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Preparation and characterization of polyseudorotaxanes based on adamantane-modified polybenzoxazines and β-cyclodextrin

Yi-Che Su, Wan-Chun Chen, Feng-Chih Chang*

Institute of Applied Chemistry, National Chiao-Tung University, Hsin-Chu 30050, Taiwan, ROC

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Abstract

β-Cyclodextrin (β-CD) forms inclusion complexes (ICs) with adamantane-modified benzoxazines (**2** benzoxazine and **3** benzoxazine). These benzoxazines can readily penetrate into the CD's hydrophobic cavity, causing turbidity of their solutions, from which fine crystalline powders are obtained. We characterized these complexes by powder X-ray diffraction, ^{13}C and ^{13}C CP/MAS NMR spectroscopies, DSC, and TGA. The X-ray diffraction and solid-state ^{13}C CP/MAS NMR spectroscopy indicate that the IC domains of the polypseudorotaxanes maintain their channel-type structures after the ring-opening curing reactions have occurred. Furthermore, DSC measurements indicate that complexing the adamantane-modified benzoxazine units with β-CDs result in stiffer main chains and, thus, higher glass transition temperature. TGA also indicates that the inclusion complexes have enhanced its thermal stability.

Keywords: Cyclodextrin; Benzoxazine; Polypseudorotaxane

1. Introduction

Cyclodextrins (CDs) are water-soluble, homochiral, cyclic oligosaccharides containing six, seven, or eight α-1, 4-linked D-glucopyranose units (α-, β-, and γ-cyclodextrins), and have pore sizes ranging from 4.9 to 7.9 Å (Scheme 1) [1–5]. Moreover, the C_2-OH group of the glucopyranoside unit can form a hydrogen bond with the C_3-OH group of its adjacent glucopyranose unit. In the β-CD molecule, a complete secondary belt is formed by these hydrogen bonds, therefore, this molecule has a rather rigid structure. Such intramolecular hydrogen bond formation is probably responsible for the β-CD having the lowest water solubility among all CDs. The hydrogen bond belt is incomplete in the α-CD molecule because the glucopyranose units are distorted; as a consequence, only four of the six possible intramolecular H-bonds can be fully established in the α-CD. Although γ-CD is quite nonpolar, it has more flexible structure, therefore, it is the most soluble among these three CDs [5–7].

The most interesting property of these CDs is that they can include a wide range of guest molecules selectively within their cavities. These internal cavities are rather hydrophobic and can accommodate suitable sized hydrophobic molecules. Since both primary and secondary –OH groups are positioned at the upper and lower rims of CD's, these rims are, therefore, hydrophilic [5,8]. In the presence of hydrophobic species, the water molecules that usually are associated with the CDs are readily expelled to allow the guest molecules to penetrate into the empty cavity. As a result, inclusion complexes are formed that are stabilized thermodynamically by relevant hydrophobic interactions. In addition, the water molecules re-entering the aqueous phase results in an overall positive Δ*S* contribution [9]. Besides being used as carriers, CDs have also been applied as components of supramolecular assemblies [10] for the creation of novel molecular materials. Additionally, they are capable of forming supramolecular nano-objects [11] with almost all kinds of polymers (e.g. alkanes, ethers, amines, and esters). The kinetics and the yield of such processes depend on the structure of both the CD and the polymer, the polymer's molecular weight, the temperature, the solvent, and the nature of other solutes present in the solution [1].

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* Corresponding author. Tel.: +886 357 270 77; fax: +886 357 195 07.
E-mail address: changfc@cc.nctu.edu.tw (F.-C. Chang).

