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Inclusion Compounds Formation of Poly(azomethine ether)s and β-Cyclodextrin

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In this study, two poly(azomethine ether)s were synthesized and they can form inclusion compounds (ICs) with β-cyclodextrin (β-CD). Fourier transform infrared (FTIR) spectroscopy, ^{1}H nuclear magnetic resonance spectroscopy (^{1}H-NMR), thermogravimetric analysis (TGA), X-ray diffraction (XRD) have been utilized to observe the formation of polymer-CD-ICs. The differentiation in their FTIR spectra may indicate the formation of the inclusion compounds between poly(azomethine ether)s and β-CD. Compared the ^{1}H-NMR of polymer-CD-ICs with β-CD, proton signals belonging to both β-CD and poly(azomethine ether)s can be found in the spectrum. The chemical shift of the protons H-3, H-5 has changed after the formation of inclusion compounds, which is perhaps due to the interaction of these protons with polymers. TGA scans showed the much higher decomposition temperatures observed for two polymer-CD-ICs may imply that polymer chains included inside the β-CD's cavity can greatly improve β-CD's stabilities. The X-ray diffraction patterns were confirmed to be the new crystal structures.

Keywords: cyclodextrin; poly(azomethine ether)s; inclusion compounds

1 Introduction

In recent years, supramolecular polymer chemistry has become a new domain of macromolecular research. A great deal of unique supramolecular architectures have been prepared as novel composite host-guest polymeric assemblies (1, 2). Cyclodextrins (CDs) is one of the most important host molecules which could construct molecular assemblies. CDs are cyclic oligosaccharides consisting of six, seven, or eight glucose units linked by 1,4-glucosidic bonds. They have rigid, well-defined ring structures and the ability to include various compounds. The cone-shaped cavities of CDs can act as hosts for a great variety of molecular guests. Supramolecular inclusion compounds stabilized by noncovalent interactions can be formed by threading CD molecules onto polymer chains. Since Harada's group reported (3) the first inclusion compounds of α-CD with poly(ethylene glycol), a great number of reports have described various kinds of polymeric guest, possessing either hydrophilic or hydrophobic properties, have the ability to form inclusion compounds with the different types of CDs (1–22).

Poly(azomethine ether)s, as a kind of particularly attractive polymers, have received considerable attention in the recent years owing to their potential applications such as information storage, nonlinear optics, laminates and films with good thermal stability and chemical resistance (23–28), fibers possess excellent mechanical properties (29). Poly(azomethine)s was first prepared by Adams' group from terephthalaldehyde and dianisidene (30). However, poor solubility in common organic solvents and difficult to liquate limited poly(azomethine)s' practical applications in various fields. Thus, many research groups have committed themselves to synthesize the soluble poly(azomethine)s through introducing alkyl or alkoxy chains into the polymers or inserting solubility enhancing groups in the backbone (31). In view of these, and in continuation of our previous work on the supramolecular chemistry (32–34), we synthesized and characterized of two poly(azomethine ether)s obtained by polycondensation reactions of 4,4′-methylenedianiline with aliphatic-aromatic dialdehydes. At the same time, we prepared the inclusion compounds of poly(azomethine ether)s and β-CD. We found that linear poly(azomethine ether)s could form inclusion compounds with β-CD. Fourier transform infrared (FTIR) spectroscopy, ^{1}H nuclear magnetic resonance spectroscopy (^{1}H-NMR), thermogravimetric analysis (TGA) and X-ray diffraction (XRD) were utilized to characterize these inclusion compounds. Owing to the interesting properties of linear aliphatic-aromatic poly(azomethine ether)s, it is

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interesting to introduce them to cyclodextrins. The scope of this preliminary paper is to present the synthesis of the inclusion complexes based on aliphatic-aromatic poly(azomethine ether)s as linear polymer and β-cyclodextrin as macrocyclic compound. The next step in our studies is to analyze the structure of polymer-CD-ICs in detail and study electro-optical properties of this kind of inclusion complexes. As Tonelli's group indicated, the study of these types of inclusion compounds provides an opportunity to investigate the behavior of single polymer chains or two adjacent parallel chains in isolated and well-defined environments (10).

