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ORIGINAL PAPER

The influence of side chains on formation of inclusion complexes prepared with polyolefin and cyclodextrins

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Abstract We investigated the formation of inclusion complexes (ICs) between cyclodextrins (CDs) with different cavity size and polyolefin (PO) with different side chains by using Fourier transform infrared (FTIR) spectroscopy, wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry. The analysis of FTIR spectra revealed that the resultants were complexes of CD and PO, and the analysis of WAXD revealed that the molecules of CD had a channel structure due to the formation of ICs. We found that IC could not be obtained when the cavity size of CD was small for PO molecules to thread and it was too large for cross-sectional area of PO molecules. Thus, it was found that PO1 with few side chains could form IC with α-CD, and PO2 with ethyl side chain could form IC with β-CD and γ-CD, while the PO3 with 2-methyl-propyl side chain could form IC with γ-CD. These results suggest that the cross-sectional areas of polymer and the cavity size of CDs play critical roles in the formation of ICs. It is only possible to form ICs when the polymer chains can tread into cavities of CDs, and the space between the polymer and CD is suitable to provide enough intermolecular interaction to keep the structure of IC stable.

Keywords Cyclodextrin · Inclusion complex · Polyolefin · Side chains

Introduction

Cyclodextrins (CDs) are a series of cyclic oligosaccharides, consisting of six, seven or eight glucose units, and are named alpha (α-), beta (β-), or gamma (γ-) CDs, respectively. These molecules with truncated cone structure, have a hydrophilic

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surface and a hydrophobic cavity in which guest molecules can reside. Although the depth of the cavity for the three kinds of CDs is same about 7.9 Å as shown in Fig. 1, their cavity diameters range from 4.9 to 7.9 Å [1]. For a long time, CDs were known to form both soluble and crystalline inclusion complexes (ICs) with a variety of small molecular guests. Since Harada and Kamachi first found that CDs could form ICs with poly(ethylene oxide) (PEO), the researchers have focused on the ICs prepared with CDs and polymers.

It has been reported that CDs can form ICs with many kinds of polymers such as polycaprolactone (PCL) [2], nylon-6 [3], poly(hydroxybutyrate) (PHB) [4], poly(ethylene glycol) (PEG) [5], poly(propylene glyclol) (PPG) [6], polycarbonate (PC) [7], polypropylene (PP) [8], poly(lactic acid) (PLLA) [9], poly(ethylene terephthalate) (PET) [10], poly (methylmethacrylate) (PMMA) [11], and poly(butylene adipate) (PBA) [12]. CDs form ICs with these polymers with high selectivity. For example, PEG can form IC with α-CD [5], but cannot react with β-CD or γ-CD. PPG can form ICs with β-CD and γ-CD [6], but cannot react with α-CD. PP can form IC with β-CD and γ-CD [8, 13], but cannot react with α-CD. PCL can form IC with α-CD and γ-CD, i.e., single PCL chain is included in the cavity of α-CD, while double PCL chains are included in the cavity of γ-CD. Therefore, it is thought that the formation and characteristics of polymer-CD ICs is related with the side chains of the polymer and the kinds of CDs.

