Inclusion Complexation between Comblike PEO Grafted Polymers and α-Cyclodextrin

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Received November 2, 2004; Revised Manuscript Received January 31, 2005

ABSTRACT: The inclusion complexation of comblike poly(ethylene oxide) grafted polymers, P(PEOMA)s, with α-cyclodextrin (α-CD) was studied. The grafted polymers were prepared by atom transfer radical polymerization (ATRP) of the macromonomers containing poly(ethylene oxide) (PEOMA) of different molecular weights (M_n = 300, 475, and 1100). The grafted polymers that were made from the macromonomers of M_n 1100 and M_n 475 formed crystalline inclusion complexes (ICs) with α-CD, while the P(PEOMA) from the PEOMA of molecular weight M_n 300 failed to form ICs with α-CD. Furthermore, when the side chain length of the grafted polymers decreased, the time to form inclusion complexation with α-CD extended as well as the yields of the inclusion complexes ICs decreased significantly. X-ray diffraction (XRD) data indicated that the obtained ICs have a channel-type crystalline structure. The formation of ICs was further confirmed by differential scanning calorimetry (DSC) and ^{13}C CP/MAS NMR analysis. The stoichiometry determined by ^{1}H NMR indicated that the ratio of EO unit to α-CD of the resulted ICs is higher than 2:1 (a ratio that was expected from the ICs of linear PEO and α-CD). This can be explained that, for the ICs formed between the grafted polymers and α-CD, the spatial hindrance of the side chains and bulky size of threaded CD rings prevent the complete coverage of the EO units with CD.

Introduction

Cyclodextrins (CDs) are water-soluble cyclic oligosaccharides, which are composed of 1,4-glucopyranose units. Generally, there are three types of CDs: α-, β-, and γ-CD corresponding to 6, 7, and 8 glucopyranose units, respectively. It is well-known that CDs can form inclusion complexes (ICs) with a large number of organic compounds.[1−4] Since the first report published by Harada et al.[5] in 1990 on the ICs between α-CD and linear poly(ethylene oxide) (PEO), extensive studies have been made on ICs formation of various linear polymers with CDs.[6−36] The key factor of inclusion process is the size matching between the cross-sectional area of polymer chain and the inner diameter of CD's cavity as well as the hydrogen bonding of neighboring CDs which serves as the driving forces. Researchers have demonstrated that PEO of various molecular weights can form ICs with α-CD in high yield, but not with β-CD.[6,7] On the contrary, poly(propylene oxide) (PPO) can form ICs with β-CD and γ-CD but not with α-CD.[35,36] IC formation of CDs and block or random copolymers of EO and PO has also been studied in recent years.[25,34,37−39]

In addition to the IC formation of linear polymers with CDs, increasing attention has been paid to the complexation of branched polymers with CDs. Huh et al. have studied the inclusion complexation between PEO grafted dextrans and α-CDs in aqueous media and obtained supramolecular hydrogels which showed a unique gel−sol phase transition.[26] Jiao et al. have reported that both α-CD and γ-CD can form stoichiometric crystalline ICs with star-shaped PEOs with three, four, and six arms, respectively.[40] Also, Sabadini et al. have studied the inclusion of complexation of high-molecular-weight star-PEOs containing 13 and 15 arms and of both α-CD and γ-CD, which formed a hydrogel.[41] Very recently, Zhu et al. have synthesized a new kind of multiarm polyether with a hyperbranched poly(3-ethyl-3-oxetanemthanol) core and PEO arms and obtained lamellar crystalline complexes of multiarm polyether and α-CD.[42] The supramolecular structure based on the polymer/CD interaction may produce materials which show novel properties such as stimuli responsive gels and, therefore, have great potential in biological and biomedical applications.

Herein, we present inclusion studies between α-CD and comblike PEO densely grafted polymers. Compared with the star-shaped or hyperbranched polymers, the polymers applied here have a unique structure; that is, there are uniform side chains at every repeat unit, and hence the backbone of the comblike grafted polymers has very high grafting density of side chains. The purpose of this report is to explore whether such densely PEO grafted polymers can form ICs with α-CD. A series of such densely grafted polymers were prepared through atom transfer radical polymerization (ATRP) of PEO macromonomers, and the IC samples were prepared from these polymers and α-CD. The stoichiometry and crystal structure were established using ^{1}H NMR and XRD.