2 Experimental

2.1 *Apparatus*

Melting points were determined in open capillaries and are uncorrected. FTIR spectra were recorded with a Nexus 670X FTIR spectrometer as KBr pellets. ^{1}H-NMR spectra were recorded with a Mercury Plus-400 MHz spectrometer in DMSO-d_6 with TMS as internal standard. TGA was carried out with DT-40 thermogravimetric analyzer. Analysis was performed at room temperature to 800°C at a heating rate of 10°C/min with nitrogen used as purge gas. XRD was performed on D/MAX-IIIC X-ray Diffractometer. The radiation source used Cu Kα radiation with a wavelength of 0.154 nm. The voltage was set to be 40 KV and the current 40 mA. Samples were placed on a sample holder and scanned from 3 to 50° in 2θ at a speed of 5°/min.

2.2 *Reagents*

4,4'-methylenedianiline, *p*-hydroxybenzaldehyde and α, ω-dibromoalkane were supplied by Shanghai Reagent Factory (China). β-CD was recrystallized twice from distilled water and dried in vacuum prior to use. Other chemicals were used as received without further purification.
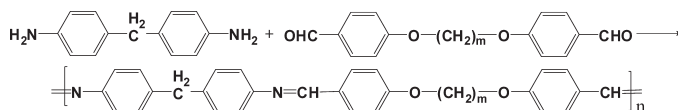
2.3 *Synthesis*

2.3.1 *Syntheses of Dialdehydes of Monomer*

Dialdehydes were synthesized according to the reactions presented in Scheme 1.

4,4'-Diformyl-α,ω-diphenoxyalkane were prepared as follows (35): Anhydrous sodium carbonate (0.25 mol) and the appropriate dibromoalkane (0.1 mol) dissolved in DMF (25 ml) were added into a 250 ml three-necked flask equipped with a condenser and magnetic stir bar. Then,
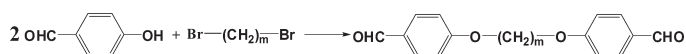
Sch. 1. Synthesis of the aliphatic-aromatic dialdehydes M$_1$: m = 2 M$_2$: m = 4.

Sch. 2. Synthesis of poly(azomethine ether)s P$_1$: m = 2, P$_2$: m = 4.

a solution of 4-hydroxybenzaldehyde (0.2 mol) in DMF (25 ml) were also added to the reaction flask. The mixture was stirring and then refluxed at 120°C for 4 h. After cooling, the product was poured into cold water (about 500 ml) and allowed to stand overnight in a refrigerator. The precipitate was filtered off, washed with water, dried under vacuum and recrystallized from ethanol.

4,4'-(Propane-1,3-diylbis(oxy))dibenzaldehyde (n = 2). Yield: 55%. M.p.: 110−112°C. ^{1}H-NMR (DMSO-*d6*) (δ, ppm): 9.79 (s, 1H, -CHO), 7.19−7.91 (s, 8H, aromatic protons), 4.50 (t, 4H,-O-CH$_2$-).

4,4'-(Butane-1,4-diylbis(oxy))dibenzaldehyde (n = 4): Yield: 60%. M.p.: 102−104°C. ^{1}H-NMR (DMSO-*d6*) (δ, ppm): 9.88 (s, 1H, -CHO), 7.13−7.89 (s, 8H, aromatic protons), 4.18 (t, 4H, -O-CH$_2$-), 1.93 (m, 4H, -CH$_2$-).

2.3.2 *Synthesis of Poly(azomethine ether)s*

The synthesis of polymers and the structure of the poly(azomethine ether)s are given in Scheme 2.

4,4'-Methylenedianiline (1 mmol) dissolved in absolute ethanol (20 ml) were added into a 250 ml three-necked flask equipped with a condenser and a magnetic stir bar. Then, the dialdehydes (1 mmol) was added to this solution. The mixture was stirred 6 h at reflux under dry nitrogen. The polymer precipitate was isolated by filtration, and then washed with hot methanol, hot acetone and then dried in vacuum.

