

FORMATION OF THE CRYSTALLINE INCLUSION COMPLEX BETWEEN β -CYCLODEXTRIN AND POLYPROPYLENE*

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Abstract PP can be included in the cavities of cyclodextrin (CD). The crystalline inclusion complex between β -CD and low molecular weight polypropylene (PP) was obtained and investigated. α -CD and γ -CD did not form crystalline inclusion complexes with PP. The FTIR spectra, TGA, X-ray diffraction spectra were studied, ¹H-NMR spectra and ¹³C CP/MAS NMR spectra were used to characterize the crystalline inclusion complexes.

Keywords Cyclodextrin, Self-assembling, Crystalline inclusion complex, Polypropylene

INTRODUCTION

Cyclodextrins (CDs) are a series of cyclic oligosaccharides produced by *Bacillus macerans* during the enzymatic degradation process of starch. The three natural CDs are called α -, β - and γ -CD which consist of six, seven and eight glucose units respectively. CDs are very important host molecules in supramolecular chemistry because they can form inclusion complexes with a wide variety of guest molecules via self-assembling procedures^[1].

In the past decade, many linear polymeric guests were reported to form inclusion complexes with CDs resulting in main-chain pseudopolyrotaxanes^[2–11]. Many kinds of polymers were found to form crystalline inclusion complexes with one or more kinds of CDs. Recently, we reported that poly(1,3-dioxolane) (PDXL) can form crystalline inclusion complexes with all three kinds of CDs^[12, 13].

Some low molecular weight polyolefin chains were also included in the cavities of CDs. Polyisobutylene (PIB) can form crystalline inclusion complexes with β -CD and γ -CD^[14, 15]. Oligoethylene (OE) can form crystalline inclusion complexes with CD^[16].

Here we report that another polyolefin, polypropylene (PP), can form a crystalline inclusion complex with β -CD but not with α -CD and γ -CD. As our work was carrying on, Harada *et al.* has claimed in a review that they had prepared the crystalline inclusion complex β -CD/PP^[17]. But they did not publish their results in detail.

EXPERIMENTAL

Materials

Low molecular weight PP was synthesized as reported before^[18]. The number average molecular weight (M_n) of PP is 1176, which was calculated from the ¹H-NMR spectrum. β -CD provided by Yunan Cyclodextrins Co.,

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Guangdong, China was recrystallized in water. α -CD and γ -CD were kindly supplied by Rohm & Haas Co., and used without further purification.

Measurements

X-ray powder diffraction patterns were taken with Rigaku III Dmax 2500 instrument using Cu-K α radiation. The voltage and the current were set to 25 kV and 25 mA, respectively. Data were collected at a rate of 4 degrees per minute with a step of 0.02 degree over the range $2\theta = 5^\circ$ – 50° . TGA was performed with a Perkin-Elmer Model 7 thermogravimetric analyzer. The samples were put inside the platinum pans, which was hanged in the heating furnace. The weight percentage of remaining material was recorded while the furnace was heating from 50 to 550°C. Nitrogen was used as the purge gas and a heating rate of 10 K/min⁻¹ was employed. ¹H-NMR spectra were recorded with a Bruker AVANCE 500 spectrometer operated at 500 MHz. Solid state ¹³C cross-polarization (CP), magic-angle spinning (MAS) NMR spectrum was recorded with a Bruker DSX-300 spectrometer operated at 75.47 MHz with a sample spinning rate of 4–6 kHz at room temperature. Chemical shifts were referenced to a external standard TMS. CP spectra were acquired with a 3.6 μ s proton 90° pulse, a 1 ms contact time, and a 5 s repetition time.

Preparation of the Crystalline Inclusion Complex

0.5 g β -CD was dissolved in 40 mL water and then 0.05 g PP was added. The mixture was stirred for 24 h at room temperature and allowed to stand overnight. The solution was centrifuged and then the precipitate was washed with water several times, and finally washed with chloroform to remove non-included materials. The product was dried under vacuum up to 90°C for 24 h.

RESULTS AND DISCUSSION

Formation of the Crystalline Inclusion Complex

The appearance of precipitate is considered as the potential evidence for the formation of crystalline inclusion complexes between CDs and polymer chains^[2]. When the β -CD solution and PP were mixed and stirred, white precipitate appeared gradually. The white precipitate is apparently differed from PP, and should be the crystalline inclusion complex formed between β -CD and PP. The yield of the crystalline inclusion complex between β -CD and PP is 67%. Under the same conditions, no precipitate will be produced from the mixture of PP with α -CD or γ -CD. This means only β -CD can form the crystalline inclusion complex with PP. According to molecular modeling, when the PP molecule takes the zigzag conformation, it fits quite snugly in the β -CD's cavity but is too big for α -CD's cavity due to the steric hindrance induced by methyl groups on the main chain. The γ -CD's cavity is apparently too large for a snug fit of the PP.