Experimental Section

Materials. Poly(ethylene oxide) methyl ether methacrylates (PEOMA) of three molecular weights (M_n = 300 g/mol, DP_{PEO} = 5; M_n = 475 g/mol, DP_{PEO} = 9; and M_n = 1100 g/mL, DP_{PEO} = 23) were obtained from Aldrich. Symbols of PEOMA300, PEOMA475, and PEOMA1100 were used to represent three macromonomers. The inhibitors in PEOMA300 and PEOMA475 were removed by passing through an alumina

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10.1021/ma047748c CCC: $30.25
Published on Web 03/17/2005

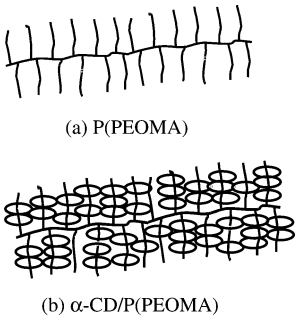
column. PEOMA1100, which is a solid at room temperature, was dissolved in toluene first; the solution was then passed through an alumina column to remove inhibitor before use. (*p*-Methoxy)benzene 2-bromoisobutyrate and CuBr were prepared according to procedures reported in the literature.[43,44] *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA, 99%) and α-CD were obtained from Aldrich and used without any treatment. All other reagents were commercially available chemicals and used as received.

Measurement. Gel permeation chromatography (GPC) was performed on a Waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3, and HT4) using THF as eluent at a flow rate of 1.0 mL/min at 35 °C. Polystyrene standards were used for calibrations. ^{1}H NMR spectra were recorded with Bruker AV 400 and 600 MHz NMR spectrometers in $CDCl_3$ or DMSO-d_6 with tetramethylsilane (TMS) as standard at room temperature. Chemical shifts of the complexes were referenced to δ = 7.26 ppm for $CDCl_3$ and δ = 2.50 ppm for DMSO-d_6. The solid-state ^{13}C CP/MAS NMR spectra were measured on a Bruker AV-300 NMR spectrometer at 75 MHz with a sample spinning rate of 5 kHz at room temperature. The spectra were acquired with a 4.75 μs proton 90 pulse and a 4 ms contact time. Chemical shifts were referred to external standard adamantane. XRD patterns of the complexes were recorded on a Rigabu D/max 2500 X-ray powder diffractometer with Cu Kα (1.541 Å) radiation (40 kV, 40 mA). Powder samples were mounted on a sample holder and scanned with a step size of 0.01° between 2θ = 3° and 50°. DSC measurements were performed under nitrogen at a flow rate of 30 mL/min on a DSC822^e differential scanning calorimeter. Each sample was heated from −20 to 160 °C at a heating rate of 10 °C/min and scanned two times to erase thermal history. TGA analyses were made with a TA Instruments Thermal Analyst 2100. Samples were heated at 20 °C/min from room temperature to 800 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL/min).

Synthesis of Densely Grafted Polymers P(PEOMA)s. A typical procedure is as follows: In a 25 mL Schlenk flask, CuBr (11.5 mg, 0.08 mmol) was added, air was exchanged with N_2 for three times, and then deoxygenated PMDETA (17 uL, 0.08 mmol) and PEOMA1100 (2.2 g, 2.0 mmol) were added. Afterward, a deoxygenated mixture of (*p*-methoxy)benzene 2-bromoisobutyrate (21.8 mg, 0.08 mmol) and toluene (3.3 mL) was transferred to the flask, and then the flask was placed in an oil bath at 60 °C with stirring. Samples at different time intervals were taken to analyze PEOMA conversion by GPC. The catalyst was removed by passing through a basic alumina column prior to GPC analysis. After a predetermined time, the polymerization was stopped by opening the flask and exposing the catalyst to air. The reaction mixture was then diluted with THF and passed through an alumina column to remove the copper complex. After condensation, the unreacted PEOMA1100 was removed through grade precipitation by ethanol/hexane (1:1 v/v). For the preparation of P(PEOMA300), the crude product was precipitated in ethyl ether for two times to remove the unreacted PEOMA macromonomer. Finally, the pure polymer was dried under vacuum to a constant mass. For monomer PEOMA475, the polymerization was carried out in the mixture of water and methanol (1:3 v/v) at 25 °C. The polymers were purified through precipitation in ether for twice.

Preparation of Inclusion Complexes. The α-CD/P(PEOMA) inclusion complexes were prepared as follows: A solution of P(PEOMA1100) sample (110 mg, 0.10 mmol of monomer) in deionized water (0.5 mL) was mixed with a saturated solution of α-CD (1.20 g, 1.23 mmol) in 8.6 mL of water at room temperature, and the mixture was sonicated for 10 min, followed by standing overnight at room temperature. The solid inclusion complex was isolated by centrifugation, washed with a limited amount of water, and dried in a vacuum at 60 °C for 1 day. The stoichiometry was measured by ^{1}H NMR, and the yields were calculated on the basis of the amount of polymers and α-CD used. A feed ratio of 2:1 (EO unit:α-CD) was used for all three polymers.