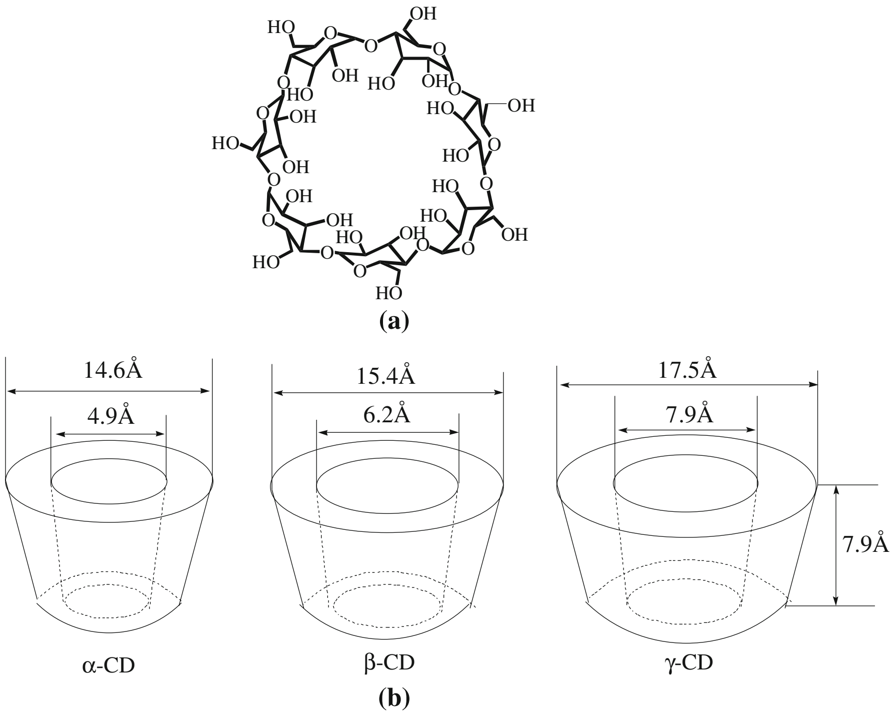

Fig. 1 Structure of β-CD (**a**) and molecular dimensions of CDs (**b**)

In this paper, we used three kinds of polyolefin (PO) with different side chains as guest molecules and investigated the possibility to form ICs with different kind of CDs (α-CD, β-CD and γ-CD), by analyzing the results of Fourier transform infrared spectroscopy (FTIR), wide angle X-ray diffraction (WAXD), and differential scanning calorimetry (DSC). The preparation of ICs with PO and CD was discussed in terms of the side chains of guest molecules and cavity size of CDs.

Experimental

Materials

Three kinds of PO specimens were purchased from Prime Polymer Co., Ltd., Japan, and the structure is shown in Fig. 2. PO1 was polymer of ethylene with few branch chains, PO2 was copolymer of ethylene and 1-butene, and PO3 was copolymer of ethylene and 4-methyl-pentene. 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. A concentration of 0.2 g dL^{-1} was used, and the calculated M_V of the PO1, PO2 and PO3 was 52,000, 68,000 and 62,000, respectively. The degree of branching of POs was determined by ^1H NMR at 110 °C in 1,1,2,2-tetrachloroethane-d_2 solution and found that n:m of PO2 was 57:1 and n:m of PO3 was 41:1.

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

Formation of ICs

0.15 g (2.38 mmol) of PO was dissolved in 70 mL of TCB to obtain a clear solution at 100 °C with continuous vigorous stirring under nitrogen atmosphere. 7 mL of hot (100 °C) α-CD solution (2.3 g, 2.38 mmol) in DMSO was added dropwise to the polymer solution, while stirring was maintained at 100 °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 (100 °C), water and acetone respectively to remove uncomplexed PO and α-CD.

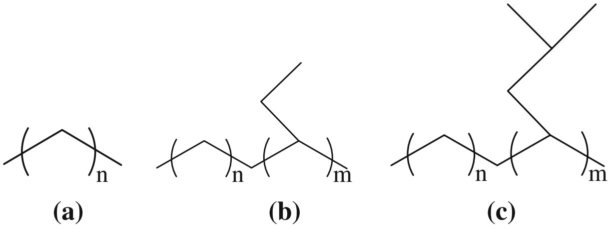

Fig. 2 Structure of PO1 (**a**), PO2 (**b**) and PO3 (**c**)

The product was vacuum-dried at 40 °C for 24 h. The synthesis process of ICs is shown in Fig. 3.

β-CD–PO ICs and γ-CD–PO ICs were also prepared by the same method to the formation of the α-CD–PO ICs.

Measurements

Fourier transform infrared spectroscopy (FTIR)

A 460P FTIR spectrometer (Japan Spectroscopic Co., Ltd) was utilized to obtain the infrared spectra. The samples were mixed with potassium bromide (KBr) and pressed into film. The spectra was recorded over a range of 4,000–400 cm^{-1} with a resolution of 2 cm^{-1} and 20 scans.

Wide angle X-ray diffraction (WAXD)

Wide angle X-ray diffraction measurement was performed with a Rigaku RAD-2C X-ray diffractometer using a Ni-filtered Cu Kα radiation source ($\lambda = 1.54$ Å). The diffraction intensities were measured from $2\theta = 5$ to 30° at a rate of $2\theta = 3°$/min with data collection at every 0.1° of 2θ. The supplied voltage and current were 40 kV and 30 mA, respectively.

Differential scanning calorimetry (DSC)

The DSC experiments were performed with a Perkin–Elmer Pyris1 DSC under the nitrogen atmosphere. Indium was used as a standard for calibration. In the nonisothermal crystallization, all ICs specimens of about 3 mg were heated from 50 to 150 °C at a heating rate of 20 °C/min and maintained at 150 °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 obtain the crystallization behavior.

