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Synthesis and Characterization of a Novel Diblock Copolymer with a Polyrotoxane Block

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Summary

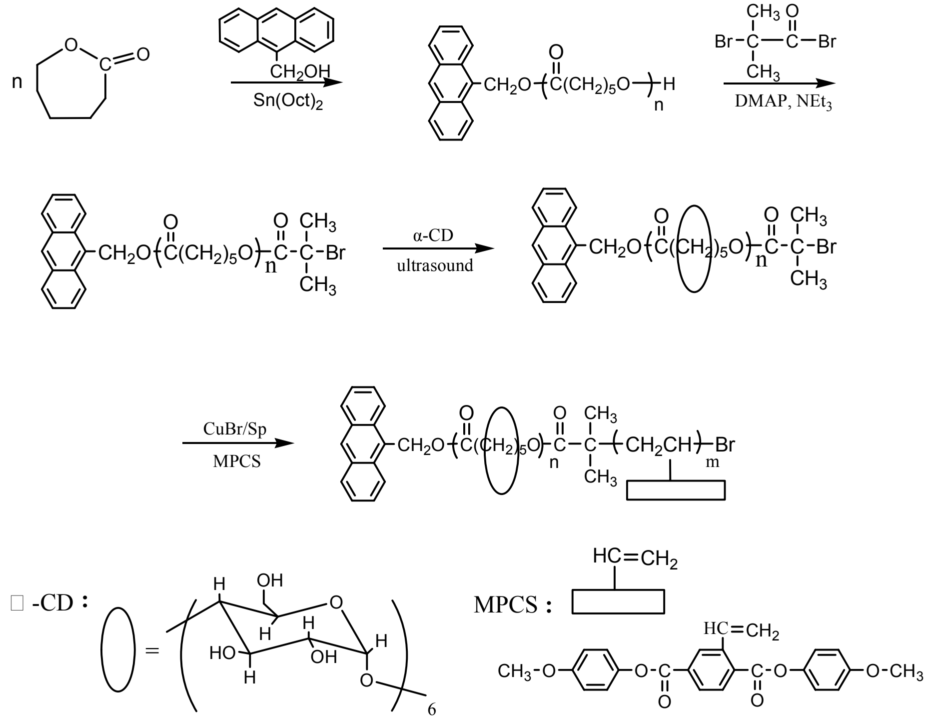
A novel diblock copolymer with a polyrotaxane block α-cyclodextrins-poly (ε-caprolactone)-b-poly{2,5-bis[(4-methoxypheny)oxycabony]-styrene} (α-CD-PCL-b-PMPCS) was successfully synthesized by combining ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP). The diblock copolymer was confirmed by ^{1}H NMR, GPC and solid-state ^{13}C CP/MAS NMR spectroscopic analysis. Its phase structures and phase transitions were investigated by thermogravimetric analyses and wide-angle X-ray diffraction (WAXD). WAXD and solid-state ^{13}C CP/MAS NMR spectroscopic study confirmed that inclusion complexes domains of the polyrotaxanes assumed a channel-type structure.

Introduction

Recently, polypseudorotaxanes (PRs), or inclusion complexes (ICs) with necklace like supramolecular structures have attracted special interest[1-7]. Polypseudorotaxanes are self-assembled supramacromolecular consisting of cyclic host materials and threaded guest molecules. Cyclodextrins (CDs), cucurbiturils, and porphyrins have been investigated extensively as host molecules for specific assembled structures.

Cyclodextrins are a series of cyclic oligosaccharides composed of six, seven, or eight glucose units linked by α-1,4 linkage, (called *α*-, *β*-, or *γ*-CD, respectively) which form inclusion complexes with a wide range of low molecular weight compounds[8,9]. In this process, the key factor is the size matching between the cross sectional area of polymer chain and the inner diameter of the CD cavity, as well as the hydrogen bonding of neighboring CDs which functions as the driving force[10].

