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Formation of the crystalline inclusion complex between γ-cyclodextrin and poly(*N*-acetylethylenimine)

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Abstract

Poly(*N*-acetylethylenimine) was found to form a crystalline inclusion complex with γ-cyclodextrin (CD). It did not form crystalline inclusion complexes with α-CD or β-CD. It is a hydrophilic, nitrogen atom-containing polymer that forms a crystalline inclusion complex with CD. FT-IR spectroscopy, thermogravimetry analysis, X-ray diffraction, ^{1}H NMR spectra and ^{13}C CP/MAS NMR spectra were used to characterize the structure and property of the crystalline inclusion complex. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: γ-Cyclodextrin; Crystalline inclusion complex; Poly(*N*-acetylethylenimine)

1. Introduction

Cyclodextrins (CDs) are well-known as molecular hosts for they can form inclusion complexes with a wide variety of low molecular weight compounds ranging from non-polar organic molecules to rare gases [1]. They are a series of cyclic starch oligomers consisting of six, seven and eight glucose units called α-, β- and γ-CD, respectively. The formation of the host–guest inclusion complexes is very useful in designing and constructing the nanometer scale ordered structures.

Much attention has been given in recent years to the formation between linear polymeric guests and CDs resulting in main-chain pseudopolyrotaxanes [2–5]. Among those linear polymers that can form inclusion complexes with CDs, poly(iminooligomethylene)s [6,7], viologen polymers and ionene polymers [8–11] are the special ones. They contain nitrogen atoms on their main chains and form soluble inclusion complexes with geometric available CDs. The reason given by the authors of the solubility of those inclusion complexes is that the hydrophilic groups on the main chains, those imino groups and cationated nitrogen atoms, are not included in the CDs' cavities.

Here we report that a hydrophilic polymer, poly(*N*-acetylethylenimine) (PAEI), which contains nitrogen atoms on its main chain, can form crystalline inclusion complex with γ-CD. But it did not form crystalline inclusion complexes with α- and β-CDs because of the geometric unfitness.

2. Experimental

2.1. Materials

2-Methyl-2-oxazoline was purchased from Aldrich Co. and used as received. β-CD (Yunan Cyclodextrins Co., Guangdong, China) was recrystallized in water. α-CD and γ-CD (Cavamax W6 and W8) were kindly supplied by Rohm and Haas Co., and used without further purification. Benzyl bromide of analytical degree was brought from Shanghai Xinda Chemical Factory.

2.2. Measurements

FT-IR spectra were measured with a Perkin–Elmer Paragon 1000 spectrometer. Samples were pressed into KBr pellets and recorded at frequencies from 4400 to 450 cm^{-1} with resolution of 4 cm^{-1}. Number average molecular weight measurement was performed with a K-7000 (Knauer Co., German) vapor pressure osmometer (VPO) using $CHCl_3$ as solvent and polyethylene glycol (for HPLC, $M_n = 6000$) as standard material. The working temperature was 35 °C. X-ray powder diffraction patterns were taken by a Rigaku III Dmax 2500 using Cu-Kα

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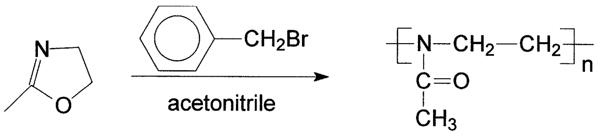

Scheme 1. Synthesis of poly(*N*-acetylethylenimine).

radiation. The voltage was set to 25 kV and the current was set to 25 mA. Data were collected at a rate of 4° $\min^{-1}$ with a step of 0.02° over the range $2\theta = 5$–50°. Thermogravimetry analysis (TGA) was determined with a Perkin–Elmer Model 7 thermo gravimetric analyzer. The samples were put inside the platinum pans, which were hanging 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 °C $\min^{-1}$ was employed. ^{1}H NMR spectra were recorded with a Brucker AVANCE 500 spectrometer operated at 500 MHz. Solid state ^{13}C cross-polarization (CP), magic-angle spinning (MAS) NMR spectrum was recorded with a Brucker DSX-300 spectrometer operated at 75.47 MHz with a sample spinning rate of 4–6 kHz at room temperature. CP spectra were acquired with a 3.6-μs proton 90° pulse.

