. The result indicates that ICs play a role of nucleating agents of high efficiency, although nucleation efficiency of γ -CD and IC4 is low. This suggests that the guest molecules inside the cavity of CDs play an important role of the nucleation effect on the crystallization of iPP.

The nucleation effect of ICs including PO with higher T_C as guest molecules is higher than that of IC including PO with lower T_C as guest molecules or γ -CD (IC1 > IC2 > IC3 > IC4 \approx γ -CD). Inoue and coworkers suggest that the crystallization of guest molecules affected the nucleation effect of the ICs remarkably, and the difference in the interfacial interaction between bulk polymers and ICs is responsible for the difference in the nucleation effects.⁴

POM observation

Figure 4 shows the crystalline morphologies of neat iPP and the blends with γ -CD and γ -CD-PO ICs observed at 130°C for 30 s during the crystallization after quenching from the melt state at 200°C. Spherulites of iPP having a size of several ten micrometers

in diameter are seen [Fig. 4(a)]. The spherulite size of iPP blended with γ -CD is slightly different comparing with that of neat iPP, but the number of the spherulite increases drastically [Fig. 4(b)]. This result suggests that the radial growth rate of the spherulite is not changed but the nucleation rate is accelerated and the number of the nucleus increases by blending the γ -CD. By blending the IC1, IC2, and IC3, the spherulites are volume filled before 30 s and the size of the spherulites is much smaller than that of the neat iPP and the blend with γ -CD. This indicates that the nucleation effect of these ICs on the crystallization of iPP is higher than that of γ -CD. However, by blending IC4, the change of the spherulites is small comparing with those of the blends with IC1, IC2, and IC3, and spherulites of iPP/IC4 blend are similar with that of iPP/ γ -CD blend. The POM results are consistent with the DSC results shown in Figure 3. Thus, the accelerated crystallization behavior of iPP blended with ICs and γ -CD demonstrated by the DSC measurement is attributed to the nucleation effect of ICs and γ -CD.

Light scattering measurement

To discuss the kinetic aspects of the crystallization, it is convenient to use the integrated scattering intensity in Hv mode,²² that is, the invariant Q_{Hv} defined by previous research.^{23,24}

$$Q_{Hv} = \int_0^\infty I(q)q^2 dq \quad (1)$$

where I is the intensity of scattering light at the scattering vector q , $q = (4\pi/\lambda)\sin(\theta/2)$, λ and θ being the wave length of the light and scattering angle, respectively.

The Hv light scattering pattern from the iPP is a circular-symmetric type. This suggests that the optical axes of the crystals are randomly oriented in the spherulite. In this case, Q_{Hv} is described by the mean square optical anisotropy δ .

$$Q_{Hv} \propto \langle \delta \rangle^2 = \phi_s (\alpha_r - \alpha_t)^2 \quad (2)$$

where ϕ_s is the volume fraction of spherulites, and α_r and α_t are the radial and tangential polarizabilities of the spherulite, respectively. Hence, Q_{Hv} is expected to increase with increasing volume fraction

TABLE III
Crystallization Time of iPP and the Blends Obtained from Figure 5

Specimen	iPP	iPP/ γ -CD	iPP/IC1	iPP/IC2	iPP/IC3	iPP/IC4
Time (s)	525	260	115	180	225	255

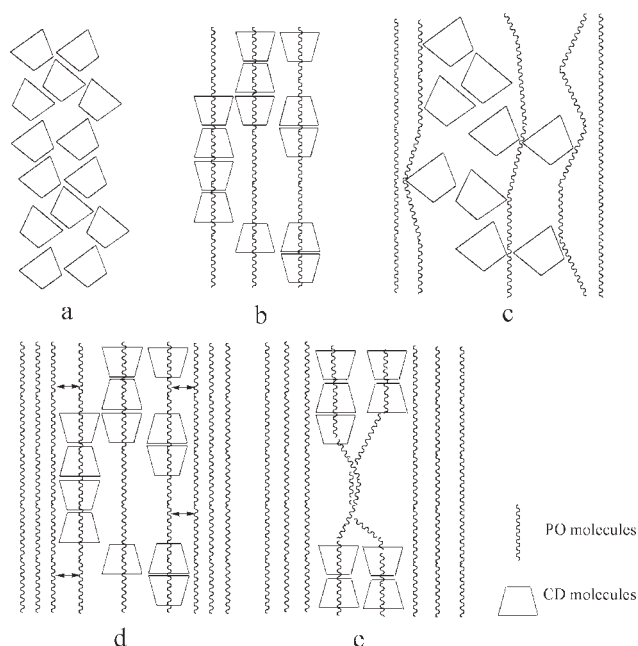


Figure 6 The crystallization growth of iPP blended with γ -CD and ICs: cage-type γ -CD (a), channel-type ICs (b), iPP/ γ -CD blend (c), iPP/IC1 blend (d), and iPP/IC4 blend (e).