Formation of PRs with cyclodextrins proceeds by threading of a polymer backbone in solution, followed by aggregation of the threaded segments and precipitation of a solid inclusion complex. The resulting poly-pseudorotaxa-cyclodextrins will dissolve



Scheme 1. Strategy for the Preparation of the α-CD-PCL-b-PMPCS

in water and dimethyl sulfoxide (DMSO), but dethreading rapidly. So, the PRs must be end capped to give the corresponding polyrotaxanes in the study of the threaded-cyclodextrin architectures in solution. The first reported poly-rotaxa-cyclodextrin results from the reaction of 2 equiv of 2,4-dinitrofluorobenzene with a threaded α,ω-diamino-terminated poly(ethylene glycol) (PEG) suspended in DMF[11-13]. In these end capping reactions, the number of cyclodextrins permanently trapped onto the polymer is governed by the competition between the reaction and dethreading.

To our knowledge, only a few examples of rod–rod diblock copolymers have been investigated[14]. Block copolymers with novel chemical structures and molecular architectures are highly desirable, in which the self-assembly behavior is suspected to be new and interesting[15].

In this paper, we will introduce the α-CD to one side end capped macro-initiator PCL-Br to form α-CD inclusion complexes, which consisted of growing a rigid rod block (PMPCS) by ATRP. This process led to the preparation of a novel diblock copolymer with a polyrotaxanes block and the α-CDs could move along the PCL chain. The synthetic route of α-CD-PCL-b-PMPCS is shown in scheme 1.

Experimental

Materials

ε-Caprolactone (CL. from Aldrich) was vacuum distilled over calcium hydride. $Sn(Oct)_2$ (Aldrich) and 9-Anthracenemethanal (Aldrich) were used as received.

α-Cyclodextrin (α-CD) was purchased from Wacker Chemical Corp. CuBr was prepared from $CuBr_2$ and purified by stirring in acetic acid, washing with methanol and then drying in vacuum. Sparteine (Spt. from Aldrich) was distilled under reduced pressure over calcium hydride and stored under nitrogen atmosphere at 4°C in the dark. *N,N'*-Dimethylformamide (DMF) (anhydrous, 99.9%), other solvents and reagents were purchased from commercial sources and used as received unless otherwise noted.

Measurements

The M_n and molecular weight distribution (M_w/M_n) were measured on a WATER 2414 gel permeation chromatography (GPC) instrument with a set of HT3, HT4 and HT5, μ-styrayel columns with DMF as an eluent (1.0mL/min) at 45°C. Calibration was made with polystyrene (PSt) standard. The ^1H NMR spectrum was taken at 25°C on a Bruker 400 NMR spectrometer with chloroform-*d* or DMSO-*d* as the solvent. Thermogravimetric analyses (TGA) were made using a 7 Series thermal analysis system (Perkin-Elmer). Samples were heated at 20°C/min from room temperature to 800°C in a dynamic nitrogen atmosphere at a flow rate of 70 ml/min. The ^{13}C NMR spectra were recorded on a Bruker AV-400 NMR spectrometer at 100 MHz at room temperature. Wide angle X-ray scattering (WAXS) was carried out on D/max-RA X-ray spectrometer using CuKα (1.54056 Å) radiation (50 kV, 100 mA). All powder samples were mounted on a sample holder and scanned from 3° to 50° in 2θ at a speed of 10°/min.

Synthesis of Macro-Initiator Linear Bromoisobutyryl PCL (PCL-Br)

The PCL was obtained from CL initiated by 9-anthracenemethanal with $Sn(Oct)_2$ as the catalyst. Then macro-initiator linear bromoisobutyryl PCL (PCL-Br) for ATRP was obtained via the modification of PCL by 2-bromoisobutyryl bromide according to the method described by Dong et al[16]. The chemical structure of PCL-Br was identified by ^1H NMR spectroscopy.