2.3. Synthesis of the polymer

PAEI was prepared via ring-open isomerization polymerization under nitrogen atmosphere using benzyl bromide as the initiator at 80 °C for 24 h [12,13]. The product was then solved in methanol and precipitated out. It was dried under vacuum at 70 °C for 24 h. The number average molecular weight of PAEI is 1824, which was determined by VPO in ethanol (Scheme 1).

2.4. Preparation of inclusion complexes

Normal method. 1.0 g γ-CD was dissolved in 10 ml water, and then 0.1 g PAEI was added. The mixture was stirred at room temperature for 3 days, and allowed to stand overnight. The precipitate was centrifuged, and then washed with water several times to remove those non-included materials. The product was dried under vacuum up to 90 °C for 24 h.

Ultrasonic method. Ultrasonications were performed in a Brason B-52 ultrasonic cleaner with power of 248 W. PAEI was added into the saturated γ-CD solution, and then the mixture was ultrasonicated for 30 min at room temperature, and allowed to stand overnight. The precipitate was filtered, washed with water several times to remove those non-included materials. The product was dried under vacuum up to 90 °C for 24 h.

2.5. Molecular weight of uncomplexed polymer

The solution after centrifugation was collected. $CHCl_3$ was used to extract uncomplexed polymer and then was vaporized. The number average molecular weight of uncomplexed PAEI is 1978, which was determined by VPO in ethanol.

3. Results and discussion

3.1. Formation of the crystalline inclusion complex

When the mixture of PAEI with γ-CD was stirred at room temperature, white precipitates gradually appeared. The appearance of precipitate is considered as potential evidence for the formation of crystalline inclusion complexes between CDs and polymer chains [2–5]. The white precipitates should be the crystalline inclusion complex between PAEI and γ-CD, because both PAEI and CD are water-soluble. Under the same conditions, there was no product when PAEI was mixed and stirred with α- and β-CD solutions and the solutions kept clear.

The yield of the crystalline inclusion complex between PAEI and γ-CD is about 15%, which is very low. The precipitate procedure is rather slow under the normal method and it needs 3 days to reach such yield. The ultrasonic method can speed up the procedure and in 30 min the yield can reach 15%. But it cannot improve the yield with prolonged ultrasonic reaction time.

The number average molecular weight of those uncomplexed polymer is slightly higher than that of the original PAEI used. This means that the γ-CD tend to form crystalline inclusion complex with low molecular weight analogs of the polymer. From the result of VPO, we can calculate that the number average molecular weight of the complexed polymer is about 951.

From the molecular modeling, the chains of PAEI are too big for α- and β-CD due to the acetyl side-groups. So only the γ-CD which has the biggest cavity size among the three natural CDs can form inclusion complex with PAEI.

3.2. FT-IR study

FT-IR is a useful tool to prove the presence of both guest and host components in the inclusion complex. The FT-IR spectra of PAEI, γ-CD and the crystalline inclusion complex between γ-CD and PAEI in the region from 450 to 4400 cm^{-1} are presented in Fig. 1. The γ-CD spectrum shows a band at 3414.0 cm^{-1} due to the symmetric and antisymmetric O–H stretching mode, a band at 2930.4 cm^{-1} due to the C–H stretching mode, and other bands at low wave number. In the spectrum of PAEI, the band at 3445.5 cm^{-1} is caused by the water absorbed by the hydrophilic polymer. Some bands of the host and guest are affected by the formation of the inclusion complex resulting in a change of position and relative intensities. The band at 3414.0 of the γ-CD is shifted to lower frequency at 3369.2 cm^{-1} in the inclusion complex. The most distinctive

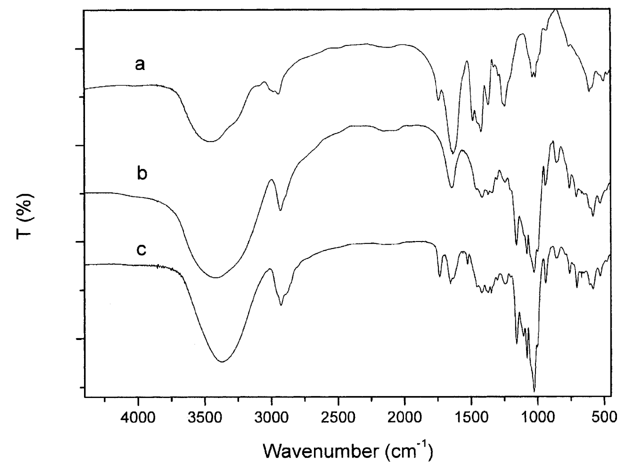

Fig. 1. FT-IR spectra of (a) PAEI, (b) γ-CD and (c) the crystalline inclusion complex between γ-CD and PAEI.