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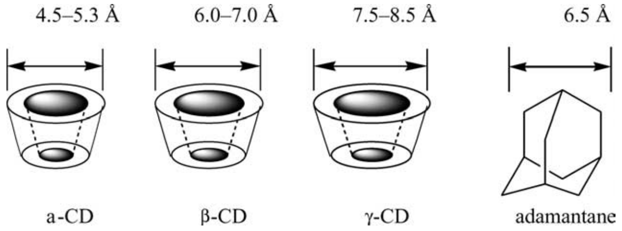
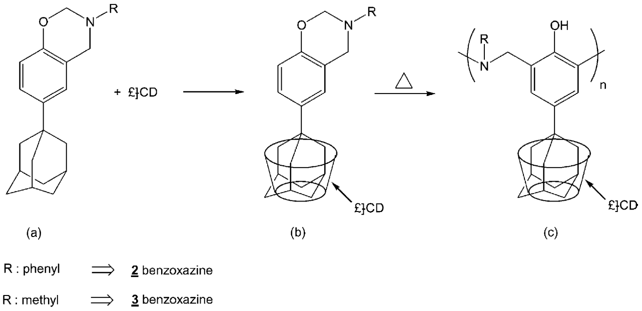


Scheme 1. Structure and dimensions of α-, β-, and γ- CD and the guest molecule, adamantine.

When the CD forms complex with low-molecular-weight guest, the aggregate of the IC can be either channel or cage structure [12]. In the channel structure, the CD rings are stacked on top of one another to produce extended cylindrical central cavities. In the cage structure, the cavity of one CD molecule is closed on both sides by adjacent molecules. Because of the long chain lengths of polymers, polymer–CD complexes are expected to possess channel-type crystal structures. The formation of polymer–CD complexes also provides a unique opportunity to study single polymer chains isolated from their neighboring chains. Such studies may eventually provide valuable insight into the single-chain electrical and optical properties of polymers in the solid state.

The polymer–CD inclusion complexes that have been reported to date mainly the main-chain polypseudorotaxanes and polyprotaxanes. In this study, we focused on the formation and characterization of side-chain polypseudorotaxanes. In an earlier publication, we reported the successful syntheses of two adamantane-modified benzoxazines are shown in Scheme 2(a) [13]. A unique feature of this study is the self-assembly of β-CD with the adamantane-modified benzoxazines. We selected the adamantane unit because it is able to fit precisely into the slightly polar β-CD cavity [14,15]. In an aqueous solution, water molecules in the CD cavity are energetically unstable and can be readily substituted by a less-polar guest molecule having appropriate dimension [16].



Scheme 2. Synthesis of β-CD/**2** benzoxazine IC, β-CD/**3** benzoxazine IC, poly(β-CD/**2** benzoxazine IC), and poly(β-CD/**3** benzoxazine IC).

2. Experimental

2.1. Materials

1-Bromoadamantane, methylamine and β-cyclodextrin were purchased from the Acros Chemical Company (USA). Formaldehyde and aniline were purchased from the Aldrich Chemical Company (USA).

2.2. Nuclear magnetic resonance (NMR)

High-resolution solid-state ^{13}C NMR spectroscopy experiments were carried out at room temperature using a Bruker DSX-400 Spectrometer operating at a resonance frequency of 100.47 MHz. The high-resolution solid-state ^{13}C NMR spectra were acquired by using the cross-polarization (CP)/magic-angle spinning (MAS)/high-power dipolar decoupling technique, using a 90° pulse width of 3.9 ms, a 3 s pulse delay time, and an acquisition time of 30 ms with 2048 scans. A magic-angle sample-spinning rate of 5.4 kHz was used to avoid absorption overlapping. The proton spin-lattice relaxation time in the rotating frame $T_{1\rho}^{\mathrm{H}}$ was determined indirectly via carbon observation using a 90°-τ-spin lock pulse sequence prior to CP. The data acquisition was performed using delay time (τ) ranging from 0.1 to 15 ms.

2.3. Wide angle X-ray diffraction (WAXD)

Wide-angle X-ray diffraction patterns of powder samples were obtained at ambient conditions on a Siemens type-F X-ray Diffractometer equipped with a nickel-filtered Cu Kα radiation source (wavelength = 1.54 Å). The supplied voltage and current were set at 50 kV and 200 mA, respectively. Sample was mounted on a sample holder with Scotch tape and the diffracting intensities were recorded every 0.02 from 2θ scans in the range 3.5–50°.