2.3.3 *Synthesis of Inclusion Compounds*

A small amount of NMP solution of poly(azomethine ether)s (0.05 wt.%) was mixed with a certain amount of saturated aqueous solution of β-CD with the ratio of 1:24 at 70°C. The mixed solutions of polymer and β-CD were stirred on a hot plate at 70°C for 9 h. After storing quiescently overnight at room temperature, the white precipitate was filtered and dried in a vacuum oven at 60°C for at least 24 h.

3 Results and Discussion

Because neither polymer is soluble in common organic solvents, their molecular weights could not be obtained. We did not perform viscosity measurements because the solubilization of poly(Schiff base)s in sulphuric acid leads to the scission of azomethine linkage. It has already indicated by the IR spectra recorded for 1,3,4-oxadiazole containing polyazomethine before and after viscosity measurements by Yasuo Saegusa (36).
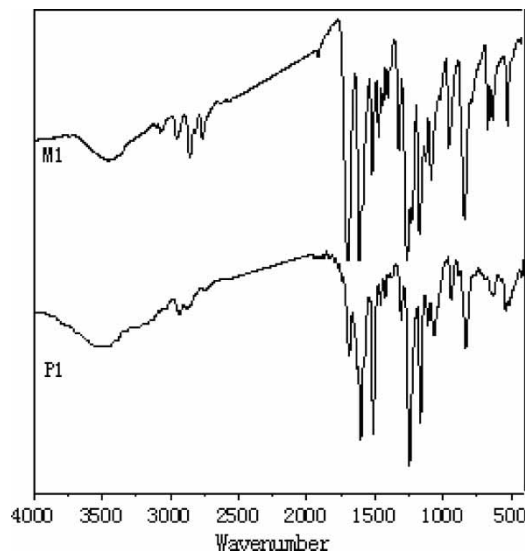
Fig. 1. IR spectra of P_1 and M_1.

Fig. 3. IR spectra of β-CD, P_1 and P_1-CD-IC.

3.1 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra showed the obvious differentiation in the spectra of two polymers in comparison with the spectra of the corresponding monomers, respectively. The IR spectra of monomers show the strong bands at $825-830 \text{ cm}^{-1}$ maybe attributed to out of plan bending of aromatic rings. The appearance of the bands at $2943-2949 \text{ cm}^{-1}$ is the characteristic peak of C-H aliphatic. The appearance of band at 1683 cm^{-1} indicates the aldehyde end group.

There are visible and significant changes in the spectra of the polymers. The characteristic absorption band of azomethine(-CH=N-) appeared at 1601 cm^{-1} with diminution of the absorption bands of aldehyde at 1683 cm^{-1} which confirms the formation of azomethine linkages in the polymer backbone. The intense bands in the region $1240-1250 \text{ cm}^{-1}$ and at 1164 cm^{-1} in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the ether linkage (Figures 1 and 2).

It has been demonstrated that FTIR is a very useful tool to prove whether there are supramolecular interactions in inclusion compounds. Figures 3 and 4 present the FTIR spectra of β-CD, polymer and polymer-CD-ICs in the region from 4000 cm^{-1} to 400 cm^{-1}.

The pure β-CD spectrum shows the broad band at 3404 cm^{-1} was assigned to symmetric and anti-symmetric O-H stretching modes. It shifted slightly to a lower frequency at 3378 cm^{-1} after the formation of the inclusion compounds. This may be caused by the non-covalent interaction between β-CD and the polymer backbones. Bands in the $1200-800 \text{ cm}^{-1}$ region were very similar for both β-CD and polymer-CD-ICs. These