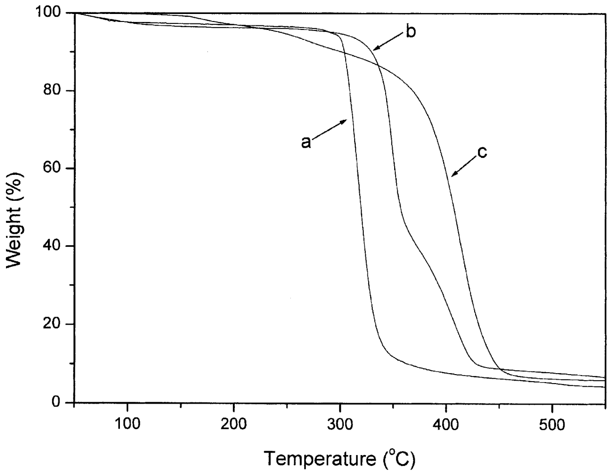

Fig. 2. TGA thermograms of (a) γ-CD, (b) the crystalline inclusion complex between γ-CD and PAEI and (c) PAEI.

band at 1741.5 cm^{-1}, which is assigned to the C=O stretching band for PAEI can also be found in the crystalline inclusion complex, but it is shifted down to 1734.9 cm^{-1}. In the region from 1500 to 450 cm^{-1}, the positions and relative intensities of the bands of the inclusion complex are very similar to those of the γ-CD. This means that the polymer chains were included into the CD's cavities.

3.3. Thermogravimetry analysis

The TGA thermograms for γ-CD, PAEI and the crystalline inclusion complex between γ-CD and PAEI are presented in Fig. 2. We can find that γ-CD started to decompose at 299 °C. PAEI began to decompose from about 160 °C with a slow-down curve and when the temperature was up to 370 °C the curve was sharply down. However, the crystalline inclusion complex started to decompose at 325 °C, which is also higher than that of the pure γ-CD. This indicates that the aggregation of the γ-CD molecules can improve their thermal stability. Because the guest polymer is in the cavity of the γ-CD molecules, it should decompose after the decomposition of the host molecules.

3.4. Crystal structure

The X-ray powder patterns of γ-CD and those of the inclusion complex between γ-CD and PAEI are displayed in Fig. 3. The pattern of the crystalline inclusion complex between γ-CD and PAEI is different from that of pure γ-CD where CDs are arranged in a cage type packing [14–16]. The pattern of the crystalline inclusion complex between PAEI and γ-CD has two main peaks at $2\theta = 15.2$ and 21.5°. It is similar to those of the inclusion complexes between γ-CD and poly(alkyl vinyl ether) [17]or poly(1,3-dioxolane) [18] and so on, which have been reported to have the columnar structure. Therefore, the inclusion complex of PEAI with γ-CD assume a columnar structure rather than a cage type structure.

3.5. Stoichiometry of the complex

Fig. 4 shows the ^{1}H NMR spectra of PAEI and that of the inclusion complex between PAEI and γ-CD in DMSO-d_6. In the ^{1}H NMR spectra of the dissolved inclusion complex, we find hydrogen atom signals assigned to both CD and PAEI molecules. According to the molecular modeling, if a