Scheme 1. Schematic Structure of (a) the PEO Comblike Grafted Polymer and (b) Possible Structure of Inclusion Complex with α-CD



Results and Discussion

Polymer Synthesis. The PEO densely grafted polymers were synthesized by homopolymerization of the macromonomers using the ATRP approach to obtain well-defined polymers. The macromonomers poly(ethylene oxide) methyl ether methacrylates with three different lengths of PEO (PEOMA, M_n = 300, 475, and 1100 g/mol) were used.[45−47] Since these macromonomers had very low polydispersities, the generated grafted polymers, P(PEOMA)s, have very uniform PEO branches. Furthermore, the PEO side chains were formed in situ during the polymerization. Therefore, the produced polymers bear PEO side chains at every repeating unit, and the schematic structure is shown in Scheme 1a. Figure 1 gives the GPC traces of three samples of P(PEOMA)s used to form inclusion complexes with α-CD, and the curves indicate that the polydispersity index was low (M_w/M_n < 1.25). Some characteristics of P(PEOMA) used in the experiments are listed in Table 1. Since the M_n given by GPC was calibrated with the linear polystyrene standard, molecular weights given by GPC are apparent; therefore, the degree of polymerization of the main chain was estimated from the conversion of monomers.

Inclusion Complexation of P(PEOMA) with α-CD. The aqueous solution of P(PEOMA1100) became turbid immediately after the addition of α-CD solution, indicating the rapid formation of the crystalline inclusion complexes. The precipitates were collected by filtration after standing for 12 h. For polymer P(PEOMA475), which has shorter side chains, it took about 2 weeks to form the precipitates with α-CD. However, the yields

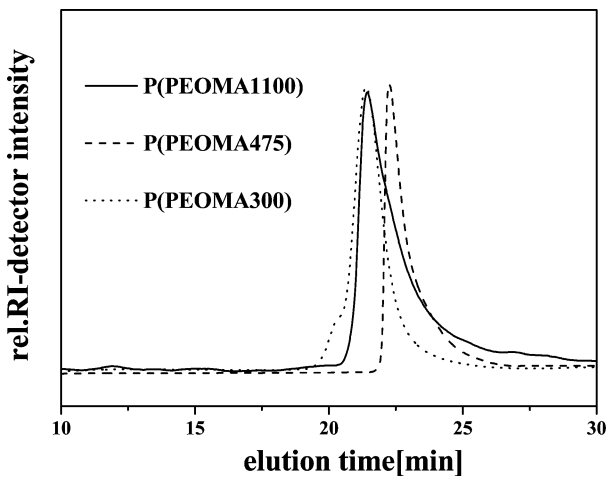


Figure 1. GPC traces of three PEO grafted polymers, P(PEOMA1100), P(PEOMA300), and P(PEOMA475).

Table 1. Preparation and Characterization of the PEO Comblike Grafted Polymers and Their Inclusion Complexes with α-CD

polymer	condition[a]	time (h)	DP (conv)[d]	M_w/M_n[e]	yield (%) of ICs	EO/α-CD
P(PEOMA300)	100:1:1:1[b]	1.0	44	1.22		
P(PEOMA475)	100:1:1:1[c]	0.75	50	1.17	14.9	2.9:1
P(PEOMA1100)	25:1:1:1[b]	7.0	21	1.14	40.1	4.2:1

[a] Feed: [monomer]:[initiator]:[CuBr]:[PMDETA]. [b] In toluene, 60 °C. [c] In mixture of water and methanol (1:3 v/v), 25 °C. [d] Estimated by [monomer]:[initiator] × conversion. [e] Determined by GPC calibrated with polystyrene standards.

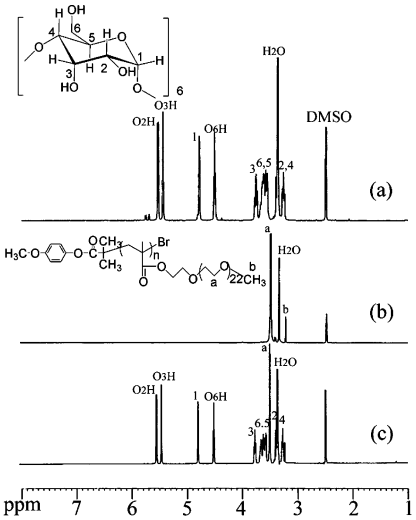


Figure 2. ^{1}H NMR spectra of (a) α-CD, (b) P(PEOMA1100), and (c) α-CD/ P(PEOMA1100).

of ICs for P(PEOMA475) were much less compared to that of P(PEOMA1100), whereas the mixed solution of P(PEOMA300) and α-CD only became cloudy with no precipitates obtained even after standing for about 4 weeks. The above results indicate that the time needed for the complexation and the yields for ICs were dependent on the side chain length of the grafted polymers: the longer the side chain is, the faster the complexation forms and the higher the yields are. Therefore, such densely grafted PEO chains can form ICs with α-CD, but short side chains are more difficult to be threaded than the long side chain due to the steric hindrance from the backbones.