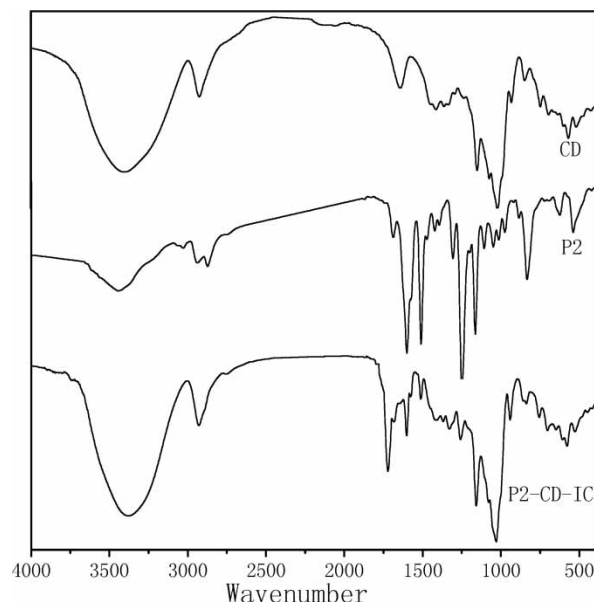**Fig. 2.** IR spectra of P_2 and M_2.

Fig. 4. IR spectra of β-CD, P_2 and P_2-CD-IC.

bands are referred to as stretching modes of the glucosidal group coupled with C-C and C-O stretching modes (37).

The intense peak at 1601 cm^{-1} attributed to the -CH=N- stretching vibration diminished after formation of polymer-CD-ICs. This may be due to the interaction between β-CD and polymers. The band at 1030 cm^{-1} was greatly enhanced, which showed that bend vibration of O-H in the molecule of β-CD was increased. The band at 1156 cm^{-1} was also greatly enhanced, which showed that the C-C bond was stretched in the ring of β-CD. These results might be contributed by the effect between poly(azomethine ether)s and β-CD.

3.2 ^{1}H Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR)

^{1}H-NMR spectroscopy is found to be the most effective tool for the study of inclusion compounds formation between cyclodextrins and guest molecules (38). To attribute to the poor solubility of the poly(azomethine ether)s in common organic solvents, their ^{1}H-NMR spectra could not be properly recorded. They were only obtained and compared to the β-CD with polymer-CD-ICs' ^{1}H-NMR spectra.

Figure 5 shows the ^{1}H-NMR spectrum of β-CD and polymer-CD-ICs in DMSO-d_6. Proton signals belonging to both β-CD and poly(azomethine ether)s can be found in the spectrum. The

azomethine (-CH=N-) proton appeared at 9.9 ppm, the aromatic protons ortho to the -OCH$_2$- appeared at 6.1 ppm and the aromatic protons meta to the -OCH$_2$- resonate at 7.9 ppm, the azomethine containing phenyl ring resonate at 8.2 ppm. The -OCH$_2$- groups of the spacer appeared at 3.6 and 4.2 ppm, while the -CH$_2$- spacers resonate in the region of 1.9 ppm.

Usually slight changes in the chemical shifts of β-CD can be observed due to the change of chemical environments as a consequence of the inclusion compounds. The resonances of β-CD protons located in the interior of the cavity (H-3 and H-5) show remarkable chemical shifts upon inclusion of the guest molecule. A small shift is observed for the resonances H-1, H-2, and H-4, which are in the exterior of the cavity. The H-6 protons are at the smaller rim of the cavity and in most cases show a chemical shift slightly larger than those of the exterior protons (H-1, H-2, and H-4).

3.3 Thermogravimetric Analysis (TGA)

The thermal stabilities of β-CD, polymer and polymer-CD-ICs were investigated by TGA. Figures 6 and 7 display the TGA of β-CD, polymer and polymer-CD-ICs up to 800°C, respectively.

The decomposition point of two poly(azomethine ether)s are at 400°C, 97% (P$_1$) of original weight was lost at 792°C