of the spherulites and then level off when the spherulites are volume filled.^{18,24}

Figure 5 shows the time variations of invariant Q_{Hv} for neat iPP and iPP blended with γ -CD and ICs during the crystallization at 130°C. The Q_{Hv} increases with time and levels off as expected from eq. (2), that is, ϕ_s of the spherulites increases and attains a maximum when spherulites fill the whole space. The induction period for the crystallization of iPP becomes shorter by blending γ -CD and ICs. The short induction period of the blends is attributed to the nucleation effect of the γ -CD and ICs. The crystallization time for the blends in which the spherulites are volume filled is shown in Table III. The crystallization rate is faster as the crystallization time is shorter. Thus, the crystallization rate of the blends increases in the order of neat iPP < γ -CD \approx IC4 < IC3 < IC2 < IC1. These results indicate that the crystallization of iPP is exceedingly accelerated by blending γ -CD and ICs due to the nucleation effect. The nucleation effect of IC with PO having higher T_C as guest molecules is higher than that of IC with PO having lower T_C as guest molecules.

Discussion

It has been demonstrated that the γ -CD and ICs could accelerate the crystallization of iPP remarkably. For the iPP/ γ -CD blend, γ -CD can act as nucleating agent, resulting in heterogeneous crystallization of iPP, and the schematic illustration of the crystallization growth is shown in Figure 6(c). The

pure γ -CD is cage type [Fig. 6(a)], and the crystallization may occur in the surface of γ -CD. However, the disordered arrangement of γ -CD may suppress the crystallization arrangement of iPP molecules. Thus, the γ -CD does not exhibit excellent nucleation effect on the crystallization of iPP.

It has also been demonstrated that the ICs have higher nucleation effect on the crystallization of iPP than γ -CD, and the kind of guest molecules favorably affects the nucleation effect of ICs on the crystallization of polymers. It has been widely reported that the crystallization structure of the IC is channel structure, and the crystalline form of γ -CD ICs is monoclinic form.²⁵ Therefore, the ordering of the crystal arrangement of ICs is much higher than that of γ -CD, and the monoclinic crystalline form of γ -CD ICs is same to the crystalline form of iPP. This enhances the nucleation effect of ICs on the crystallization of iPP as Binsbergen and Beck have reported that nucleating agent will have better nucleation effect if the nucleating agent has the same crystalline form to the bulk polymer.^{26,27} Thus, the ICs have higher nucleation effect than that of γ -CD, and the kind of the guest molecules of ICs plays an important role in the nucleation effect of ICs. It has been demonstrated that the ICs with PO having higher T_C as guest molecules have higher T_C relevantly. If the ICs have higher T_C , the crystallization of guest molecules uncovered by γ -CD can proceed faster and nucleus can be formed at higher temperature and act as nucleating agent of iPP in a shorter time [Fig. 6(d)], resulting in better nucleation effect. But for the IC4 with iPB as guest molecules, the melting temperature (T_m) of guest molecule (iPB) is 113°C, which is lower than T_C of neat iPP. Therefore, in the cooling process, when temperature arrives to the onset T_C of iPP and the crystallization of iPP occurs, the temperature is still higher than T_m of iPB, and guest molecules of IC4 (iPB) are still in amorphous state. Therefore, there is no regular arrangement of IC4 molecules, and this situation is similar with the iPP blend with only γ -CD and nucleation effect is low [Fig. 6(e)]. Thus, the crystalline guest molecules of ICs play an important role in the nucleation effect on the crystallization of iPP.

CONCLUSIONS

ICs between γ -CD and four kinds of POs were prepared. The neat γ -CD and four kinds of ICs were found to exhibit nucleation effect on the crystallization of iPP. The ICs have higher nucleation effect than pure γ -CD. The nucleation effect of ICs is different and the kinds of the guest molecules of ICs play an important role in the nucleation effect on iPP. The IC with PO having higher T_C as guest

molecules has higher nucleation effect on iPP than the IC with PO having lower T_C as guest molecules.

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