Preparation of α-CD Inclusion Complexes

The ICs were prepared as follows: α-CD (5 g, 10 mmol) was dissolved in distilled water (40 mL) at 60°C. PCL (0.5 g, 0.1 mmol) was dissolved in 5 mL of acetone. Then, PCL solutions were added dropwise to the α-CD solution at 60°C. The mixtures were agitated ultrasonically for 1 h. The resulting mixtures were cooled to room temperature and further stirred for 24 h. The precipitated products, i.e., ICs, were collected by filtration, and washed with distilled water and acetone to remove free α-CD and PCL. The ICs were dried overnight in vacuum overnight (Yield: 50-65%). The chemical structures of ICs were confirmed by ^1H NMR spectroscopy.

Synthesis of MPCS Monomer

The monomer 2,5-bis[(4-methoxyphenyl) oxycarbonyl] styrene] (MPCS) was synthesized by the reaction of 2-vinylterephathalic acid according to the method described by Zhang et al[17], ^1H NMR ($CDCl_3$): $\delta = 3.83$, 6H for $-OCH_3$, 5.1-5.90, 2H for $=CH_2$, 6.60-6.95, 1H for .CH = and 7.00-8.30, 11H for the phenylene rings.

Preparation of Diblock Copolymer with a Polyrotoxane Block

A dry glass tube was charged with MPCS, α-CD-PCL-Br, CuBr, Sp and DMF solution, where the molar ratio of MPCS:α-CD-PCL-Br:CuBr:Spt was n:1:1:2. Then the system was degassed three times and the tube was sealed under vacuum. In succession the tube was placed in an oil bath at the desired temperature maintained by a thermostat. After an expected time, the tube was placed in an ice bath to stop the reaction. The reaction mixture was diluted with DMF and added dropwise into diethyl ether. The precipitate was collected by filtration, washed two times with ether, dissolved in DMSO, and precipitation into water, and then washed with water. Finally, the product was dried at 110°C overnight under vacuum. The chemical structure of the diblock copolymer was determined by ^{1}H NMR spectroscopy.

Results and Discussion

The chemical structure of the macro-initiator PCL-Br with the $M_{n,GPC}$ value of 0.48×10^4 g/mol and an M_w/M_n value of 1.18 was characterized by ^{1}H NMR spectroscopy as shown in Figure 1. The signals at 4.05, 2.30, 1.64, and 1.31 ppm represent methylene groups (peak a), methylene groups (peak d), methylene groups (peak b), and methylene groups (peak c), respectively. Moreover, characteristic resonances of 3.64ppm which showed the methylene group of terminal ($-CH_2-OH$ which consist in PCL end) was in stead of characteristic resonances of at 1.92 ppm (peak f) after ester reaction, that proved the presence of the end group, $-CH_2-OCOCBr(CH_3)_2$. The $M_{n,NMR}$ value of macro-initiator PCL-Br was estimated from the ratio of the methylene protons (a) and methylene protons (e). The $M_{n,NMR}$ value (0.55×10^4) was close to the $M_{n,GPC}$ (0.48×10^4). These data confirmed that the well-defined macroinitiator PCL-Br with terminal bromine was obtained.