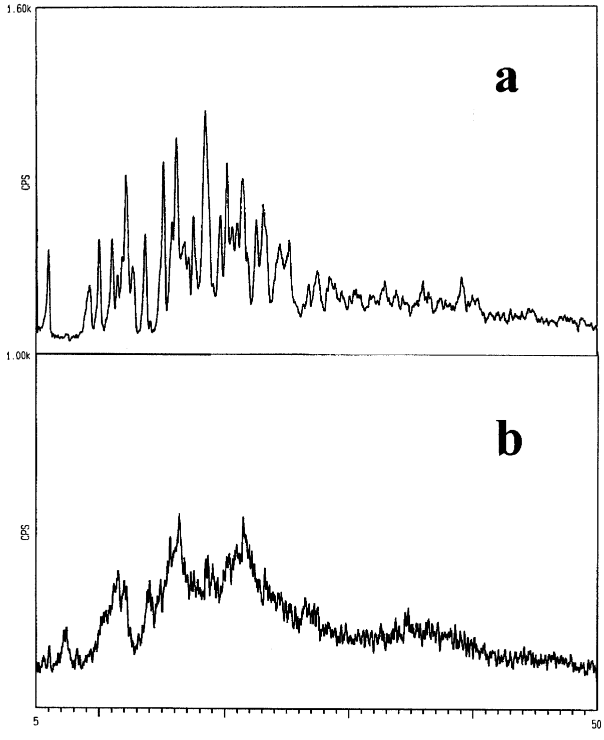

Fig. 3. X-ray powder patterns of (a) γ-CD and (b) the crystalline inclusion complex between γ-CD and PAEI.

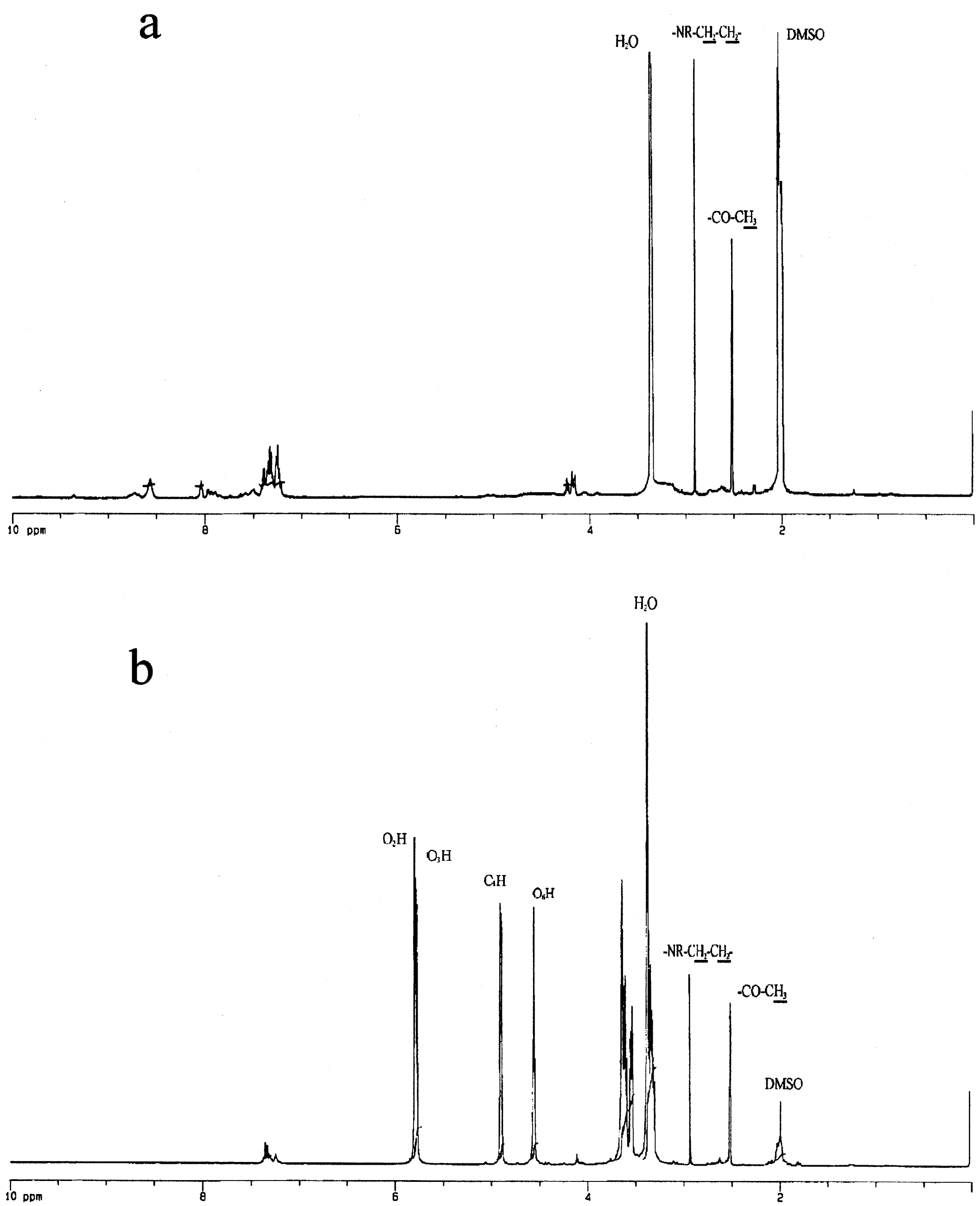

Fig. 4. ^{1}H NMR spectra of (a) PAEI and (b) the crystalline inclusion complex between γ-CD and PAEI in DMSO-d_6.