2.4. Differential scanning calorimetry (DSC)

Calorimetric measurements were performed using a TA DSC-2010 Differential Scanning Calorimeter and were conducted under a nitrogen flow of 25 mL/min and a heating rate of 20 °C/min. The sample was preheated from 30 to 240 °C and maintained at 240 °C for 2 min. The measurement was made using 5–10 mg of sample in a DSC sample cell by cooling to 30 °C quickly from the melt of the first scan. The second scan involved heating the sample from 30 to 300 °C and the value of T_g was taken as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated rubbery and glassy lines.

2.5. Thermogravimetric analysis (TGA)

The thermal stability of the cured sample was investigated using a TA Instruments Q 50 apparatus. The cured sample of (10–20 mg) was placed in a Pt cell and heated from 30 to 700 °C under a nitrogen flow of 60 mL/min and a heating rate of 10 °C/min.

*2.6. Syntheses of 4-(1-adamantyl)phenol, **2** benzoxazine and **3** benzoxazine*

We have synthesized and characterized these compounds previously [13].

4-(1-Adamantyl)phenol. Yield: 28%. ^{1}H NMR (CDCl$_3$, 500 MHz): δ (ppm) 1.72 (q, 6H, adamantane), 1.85 (d, 6H, adamantane), 2.06 (s, 3H, adamantane), 4.64 (s, 1H, hydroxyl), 6.77 (d, 2H, Ar), 7.22 (t, 2H, Ar).

***2** benzoxazine*. Yield: 87.6%. ^{1}H NMR (CDCl$_3$, 500 MHz): δ (ppm) 1.72 (q, 6H, adamantane), 1.85 (d, 6H, adamantane), 2.06 (s, 3H, adamantane), 4.62 (s, 2H, Ar–C*H*$_2$–N), 5.33 (s, 2H, N–C*H*$_2$–O), 6.67–7.23 (8H, Ar).

***3** benzoxazine*. Yield: 64.5%. ^{1}H NMR (CDCl$_3$, 500 M Hz): δ (ppm) 1.72 (q, 6H, adamantane), 1.85 (d, 6H, adamantane), 2.06 (s, 3H, adamantane), 2.59 (s, 3H, methyl), 3.94 (s, 2H, Ar–C*H*$_2$–N), 4.75 (s, 2H, N–C*H*$_2$–O), 6.71–7.24 (3H, Ar).

2.7. Synthesis of the β-CD/2 benzoxazine inclusion complex

The β-CD/**2** benzoxazine inclusion complex was prepared by the sonication method according to Scheme 2(b). Both **2** benzoxazine (0.1 g was dissolved in 35.5 mL acetone) and saturated aqueous β-CD solution [5,7] (0.657 g was dissolved in 35.5 mL water) were kept in room temperature. The solution of **2** benzoxazine was added slowly over 2 h to the β-CD solution while sonicating. The mixture rapidly became turbid and a white precipitate was formed subsequently. After filtration, the white powder was washed with water and acetone several times to remove any uncomplexed β-CD and the free **2** benzoxazine. Finally, a white powder with 98.6% yield was formed which was dried in a vacuum oven at 60 °C for 12 h. Anal. Calcd for $C_{66}H_{97}NO_{36}$: C, 51.66; H, 6.70; N, 0.99; O, 40.65. Found: C, 51.54; H, 6.77; N, 0.98; O, 40.70.

2.8. Synthesis of the β-CD/3 benzoxazine inclusion complex

A similar method illustrated in Scheme 2(b) was adopted for the synthesis of the β-CD/**3** benzoxazine inclusion complex as that described above for the β-CD/**2** benzoxazine complex, except that a solution of **3** benzoxazine (0.1 g was dissolved in 43.24 mL acetone) and a saturated aqueous β-CD solution (0.8 g was dissolved in 43.24 mL water) were employed. After proceeding through same purification process, the β-CD/**3** benzoxazine inclusion complex was obtained as a white powder with 97.2% yield. Anal. Calcd for $C_{61}H_{95}NO_{36}$: C, 53.66; H, 6.57; N, 0.95; O, 39.02. Found: C, 53.60; H, 6.64; N, 0.94; O, 39.06.