FTIR Spectral Study

Figure 1 shows the FTIR spectra of β -CD, PP and their crystalline inclusion complex. In the FTIR spectrum of the complex, there are several characteristic absorption bands belonging to both β -CD and PP. The asymmetrical stretching vibration bands of methyl and methylene groups of PP appear at 2961.9 cm⁻¹ and 2920.5 cm⁻¹, respectively, in the crystalline inclusion complex. Also the absorption bands at 2871.3 cm⁻¹ and 2837.7 cm⁻¹ stand for the symmetrical stretching vibration of methyl and methylene groups of PP found in the complex. The deformation vibration of methyl and methylene groups of PP in the crystalline inclusion complex appear at 1379.1 cm⁻¹ and 1461.8 cm⁻¹, respectively. Other regions of the FTIR spectrum of the complex are similar to that of β -CD. These spectral characteristics indicate that crystalline inclusion complex is composed of β -CD and PP.

Thermogravimetric Analysis

Figure 2 shows the TGA Thermogram curves for pure β -CD, PP and the crystalline inclusion complex of β -CD and PP. We can see that β -CD started to decompose at 322°C and the polymer started to decompose at higher temperature. However, the crystalline inclusion complex started to decompose at 337°C, which is higher than that of the pure β -CD. This means the aggregation of the CDs molecules on the polymer chains improved the CD's thermal stability due to the improved interaction between neighboring CD molecules.

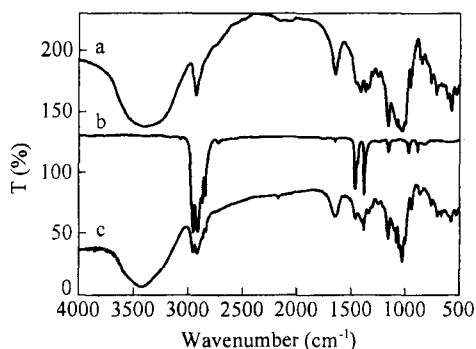


Fig. 1 FT-IR spectra of (a) β -CD, (b) PP and (c) the crystalline inclusion complex of β -CD and PP

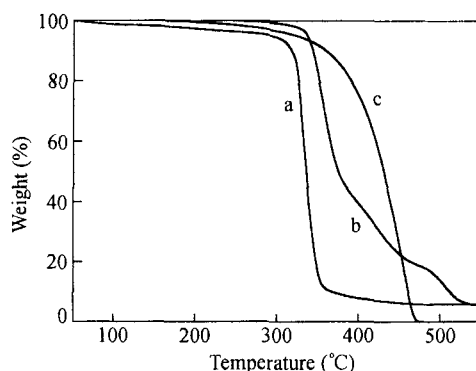


Fig. 2 TGA curves of (a) β -CD, (b) the crystalline inclusion complex and (c) PP

Crystal Structure

The X-ray powder patterns of β -CD and that of the crystalline inclusion complex are shown in Fig. 3. It is reported that the structures of the inclusion complexes of CDs with low molecular weight compounds can be classified as cage type or columnar type^[19, 20]. The number of diffraction peaks of the inclusion complexes is less than that of pure β -CD. There are two major diffraction peaks of the complex at $2\theta = 12.5^\circ$ and 19.6° . The pattern of the β -CD-PP complex is similar to that of the inclusion complex between β -CD and PDXL^[12, 13] or poly(propylene glycol) (PPG)^[21], which have been reported to have the columnar structure. Therefore, it seems that β -CD-PP complex also assumes columnar structures, implying that the PP chains take the linear zigzag conformation and the β -CDs are threaded along the polymer backbones.