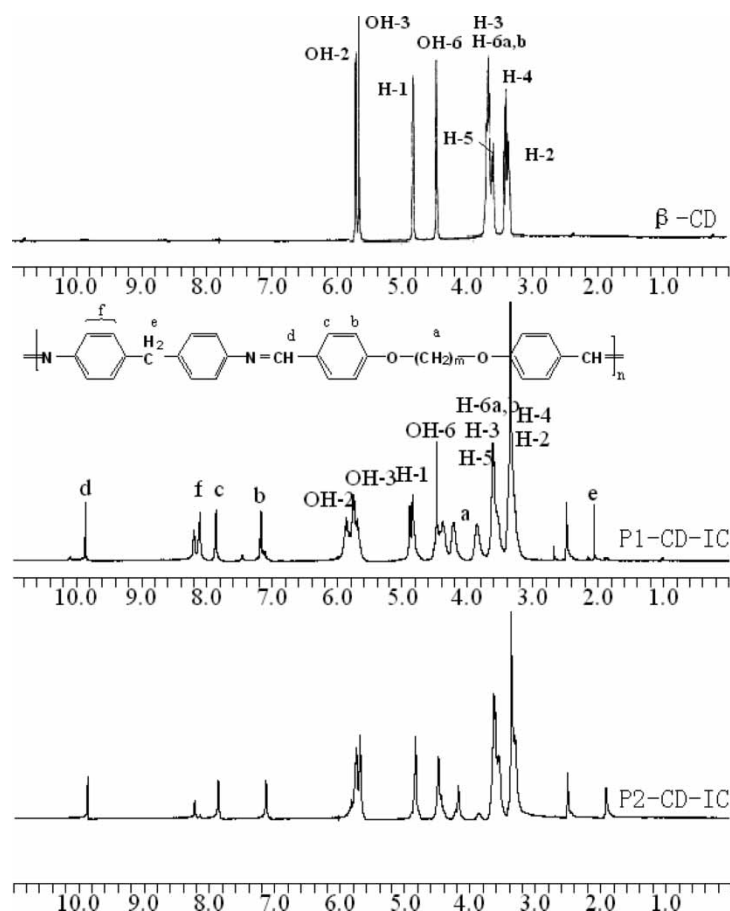**Fig. 5.** ^{1}H-NMR spectra of β-CD, P$_1$-CD-IC and P$_2$-CD-IC in D$_2$O.

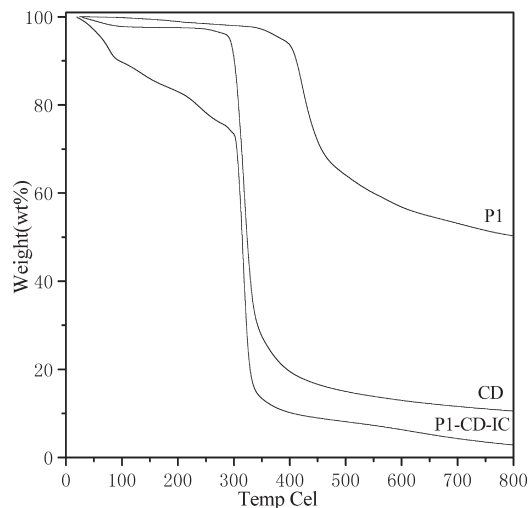**Fig. 6.** The TGA trace of β-CD, P_1 and P_1-CD-IC.

Fig. 8. XRD patterns of β-CD, P_1 and P_1-CD-IC.

and 95% (P_2) of original weight was lost at 784°C. This differentia of polymers means that the nuance in spacers (two methylene groups) has great influence on their thermal stability.

β-CD started to decompose at 275°C, while two polymer-CD-ICs showed the different decomposition temperatures at 285°C and 292°C, respectively. This phenomenon of the different decomposition temperatures in polymer-CD-ICs may imply that the polymer chains included inside the channels can change β-CD's stability.