3. Results and discussion

3.1. Wide angle X-ray diffraction analysis

The inclusion complex of CDs with low-molecular-weight compound can be classified as either ‘cage-type’ or ‘channel-type’ structure. Fig. 1(a)–(c) and Fig. 2(a)–(c) present the WAXD patterns of β-CD, **2** benzoxazine, and the β-CD/**2** benzoxazine inclusion complex and of β-CD, **3** benzoxazine, and the β-CD/**3** benzoxazine inclusion complex, respectively. These patterns indicate that both of these complexes are crystalline and which are completely different from those of β-CD and benzoxazines. The appearance of two sharp peaks in both the β-CD/**2** benzoxazine and β-CD/**3** benzoxazine inclusion complexes at ca. $2\theta = 11.6°$ ($d = 7.62$ Å) and 17.9° ($d = 4.95$ Å) is the key feature serving as a fingerprint to indicate the channel-type structures of the β-CD/polymer inclusion complex [17]. The benzoxazine complex of β-CD exhibits packing different from that of the free β-CD and possesses a channel structure similar to those of other β-CD based polypseudorotaxanes [8,17].

Figs. 1(d) and 2 (d) display the WAXD patterns of poly(β-CD/**2** benzoxazine) and poly(β-CD/**3** benzoxazine) obtained after thermal curing of the ICs at 180 °C for 4 h. The inclusion complex transforms into a side-chain polypseudorotaxane as indicated in Scheme 2(c). Intensities of these characteristic peaks of the channel-type structure at ca. $2\theta = 11.6°$ ($d = 7.62$ Å) and 17.9° ($d = 4.95$ Å) become smaller because fraction of the crystal structure has been destroyed during the cuing process. This observation indicates that the channel-type structures of the inclusion complex remains essentially intact, despite the occurrence of the ring-opening curing reaction.

3.2. Nuclear magnetic resonance analysis

Solid-state ^{13}C NMR spectroscopic study, conducted by ^{13}C cross-polarization magic-angle spinning (CP/MAS) is able to provide detailed information regarding the structure of the CD complex [18–20]. Fig. 3(a)–(c) display the ^{13}C CP/MAS NMR spectra of β-CD, β-CD/**2** benzoxazine, and β-CD/**3** benzoxazine inclusion complex, respectively. The β-CD assumes a less-symmetrical conformation in the crystal because it does not possess a guest compound included in its cavity. Fig. 3(a) displays resolved resonances for the C_1 and C_4 nuclei of each of the α-1,4-linked glucose residues. Two peaks appear at 94.2 and 96.7 ppm which have been assigned as the conformationally strained glycosidic linkages [21]. As would be expected, these two peaks disappear in the spectra of the β-CD/**2** benzoxazine and β-CD/**3** benzoxazine inclusion complexes. Furthermore, ^{13}C resonances of β-CD give multiple lines because of the asymmetric glucopyranosyl conformations, however, each carbon of the glucose of β-CD/adamantane-modified benzoxazine inclusion complexes can be observed in a sharp

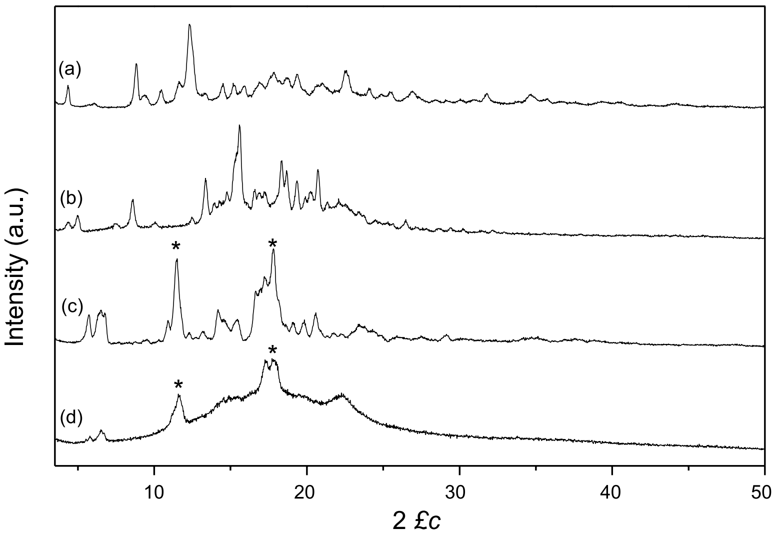


Fig. 1. Powder X-ray diffraction patterns of (a) β-CD, (b) **2** benzoxazine, (c) β-CD/**2** benzoxazine IC, and (d) poly(β-CD/**2** benzoxazine IC).