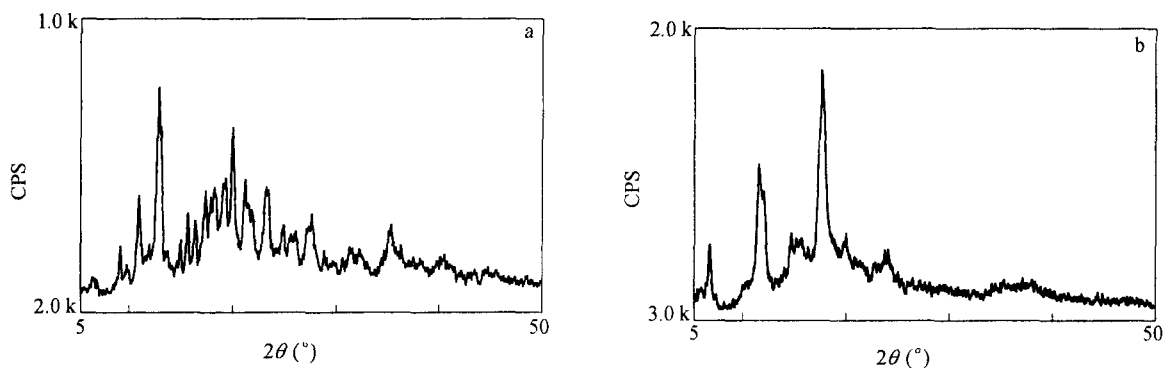


Fig. 3 X-ray diffraction patterns of (a) β -CD and (b) the crystalline inclusion complex

Stoichiometry of the Complex

Figure 4 shows the ^1H -NMR spectrum of PP in CDCl_3 and that of the inclusion complex in $\text{DMSO}-d_6$. In the ^1H -NMR spectrum of the solution of inclusion complex, we could find hydrogen atom signals belonging to both β -CD and PP molecules. From the molecular modeling, if a PP chain assumes a zigzag conformation, the length of each propylene repeating unit, propylene, will be 0.23 nm. The depth of β -CD molecules is 0.7 nm. Therefore, one β -CD molecule can hold 3 propylene repeating units theoretically. The real composition of the crystalline inclusion complex could be obtained by comparing the peak integrations for its constituents. About 3.1 repeating units were found to bind to a β -CD molecule by comparing the integrals of the peak of C1 hydrogen atom on β -CD and that of the methyl groups on propylene units. This indicates that the β -CDs are arranged one by one closely on the polymer chains.

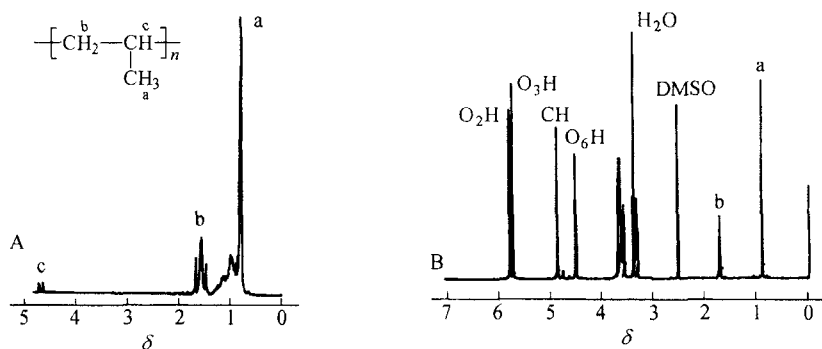


Fig. 4 ^1H -NMR spectra of (A) PP and (B) the crystalline inclusion complex in $\text{DMSO}-d_6$

CD's Conformation

Figure 5 presents the ^{13}C CP/MAS NMR spectrum of the β -CD and that of the crystalline inclusion complex. β -CD assumes a less symmetrical conformation in the crystal when it does not contain a guest in the cavity. In this case, the spectrum shows resolved C-1 and C-4 resonance from each of the α -1,4-linked glucose residues. On the other hand, in the spectrum of the β -CD-PP complex, each carbon of glucose can be observed as a single peak. These results indicate that in the crystalline inclusion complex, β -CD adopts a symmetrical conformation and each glucose unit of β -CD is in a similar environment. The X-ray study of single crystals of the inclusion complex formed between β -CD and *p*-nitroacetanilide shows that β -CD adopts a symmetrical conformation when it contains a guest in the cavity^[22]. The ^{13}C CP/MAS NMR spectrum of the β -CD and the crystalline inclusion complex is consistent with the data of X-ray studies.