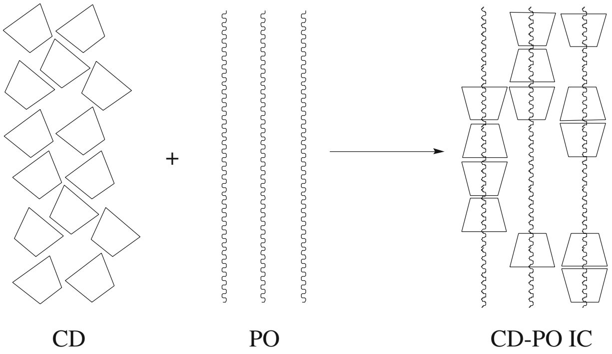

Fig. 3 The synthesis process of ICs with CD and PO

Result and discussion

FTIR measurement

Fourier transform infrared spectroscopy measurement has been used widely in the research of supramolecular complexes as a very useful tool to investigate the presence of both guest and host components of ICs. The FTIR spectra of the α-CD, pure PO1, and four kinds of CD–PO IC in the region from 400 to 4,000 cm^{-1} are presented in Fig. 4. In the FTIR spectrum, the neat PO1 shows characteristic intense peaks at 2,960 and 2,920 cm^{-1} attributed to the antisymmetric stretching vibrations of the CH_2 groups. Here, the neat PO2 and PO3 have similar FTIR spectrum with PO1 and do not show in the figure. On the other hand, α-CD shows characteristic peak at around 3,370 cm^{-1} due to the symmetric and antisymmetric O–H stretching mode and peak at around 2,930 cm^{-1} due to the C–H stretching mode [14], and the FTIR spectra of β-CD and γ-CD are similar to that of α-CD. These characteristic peaks of CDs can be also found in the spectrum of α-CD–PO1 IC, indicating that the molecules of α-CD–PO1 IC has the component of CD. The characteristic peaks of PO are also seen in the spectrum of α-CD–PO1 IC, indicating that the molecules of α-CD–PO1 IC also have the unit of PO1. Thus, the α-CD–PO1 IC consists of molecules of α-CD and PO1. The same results are observed in β-CD–PO2 IC, γ-CD–PO2 IC and γ-CD–PO3 IC. The formation of ICs with various POs and CDs are summarized in Table 1.

The peak positions of PO and CD are affected by the formation of the ICs. For example, the peak of α-CD at 3,370 cm^{-1} due to the effect of O–H stretching mode is shifted a few higher to 3,392 cm^{-1} in the spectrum of α-CD–PO1 IC. This shift of a few bands may be attributed to the CD bridged systems [15] which

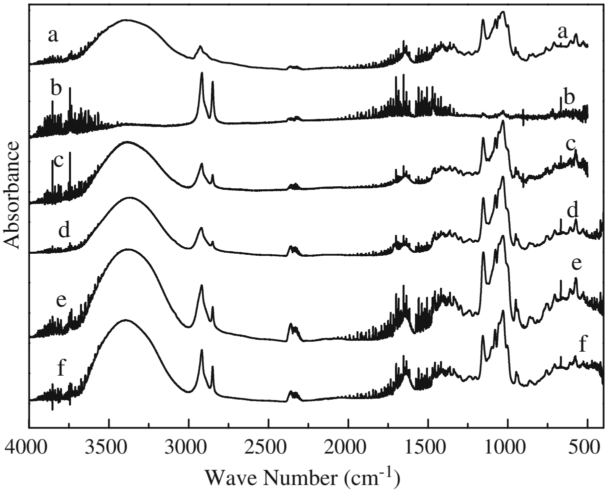

Fig. 4 FTIR spectra of as-received α-CD (**a**), PO1 (**b**), α-CD–PO1 IC (**c**), β-CD–PO2 IC (**d**), γ-CD–PO2 IC (**e**), γ-CD–PO3 IC (**f**)

Table 1 Components of POs and CDs for the formation of the ICs

PO	α-CD	β-CD	γ-CD
PO1	α-CD–PO1 IC	No reaction	No reaction
PO2	No reaction	β-CD–PO2 IC	γ-CD–PO2 IC
PO3	No reaction	No reaction	γ-CD–PO3 IC

affected the interaction of CDs and POs. The peak shift has been observed in other CD-polymer ICs [16], and is an evidence of the formation of ICs between CDs and polymer.