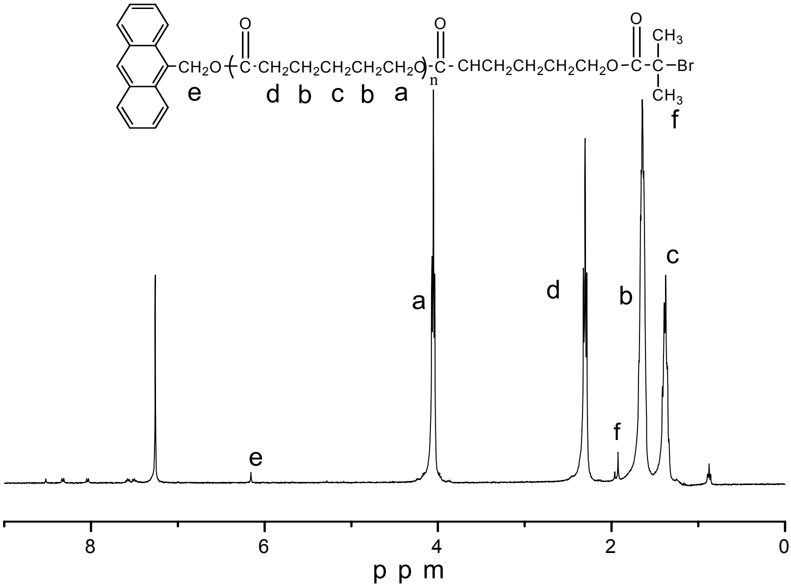


Fig.1. ^{1}H NMR spectrum of the macro-initiator PCL-Br in $CDCl_3$

When an acetone solution of PCL-Br was added into an aqueous solution of α-CD, followed by sonication, the solution became turbid quickly. Ultimately, the inclusion complexes were formed as crystalline precipitates. It has been demonstrated that WAXD, ^{13}C CP/MAS and ^{1}H NMR spectroscopy are useful tools for suggesting the presence of both the guest and host components in polypseudorotaxanes.

Figure 2 showed the ^{1}H NMR spectrum of α-CD-PCL in DMSO-d_6. The signals at 5.51, 5.42, 4.79, 4.47, 3.73-3.83, 3.54-3.73 and 3.23–3.51 ppm represented hydroxy groups (O(2)H of α-CD), hydroxy groups (O(3)H of α-CD), internal H (H(1) of α-CD), hydroxy groups (O(6)H of α-CD) and internal H (H(3) of α-CD), internal H (H(6) and H(5) of α-CD) and internal H (H(2) and H(4) of α-CD), respectively. The peaks at 3.97, 2.26, 1.53 and 1.29 ppm represented the methylene protons in PCL unit. The α-CD contents of the α-CD-PCL were quantitatively studied using ^{1}H NMR spectroscopy, based on the integral values of the peaks (at 4.47 ppm)O(6)H of α-CD and (at 2.30 ppm) methylene groups of PCL, the ratio of integral values of CL unit and α-CD as determined from ^{1}H NMR result was 1.15.

A series of diblock copolymers with polyrotaxane block were synthesized by ATRP, Figure 3 showed the ^{1}H NMR spectrum of α-CD-PCL-b-PMPCS in DMSO-d_6. The signals at 5.51, 5.42, 4.79, 4.47, 3.73-3.83, 3.54-3.73 and 3.23–3.51 ppm represented hydroxy groups (peak O(2)H of α-CD), hydroxy groups (peak O(3)H of α-CD), internal H (peak H(1) of α-CD), hydroxy groups (peak O(6)H of α-CD), internal H (peak H(3) of α-CD and -OCH_3 proton of MPCS units) and internal H (peak H(6) and H(5) of α-CD, -OCH_3 proton of MPCS units), internal H (peak H(2) and H(4) of α-CD), respectively. The broad peaks at 6.37–7.20 ppm and 7.20–8.20 ppm represented aromatic protons in PMPCS units, respectively. The peaks at 3.97, 2.26, 1.53 and 1.29 ppm represent the methylene protons in PCL unit. The host-guest stoichiometry of the ICs was estimated by ^{1}H NMR in solution. From these signals the molar ratio of α-CD molecule to the monomeric repeat unit of polymer is calculated to be 8.0. These results indicate that the polymer chain was partially covered by α-CDs in the α-CD -ICs.