single peak of the complex in the ^{13}C CP/MAS NMR. The C_1–C_6 nuclei of β-CD appear as distinct but unresolved resonances in Fig. 3(c) and (d), indicating that, in the ICs, the β-CD units adopts a more-symmetrical conformation in which each glucose unit of β-CD exits in a similar environment. It is known, from a previous X-ray crystallographic study on single crystals, that β-CD adopts a symmetrical conformation when it includes a guest in its cavity [22]. Hence, results from ^{13}C CP/MAS NMR spectra of the complexed and uncomplexed cyclodextrins are consistent with prior results from the X-ray crystallography, therefore, the adamantane units of **2** and **3** benzoxazines are indeed included within the cavity of the β-CD.

3.3. Proton $T_{1\rho}^{H}$ relaxation time analysis

Solid-state NMR spectroscopy has often been used to estimate the length scale of phase separation in semicrystalline polymers and blends because the rate of magnetization transfer via proton spin diffusion is on the correct time scale to measure phase separation over a length scale of 5–200 Å. The length scale of phase separation is of interest in many polymeric systems, and several methods have been developed to measure domain sizes using proton spin diffusion. In the present study, we have used the proton $T_{1\rho}^{\mathrm{H}}$ relaxation rates to measure the magnetization exchange between the guest polymer and the CDs [6,24]. If there is efficient magnetization exchange on a length scale of 20 Å or less, an averaged relaxation time can be observed between the polymer and the host CD. The magnetization of the resonance is expected to decay according to the following exponential function for a model spin-locking mode:

$$\ln(M_\tau/M_0) = -\tau/T_{1\rho}^{\mathrm{H}} \tag{1}$$

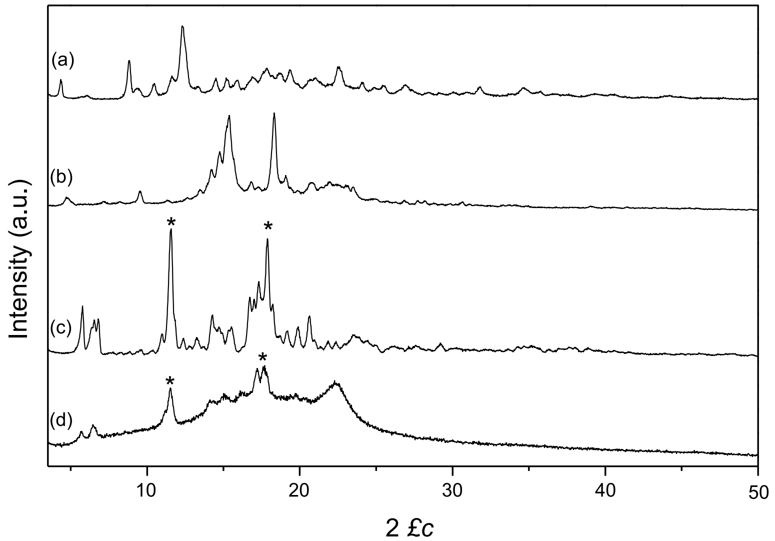


Fig. 2. Powder X-ray diffraction patterns for (a) β-CD, (b) **3** benzoxazine, (c) β-CD/**3** benzoxazine IC, and (d) poly(β-CD/**3** benzoxazine IC).