WAXD measurement

Wide angle X-ray diffraction is now a useful and common characterization method to investigate the crystalline phase between the cage structure of as-received CD and the channel structure of CD–polymer IC. If the guest polymer is threaded into the CD molecules, it has been proved that the IC with a channel-type crystalline structure will be obtained and the WAXD profiles of ICs are different with those of neat CDs and polymer.

The WAXD profiles of α-CD, β-CD, γ-CD, PO1 and CD–PO ICs are presented in Fig. 5. The profiles of CD–PO ICs (d, e, g, h) are quite different with those of neat PO (a) and CDs (b, c, f), suggesting that the CD–PO ICs are not simply a mixture of free CD and PO but crystalline ICs with supramolecular structure. Different with the tanglesome peaks of α-CD and two strong reflections at $2\theta = 21.6°$ and 24° in PO1 (the PO2 and PO3 has similar WAXD curve with PO1), the most prominent peaks for α-CD–PO1 ICs are at approximately 19.8° and 22.5° (2θ). It indicates that the inclusion complex has been formed with a channel structure as shown in Fig. 3, resulting in the characteristic peaks of WAXD [17]. Like the α-CD–PO1 diffractogram, the β-CD–PO2 IC shows characteristic peaks at about 12.5° and 19°, different with the tanglesome peaks of β-CD and two strong reflections at $2\theta = 21.6°$ and 24° in PO2, while γ-CD–PO2 IC and γ-CD–PO3 IC show characteristic peaks at $2\theta = 7.5°$, different with three strong reflections at $2\theta = 11°$, 16.8° and 22° in γ-CD and two strong reflections at $2\theta = 21.6°$ and 24° in PO3. Thus, the inclusion complex with a channel structure is formed in the β-CD–PO IC and γ-CD–PO IC [18, 19].

DSC measurement

Figure 6 shows the DSC thermograms of PO1, PO2, PO3 and four kinds of ICs during the cooling scan. It is well known that no exothermic peak is seen in the α-CD, β-CD and γ-CD at cooling process below 200 °C. On the other hand, exothermic peak due to the crystallization is seen in PO and the crystallization temperature (T_c) of neat PO1, PO2 and PO3 estimated from the peak position is 114, 107 and 103 °C, respectively. While the CD–PO ICs show small exothermic peaks due to the crystallization of POs. Since ICs were washed with hot TCB to remove

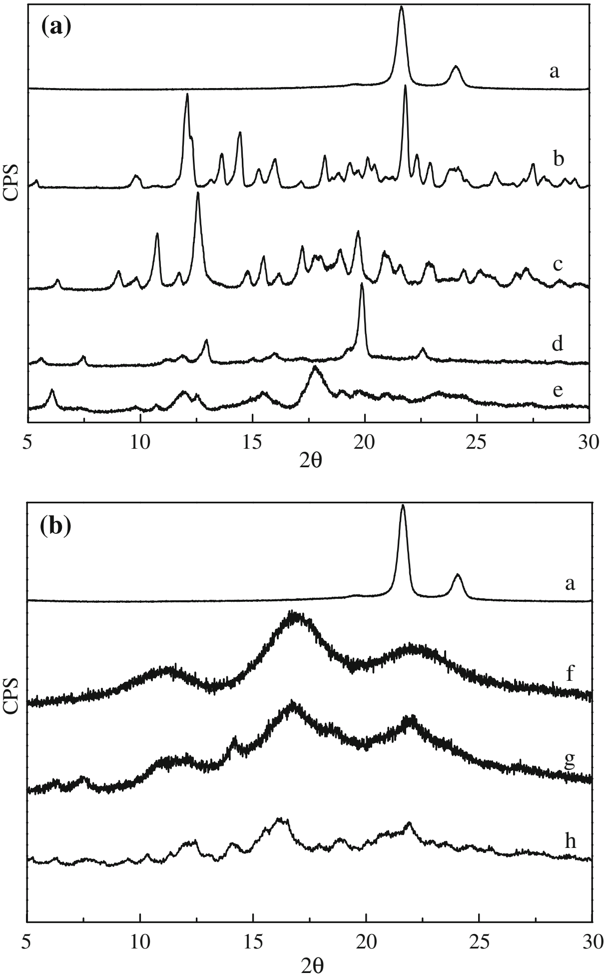

Fig. 5 WAXD patterns of PO1(**a**), α-CD (**b**), β-CD (**c**), α-CD–PO1 IC (**d**), β-CD–PO2 IC (**e**), γ-CD (**f**), γ-CD–PO2 IC (**g**), γ-CD–PO3 IC (**h**)

the free PO molecules, the exothermic peak is attributed to the crystallization of the uncovered portion of the crystalline PO. There is no exothermic peak in the DSC curve of β-CD–PO2 IC because of the high inclusion rate of the IC, resulting in few free PO2 uncovered by β-CD. Although the exothermic peaks of ICs are smaller, the peak temperature of the ICs is higher than that of respective neat POs used as guest molecules of ICs, suggesting that the crystallization in the uncovered PO portion is accelerated. Such behavior is also found in other CD–polymer ICs [20–22] and the accelerated crystallization in the uncovered PO portion is attributed to the supramolecular structure of ICs [22]. These results are another evidence of formation of ICs between CDs and POs.