The results show that the inclusion compounds started to decompose at the lower temperature than poly(azomethine ether)s. This might imply that the β-CD component in the polymer-CD-ICs lowered the thermal stability of poly(azomethine ether)s. At the same time, the polymers' thermal stability is degressive result that the practical applications of this kind of polymer maybe accessible.
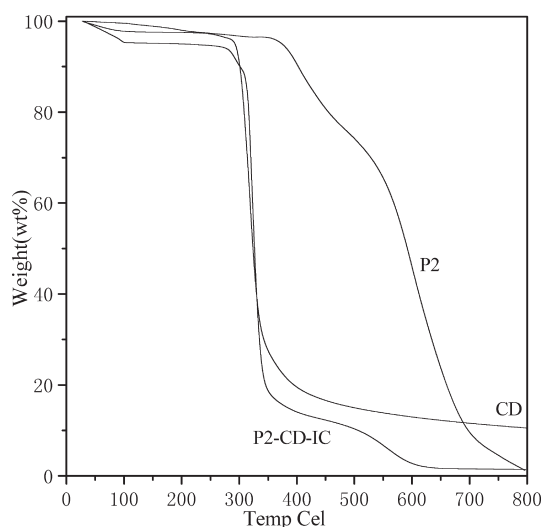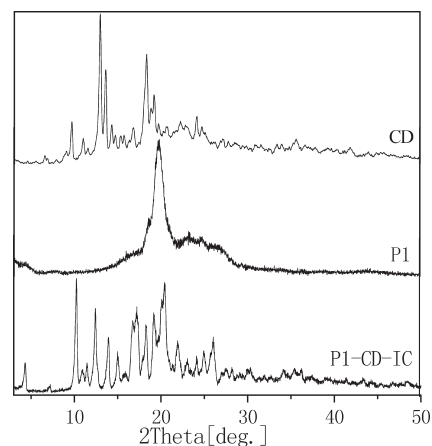
3.4 X-ray Diffraction (XRD)

XRD is a widely used technique in the study of inclusion compounds for assessing the kind of structure they form, and to check whether a new compound has been produced from the parent molecules (21).

Figures 8 and 9 present the comparison of X-ray diffraction patterns observed for β-CD, polymers and polymer-CD-ICs at room temperature from $2\theta = 3$ to $50°$. Major peaks at $12.98°$ were observed for pure β-CD. From the X-ray diffraction pattern of the poly(azomethine ether)s sample, we observed the single broad peak centered on $2\theta = 20$–$22°$. It is shown that the pattern of polymer-CD-ICs is greatly different from that of β-CD, which was reported to be a cage crystal structure when it forms a β-CD $\cdot$ $12H_2O$ complex with water (39). Furthermore, the polymer-CD-ICs showed the diffraction pattern quite different from the diffractograms of poly(azomethine ether)s and this constitutes primary evidence that a different new crystal type was formed.
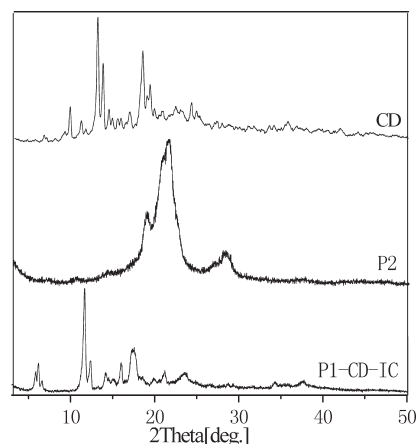

Fig. 7. The TGA trace of β-CD, P_2 and P_2-CD-IC.

Fig. 9. XRD patterns of β-CD, P_2 and P_2-CD-IC.

There is the strong diffraction peak at approximately $20.44°$ in the spectra of P_1-CD-IC, which was previously suggested to be a possible indicator for the cavity of β-CD which includes a polymer inside (9). However, the appearance of characteristic peaks of P_2-CD-IC is different from all of samples. We may require the further study on P_2-CD-ICs, because of its exceptional diffraction pattern, but the results here indicate that, in the polymer-CD-ICs sample, the β-CD exhibits a different packing from that in free β-CD.

4 Conclusions

In this study, the inclusion compounds between β-cyclodextrin (β-CD) and poly(azomethine ether)s have been successfully synthesized. FTIR, ^{1}H-NMR, TGA, and XRD have utilized and observed the polymer chains included inside the cavity formed by β-CD. In FTIR spectra, the characteristic peaks of β-CD and the intense bands of polymers changed after formation of inclusion compounds. From the ^{1}H-NMR, the change of the protons' chemical shift may indicate the interaction of the protons with polymers. Polymer-CD-ICs have very different thermal behavior and crystal structures compared to the corresponding polymers and β-CD. Further analyses of the structure, stoichiometry, and stability of these polymer-CD-ICs are in progress and this type researches may put forward some interesting research topic.

5 Acknowledgments

6 References

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