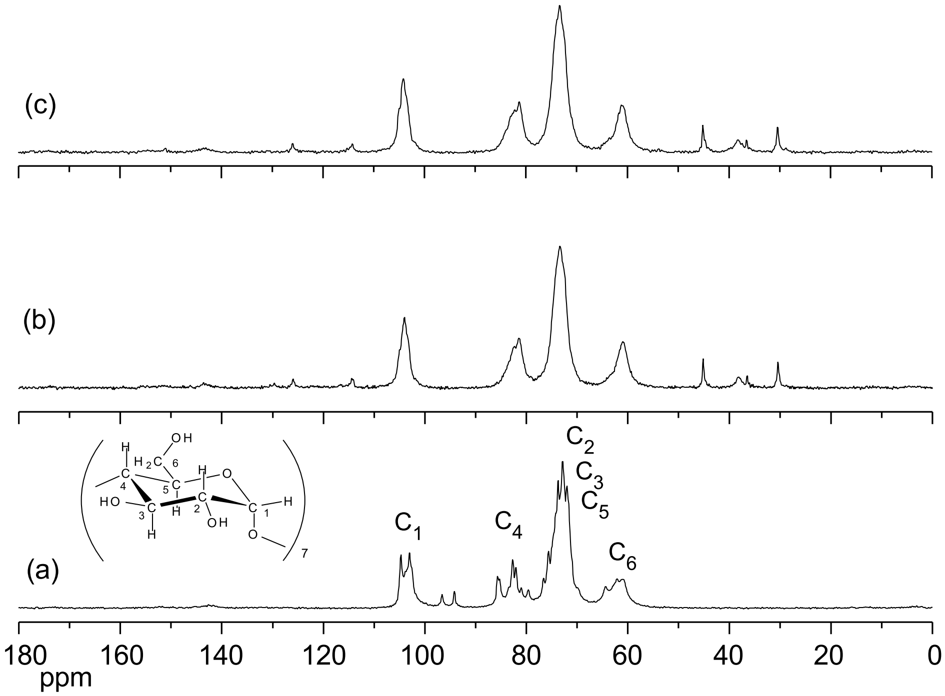


Fig. 3. ^{13}C CP/MAS NMR spectra of (a) β-CD, (b) β-CD/**2** benzoxazine IC, and (c) β-CD/**3** benzoxazine IC.

where $T_{1\rho}^{\mathrm{H}}$ is the spin-lattice relaxation time in the rotating frame, τ is the delay time used in the experiment, and M_τ is the corresponding resonance. $T_{1\rho}^{\mathrm{H}}$ can be obtained from the slope of a plot of In(M_τ/M_0) vs. τ.

Fig. 4 presents the results of the proton $T_{1\rho}^{\mathrm{H}}$ relaxation measurements for β-CD, β-CD/**2** benzoxazine and β-CD/**3** benzoxazine ICs. A slightly longer relaxation time (8.13 and 8.82 ms) has been observed for the β-CD/**2** benzoxazine and β-CD/**3** benzoxazine ICs relative to that of the pure β-CD (8.06 ms). Instead of large variation in the relaxation time, the difference is only slight because the guest adamantane-modified benzoxazine is not a macromolecule. Nevertheless, the slight difference observed indicates that some spin diffusion exists between the host and the guest. Therefore, we conclude that the environment before curing is similar for the β-CD and the β-CD/adamantane-modified benzoxazine ICs.