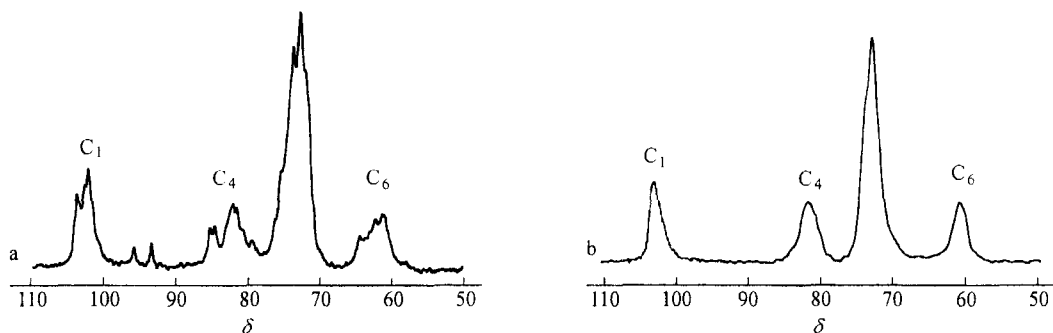


Fig. 5 ^{13}C CP/MAS NMR spectra of (a) β -CD and (b) the crystalline inclusion complex

CONCLUSION

Crystalline inclusion complex was formed between β -CDs and PP but not between α -CD, γ -CD and PP. FTIR spectra elucidate the formation of this complex. Thermograms showed that the complex formation improved the thermostability of β -CD. The X-ray powder pattern of the product demonstrated that the resultant inclusion complex is crystalline and has the columnar structure. The ^1H -NMR spectra showed that the β -CD molecules were arranged one by one closely on the polymer chains. ^{13}C CP/MAS NMR spectra of the crystalline inclusion complex indicate that CDs adopt a more symmetrical conformation in the complex, while pure CD assumes a less symmetrical conformation in the crystal without a guest inside its cavity.

REFERENCES

- 1 Szejtli, J., "Cyclodextrins and Their Inclusion Complexes", Akademiai Kiado, Budapest, 1982

- 2 Harada, A. and Kamachi, M., *Macromolecules*, 1990, 23: 2821
- 3 Wenz, G. and Keller, B., *Angew. Chem. Int. Ed., Engl.*, 1992, 31: 197
- 4 Weickenmeier, M. and Wenz, G., *Macromol. Rapid Commun.*, 1997, 18: 1109
- 5 Huang, L., Allen, E. and Tonelli, A.E., *Polymer*, 1999, 40: 3211
- 6 Lu, J., Shin, I.D., Nojima, S. and Tonelli, A.E., *Polymer*, 2000, 41: 5871
- 7 Lu, J., Mirau, P.A. and Tonelli, A.E., *Macromolecules*, 2001, 34: 3276
- 8 Li, J.Y., Yan, D.Y., Jiang, X.L. and Chen, Q., *Polymer*, 2002, 43: 2625
- 9 Li, J.Y. and Yan, D.Y., *Macromol. Chem. Phys.*, 2002, 203: 155
- 10 Jiao, H., Goh, S.H. and Valiyaveetil, S., *Macromolecules*, 2001, 34: 8138
- 11 Jiao, H., Goh, S.H. and Valiyaveetil, S., *Macromolecules*, 2002, 35: 1399
- 12 Li, J.Y. and Yan, D.Y., *Macromolecules*, 2001, 34: 1542
- 13 Li, J.Y., Yan, D.Y. and Chen, Q., *Science in China B*, 2002, 45: 73
- 14 Harada, A., Li, J., Suzuki, S. and Kamachi, M., *Macromolecules*, 1993, 26: 5267
- 15 Harada, A., Suzuki, S., Okada, M. and Kamachi, M., *Macromolecules*, 1996, 29: 5611
- 16 Li, J., Harada, A. and Kamachi, M., *Bull. Chem. Soc. Jpn.*, 1994, 67: 2808
- 17 Harada, A., Okada, M., Kawaguchi, Y. and Kamachi, M., *Polym. Adv. Technol.*, 1999, 10: 3
- 18 Zhang, F., Mu, Y., Chen, C.X., Zhao, L.G., Zhai, H.M., Zhang, Y.T. and Wang, J.H., *Proceeding of CCE Congress* 2000, 2000, p.581
- 19 Sanger, W., "Jerusalem Symposium on Quantum Chemistry and Biochemistry", ed. by Pullman, B.D., Reidel Co., Dordrecht, 1976
- 20 McMullan, R.K., Saenger, W., Fayos, J. and Mootz, D., *Carbohydr. Res.*, 1973, 31: 37
- 21 Harada, A., Okada, M., Li, J. and Kamachi, M., *Macromolecules*, 1995, 28: 8406
- 22 Harding, M.M., MacLennan, J.M. and Paton, R.M., *Nature*, 1978, 274: 621