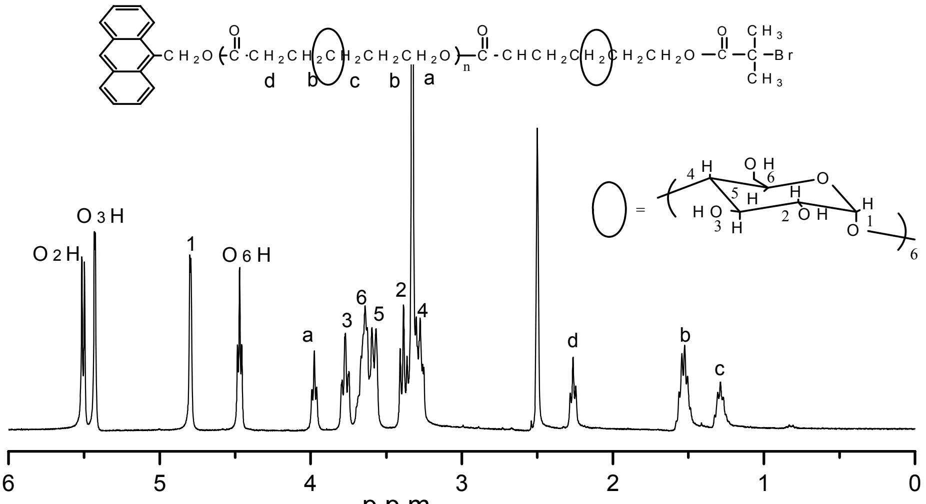


Fig.2. ^{1}H NMR spectrum of the α-CD-PCL in DMSO-d_6

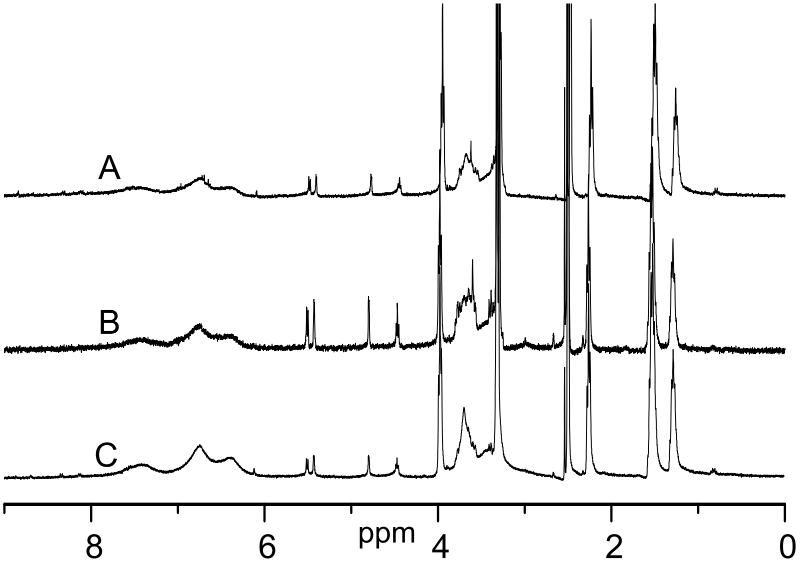


Fig.3. ^{1}H NMR spectrum of a series of α-CD-PCL-b-PMPCS in DMSO-d_6

All these data verified that reaction underwent ATRP well. Based on the conversion of MPCS and molar ratio of MPCS {$[MPCS]_0$} to α-CD-PCL {$[\alpha\text{-CD-PCL}]_0$}, the $M_{n,th}$ of diblock copolymer α-CD-PCL-b-PMPCS could be calculated according to Eq. (1).

$$M_{n,th} = Conv \times \left\{ [MPCS]_0 / [\alpha - CD - PCL]_0 \right\} \times 404 + M_{n,th}(\alpha - CD - PCL) \tag{1}$$

Where $M_{n,th}$ (α-CD-PCL) was the M_n of macro-initiator α-CD-PCL that could be calculated according to Eq. (2).

$$M_{n,th} = (number\ of\ a - CD\ in\ a\ single\ PR) \times 973 + M_n(PCL - Br) \tag{2}$$

M_n (PCL-Br) was the M_n of macro-initiator PCL-Br on the basis of GPC data, 404 was the molar weight of MPCS. 973 was the molar weight of α-CD.