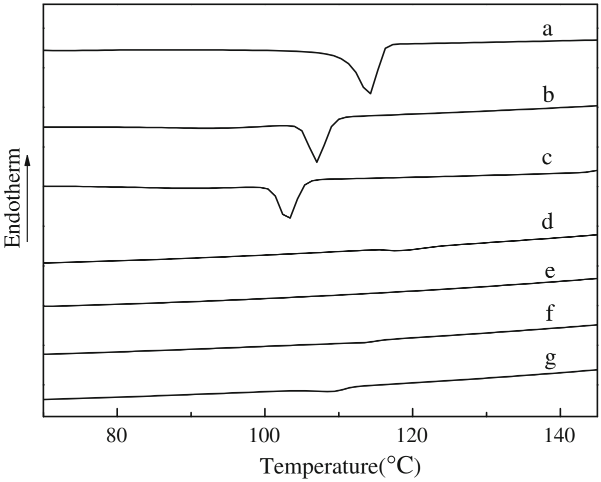

Fig. 6 DSC thermograms during the nonisothermal crystallization of PO1 (**a**), PO2 (**b**), PO3 (**c**), α-CD–PO1 IC (**d**), β-CD–PO2 IC (**e**), γ-CD–PO2 IC (**f**) and γ-CD–PO3 IC (**g**) at a cooling rate of 10 °C/min

Discussion

The formation of the ICs with different CDs and POs demonstrated above and summarized in Table 1 suggests that the cross-sectional areas of polymers and the cavity sizes of the CDs play important roles in the formation of ICs. If the cross-sectional areas of polymer can suit to the cavity size of the CDs, they can form ICs. For example, the PO1 with few side chains can thread into α-CD cavity, and the space between the guest molecule PO1 and host molecule α-CD is suitable to provide enough molecular interaction to obtain stable IC. On the other hand, the cavity space of host molecule β-CD and γ-CD is too large for PO1 to provide enough molecular interaction to obtain stable ICs. Hence, there is no report about the formation of the ICs between oligoethylene with few side chain and β-CD or γ-CD with large cavity.

Because of the large side chains of ethyl in PO2, the cross-sectional areas of PO2 is too large for the cavity size of α-CD to thread into the cavity of α-CD to form IC. On the other hand, PO2 can thread into the CDs with larger cavity size such as β-CD and γ-CD, and the space between guest molecule PO2 and host molecule β-CD (or γ-CD) is suitable to provide enough molecular interaction to form stable ICs. Since the side chain of 2-methyl-propylene in PO3 is too large for the cavity of α-CD and β-CD, it is difficult for the PO3 to thread into their cavity to form IC. On the other hand, the cavity size of γ-CD is large enough for PO3 with large cross-sectional area to thread into the cavity to form IC. Therefore the relation of cross-sectional area of polymer and the cavity size of CDs is important for the formation of IC. If the cross-sectional area of polymer is too small for the cavity size of CD, although the PO molecules can thread into the cavity of CDs, the molecular interaction between CDs and guest molecules is not enough to obtain stable ICs. While if the cross-sectional area of polymer is too large for the cavity size of CD, the polymer can not thread into the cavity of CDs. Thus, it is only possible to form ICs when the CD and polymer have suitable relation of size. Recently it is also found that if the side chain of polymer is large enough, although the main chain of the polymer can not form ICs with any kinds of CDs, the side chain can thread into the CDs and form ICs [23]. So it is a valuable research about the influence of side chain of polymer on the formation of ICs.

Conclusion

We found that IC could not be obtained when the cavity size of CD was small for PO to thread and it was too large for cross-section area of PO. The results suggest that the cross-sectional area of polymer and the cavity size of CDs play critical roles in the formation of ICs. It is only possible to form ICs when the polymer chains can thread into cavities of CDs and there is enough molecular interaction between host molecules and guest molecules.

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