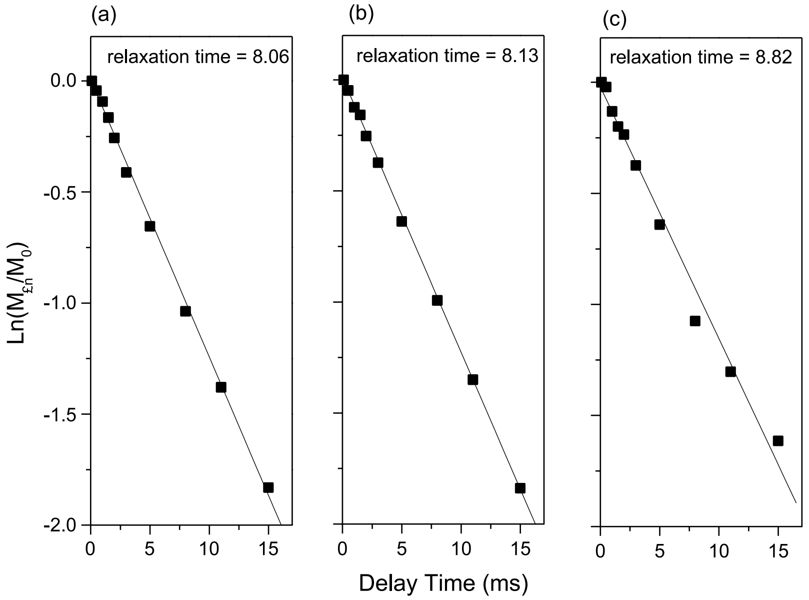


Fig. 4. Proton $T_{1\rho}^{\mathrm{H}}$ relaxations of (a) β-CD, (b) β-CD/**2** benzoxazine IC, and (c) β-CD/**3** benzoxazine IC.

3.4. Glass transition temperature analysis

Differential scanning calorimetry (DSC) has been carried out to obtain glass transition temperatures of the adamantane-modified polybenzoxazines and their polypseudorotaxanes complexed with β-CD. The side chain of the β-CD/adamantane-modified polybenzoxazine IC is included into the CD molecule, a situation would affect the mobility of the polybenzoxazine main chain. Fig. 5 displays the DSC curves of the two polybenzoxazines and their inclusion complexes, all show poorly defined single glass transition temperatures. T_gs of poly(**2** benzoxazine) and poly(**3** benzoxazine) are 109.4 and 188.8 °C, respectively, as indicated in Fig. 6(a) and (c). Fig. 6(b) and (d) present the DSC traces of poly(β-CD/**2** benzoxazine IC) and poly(β-CD/**3** benzoxazine IC). In comparison, values of T_g of these polyseudorotaxanes are increased significantly, from 109.4 to 216.6 °C and from 188.8 to 243.4 °C, respectively. These results are reasonable because of greater steric congestion existing in these complexes and cause polybenzoxazine main chains to stiffer that resulting in higher glass transition temperatures.

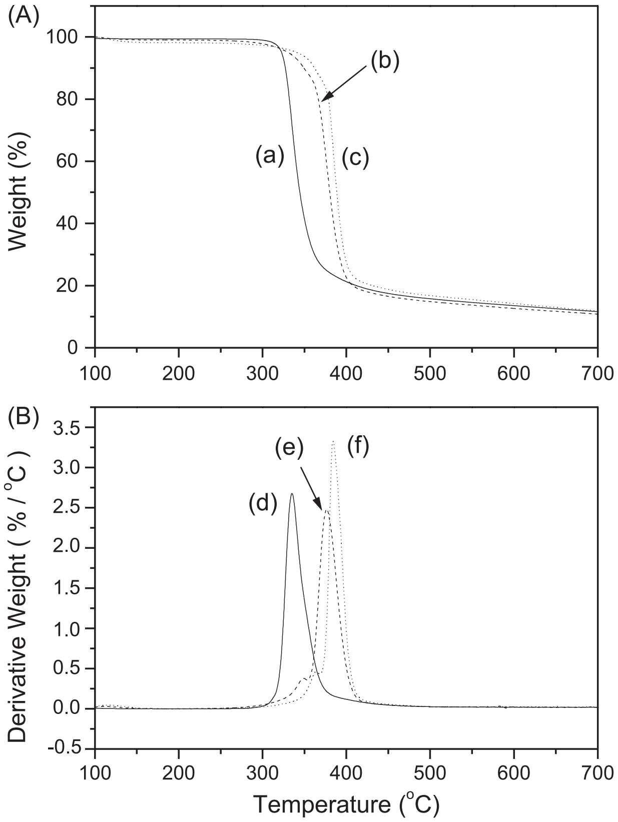


Fig. 6. (A) The TGA trace of (a) β-CD, (b) poly(β-CD/**2** benzoxazine IC), and (c) poly(β-CD/**3** benzoxazine IC). (B) Plots of derivative weight per degree C of (d) β-CD, (e) poly(β-CD/**2** benzoxazine IC) and (f) poly(β-CD/**3** benzoxazine IC)under N_2 atmospheres.