Table 1 GPC data of diblock copolymer and its precursors

Sample	$M_{n,\,th}$ $(\times 10^{-4})^1$	Yield $(\%)^2$	$M_{n,\,NMR}$ $(\times 10^{-4})^3$	$M_{n,\,GPC}$ $(\times 10^{-4})$	M_w/M_n
PCL-Br	0.50	92.5	0.55	0.48	1.18
α-CD-PCL	4.77	62.5	3.92	\	\
α-CD-PCL-PMPCS-A	5.17	51.2	1.65	220	2.84
α-CD-PCL-PMPCS-B	5.58	56.5	2.32	285	2.25
α-CD-PCL-PMPCS-C	5.98	53.6	2.53	321	2.68

[1] $Mn_{,th}$ was calculated according to Eq. (1) and Eq (2).
[2] Yield was calculated according to Yield (%) = $(W_p - W_i)/Wm \times 100\%$, where W_p, W_i and W_m were the weight of the diblock copolymer, macro-initiator α-CD-PCL and MPCS, respectively.
[3] Calculated based on ^{1}H NMR analysis.

GPC analysis was performed to determine the molecular weights and molecular weight distributions of the purified diblock copolymers α-CD-PCL-PMPCS and their macro-initiator (the data are shown in Table 1). It can be observed from Table 1 that the molecular weight which measured by GPC are lager than the theoretical molecular weights. This might be due to the difference in solvent property between diblock copolymer and standard polystyrene. Another reason is that the molecular weight dependence of the hydrodynamic volume should be different when comparing diblock copolymer with polystyrene standard.