PAEI chain takes the zigzag configuration, the length of one *N*-acetylethylenimine unit is calculated as 0.35 nm. The depth of γ-CD molecules is 0.7 nm. Therefore, one γ-CD molecule can contain 2.0 *N*-acetylethylenimine repeating units theoretically if single polymer chain was contained in the cavities of γ-CDs. The experimental ratio of the PAEI (repeating units) to γ-CD is about 0.54 by comparing the integrals of the peak of C1 hydrogen atom on γ-CD with those of the ethylene groups on *N*-acetylethylenimine units. The experimental ratio is quite coincident to the theoretical one that means the inclusion complex is near perfect in stoichiometry.

3.6. CD's conformation

^{13}C CP/MAS NMR spectra of the γ-CD and the crystalline inclusion complex between γ-CD and PAEI are presented in Fig. 5. γ-CD assumes a less symmetrical conformation in the crystal when it does not include a guest in the cavity [19]. The spectrum of the pure γ-CD shows resolved C-1 and C-4 resonance from each of the α-1,4-linked glucose residues. However, in the spectra of the crystalline inclusion complex between γ-CD and PAEI, each carbon of glucose is in a single peak. As polymer chains were included in the γ-CD molecules' cavities, one

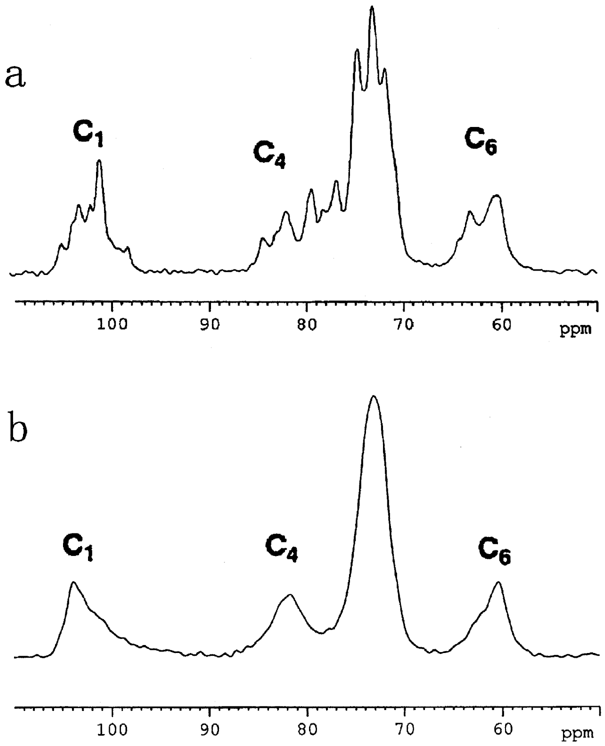

Fig. 5. ^{13}C CP/MAS NMR spectra of (a) γ-CD and (b) the crystalline inclusion complex between γ-CD and PAEI.

can visualize that the cavities were swelled up and the molecules were of cylindrical shape. Therefore, the result indicates that in the crystalline inclusion complex, γ-CDs adopt the symmetrical conformation and every glucose unit of γ-CDs is in similar environment.

4. Conclusion

The crystalline inclusion complex between PAEI and γ-CD was obtained and studied. α- and β-CDs did not form crystalline inclusion complexes with PAEI due to the geometric unfitness. FT-IR spectra show that the inclusion complex is combined by the PAEI and γ-CD. TGA shows that the formation of the crystalline inclusion complex can improve the thermo stability of γ-CD. X-ray powder patterns of those products shows that the resultant inclusion complexes is crystalline and has the columnar structure. H NMR spectra give the stoichiometry between γ-CD and polymer in the complex. ^{13}C CP/MAS NMR spectra of crystalline inclusion complex indicate that γ-CD adopts a more symmetrical conformation in the complexes, while pure γ-CD assumes a less symmetrical conformation in the crystals without guests inside its cavity.

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