3.5. Thermogravimertric analysis

We investigated the thermal stabilities of β-CD and polyseudorotaxanes by thermogravimetric analysis (TGA). Fig. 6 and Table 1 display the initial decomposition temperatures, temperatures of maximum weight loss rate, and char yields of β-CD, poly(β-CD/**2** benzoxazine IC), and poly(β-CD/**3** benzoxazine IC) under nitrogen atmosphere. The pure β-CD and their polymeric inclusion complexes begin to decompose (5 wt%) in the range from 323 to 340 °C as shown in Fig. 6(a)–(c). Furthermore, Fig. 6(d)–(f) display the traces of the derivative weight per degree C (%/°C) of β-CD, poly(β-CD/**2** benzoxazine IC), and poly(β-CD/**3** benzoxazine IC). Instead of only a slight increase in

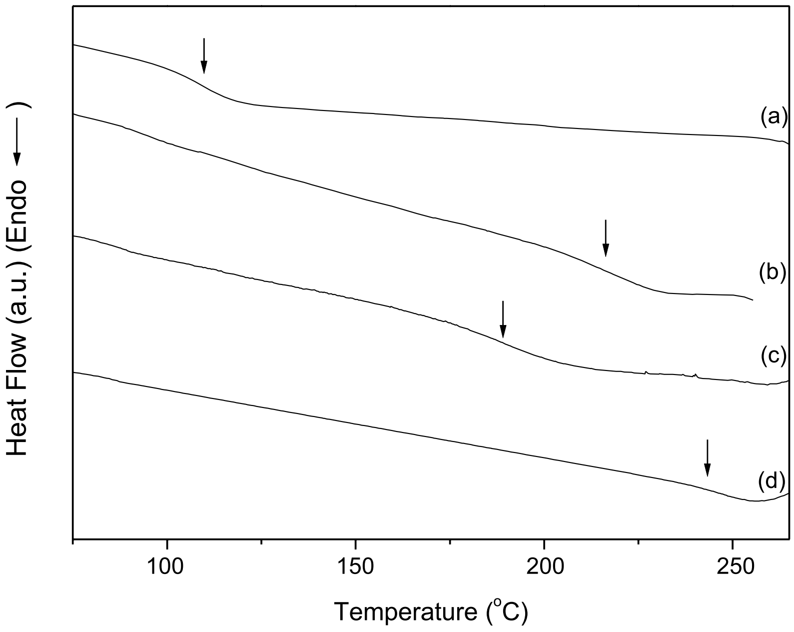


Fig. 5. DSC scans of (a) poly(**2** benzoxazine), (b) poly(β-CD/**2** benzoxazine IC), (c) poly(**3** benzoxazine), (d) poly(β-CD/**3** benzoxazine IC).

Table 1
Weight losses temperatures, temperatures of maximum weight losses rates, and char yields of (a) β-CD, (b) poly(β-CD/**2** benzoxazine IC) and (c) poly(β-CD/**3** benzoxazine IC) under N_2 atmospheres

Code	Temperature (°C)		Char yield (%) at 700 °C
	5 wt% loss	Max. weight loss rate	
(a) β-CD	323	335	11.6
(b) poly(β-CD/**2** benzoxazine IC)	330	376	10.8
(c) poly(β-CD/**3** benzoxazine IC)	340	385	11.8

the 5 wt% weight loss temperature, the temperature of maximum weight loss rate of β-CD is increased substantially from 335 to 376 °C and 385 °C for poly(β-CD/**2** benzoxazine IC) and poly(β-CD/**3** benzoxazine IC), respectively. In other words, these results indicate that the thermal stability of the CD is enhanced by the formation of inclusion complexes.

4. Conclusions

β-CD forms stoichiometric complexes with **2** benzoxazine and **3** benzoxazine. X-ray diffraction and solid-state ^{13}C CP/MAS NMR spectroscopic studies indicate that the resulting polypseudorotaxane is a channel-type structure even through the ring opening curing process occurred at high temperature. DSC measurements indicate that the inclusion of the adamantane-modified benzoxazines into β-CD units results in stiffer of the main chains and higher glass transition temperatures. TGA analyses also indicate that the thermal stability of the inclusion complexes is enhanced.

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