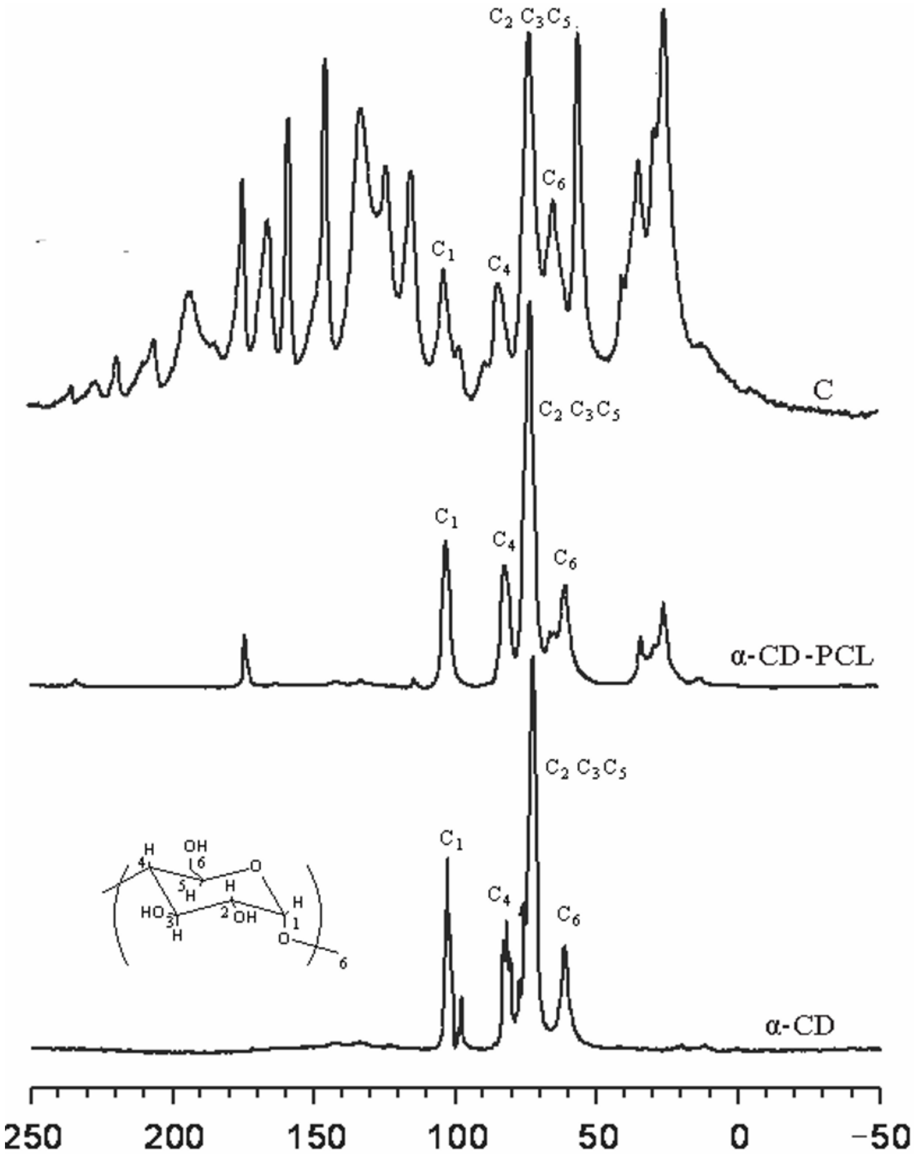


Fig.4. Soild-state ^{13}C CP/MAS NMR spectrum of α-CD, α-CD-PCL and α-CD-PCL-b-PMPCS-C

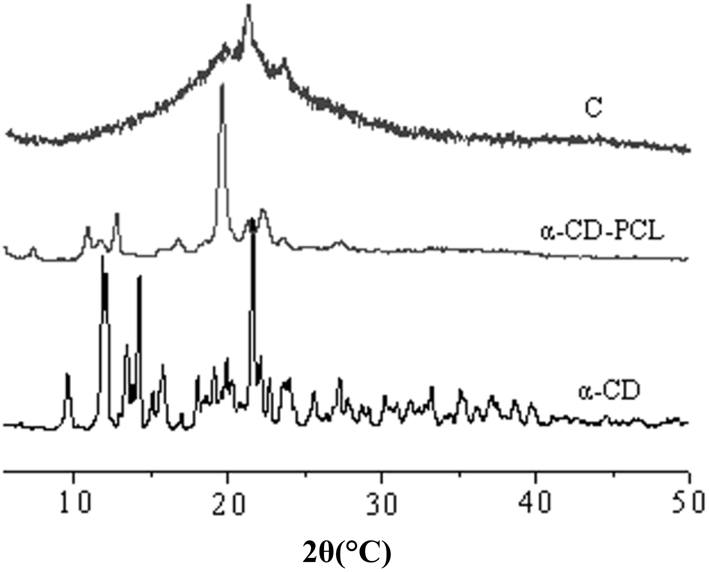


Fig.5. XRD diffraction patterns recorded at room temperature for α-CD, α-CD-PCL, and α-CD-PCL-b-PMPCS-C

Solid-state ^{13}C CP/MAS NMR spectroscopy studies could provide additional information about the structure of α-CD complexes. Figure 4 gives the Solid-state ^{13}C CP/MAS NMR spectrum of α-CD, α-CD-PCL and α-CD-PCL-b-PMPCS. α-CD was known to assume a less symmetrical conformation in its crystalline uncomplexed state. In this case, the spectrum reveals resolved C_1 and C_4 resonances; i.e., these atoms were located adjacent to a single conformationally strained glycosidic linkage. In contrast, these resolved resonances disappear. In the case of the α-CD-PCL complex, in which each carbon atom of the glucose unit of the α-CD experiences a similar environment, after growing a rigid rod block PMPCS by ATRP. As shown in Figure 4, each carbon atom of the glucose unit of the α-CD experiences a similar environment too as (compared with α-CD-PCL).

Figure 5 presented a comparison of the wide-angle X-ray diffraction (WAXD) patterns observed for α-CD, α-CD-PCL, and the α-CD-PCL-b-PMPCS complex at room temperature. Figure 5 (α-CD) displays the reflection of free α-CD, in which major WAXD peaks were observed at 2θ ca. 11.92°, 14.33° and 21.67°. Figure 5 (α-CD-PCL) displays the reflection of α-CD-PCL. The characteristic peak at 2θ ca. 19.4 demonstrated that α-CD rings were stacked along the PCL chain axis to form the necklace structure. Therefore, the WAXD results confirmed that α-CD-PCL ICs possess a column structure[18]. Compared with the reflection of α-CD-PCL, the peak of α-CD-PCL-b-PMPCS at 2θ ca. 19.4° was weakened, whereas in the diblock copolymer only a spot of α-CD stacked along the PCL chain. In PCL-b-PMPCS, PCL and PMPCS block have good compatibility [19], and in the reflection of α-CD-PCL-b-PMPCS, the crystal peaks of PCL at 2θ ca. 21.15°, 23.44° could be seen.

The thermogravimetric analysis (TGA) of free α-CD, PCL, α-CD-PCL and α-CD-PCL-b-PMPCS are shown in Figure 6. In Figure 6c, the α-CD-PCL underwent two-step thermal degradation. The first step could be mainly attributed to a decomposition of α-CD, while the second one mainly to the PCL. In Figure 6d, the

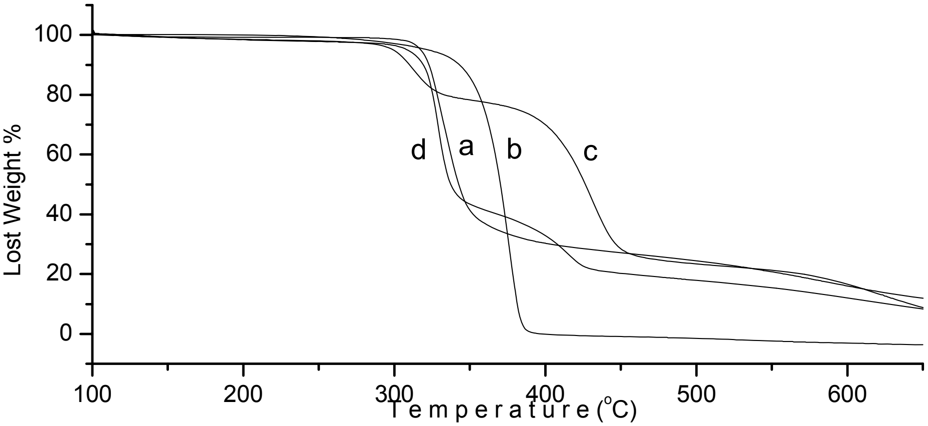


Fig.6. Thermogravimetric analysis (TGA) under nitrogen atmosphere for (a) α-CD (b) PCL (c) α-CD-PCL (d) α-CD-PCL-b-PMPCS-C

α-CD-PCL-b-PMPCS underwent two-step thermal degradation too. The first step could be mainly attributed to a decomposition of α-CD, while the second one mainly to the PCL-b-PMPCS copolymer. Free α-CD and the PCL started to decompose at 316°C and 315°C, respectively, while the α-CD-PCL started to decompose at about 308°C. As compared with its free counterparts, the decomposition temperature T_d value for α-CD in the IC was reduced about 8°C, and that for the PCL in the IC increased by 35°C. Therefore, the PCL was stabilized by the formation of IC. However, the α-CD-PCL-PMPCS started to decompose at about 303°C. As compared with its free counterparts, the decomposition temperature T_d value for α-CD in the IC was reduced by 13°C, and that for the PCL-b-PMPCS in the IC started to decompose at about 351°C. In addition, the two-step weight loss behavior could be used to estimate the ratio between α-CD and the copolymer in the ICs.

Conclusions

In this paper, we have described the preparation of a novel diblock copolymer: α-cyclodextrins-poly(ε-caprolactone)-b-poly{2,5-bis[(4-methoxypheny)oxycabony]-styrene}. WAXD and solid-state ^{13}C CP/MAS NMR spectroscopic study confirmed that the ICs domains of the polyrotaxanes assumed a channel-type structure. The TGA results revealed that the polypseudorotaxanes and polyrotaxanes had better thermal stability than free components due to the inclusion complexation. It will be of interest to investigate the self-assembly behavior and the solution properties of the rod-rod diblock copolymer. We believe that self-assembly behavior of this rod-rod diblock copolymer will be affected by both of the PMPCS and the IC segments. The relusts will be reported later.

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