Figure 2 shows the ^{1}H NMR spectrum of the α-CD/P(PEOMA1100) inclusion complex compared with its precursor. A comparison between the integral intensities of the proton peaks of α-CD and the EO protons of P(PEOMA1100) gave the composition of α-CD/P(PEOMA1100) complexes. Table 1 lists the stoichiometry of ICs. It has reported that, for a linear PEO, CDs thread as much as the chain permits, and the stoichiometry for a fully threaded IC is 2:1, which means that two EO repeat units are threaded by one α-CD ring.[7,48] As shown in Table 1, the stoichiometry values for α-CD/P(PEOMA475) and α-CD/P(PEOMA1100) are 2.9:1 and 4.2:1, respectively, indicating that fewer α-CD rings were threaded by grafted PEO chains compared to that by linear PEO. It demonstrated that some of ethylene glycol units, presumably those near the main chain or even some PEO chains, are difficult to be threaded by α-CDs due to the repulsion of side chains and the steric hindrance between backbone and side chains.

For polymers P(PEOMA1100) and P(PEOMA475), the precipitates formed in the mixture solution were treated as described in the Experimental Section and used for XRD analysis. For P(PEOMA300), the white solid

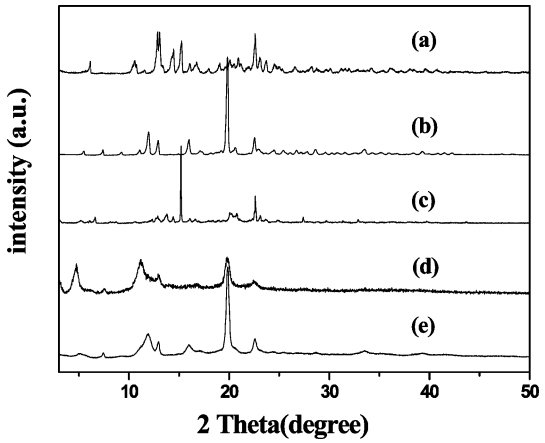


Figure 3. X-ray diffraction patterns for (a) α-CD, (b) α-CD/PEO750, (c) α-CD/P(PEOMA300), (d) α-CD/P(PEOMA475), and (e) α-CD/P(PEOMA1100).

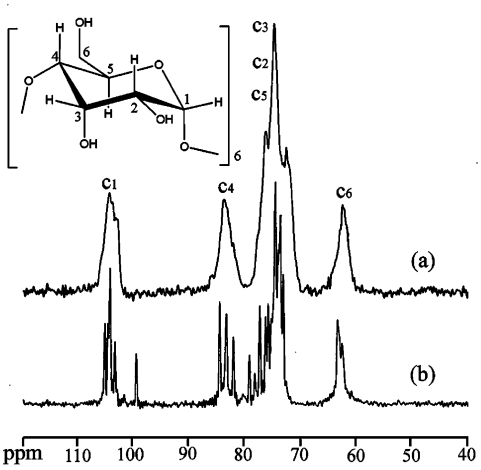


Figure 4. ^{13}C CP/MAS NMR spectra of (a) α-CD/P(PEOMA1100) and (b) α-CD.

powders were collected and used for XRD analysis directly after the water was evaporated naturally; therefore, free α-CDs were included. Figure 3 gives the XRD patterns of α-CD, α-CD/PEO750 (complex with linear polymer for comparison), α-CD/P(PEOMA300), α-CD/P(PEOMA475), and α-CD/P(PEOMA1100). As one can see, the diffraction patterns of curve d (α-CD/P(PEOMA475)) and e (α-CD/P(PEOMA1100)) are very similar to curve b (α-CD/PEO750). The characteristic peak at 2θ ca. 20° demonstrates that α-CD rings were stacked along the PEO side chain axis to form the necklace structure. Therefore, the XRD results confirm that α-CD/P(PEOMA475) and α-CD/P(PEOMA1100) ICs possess a column structure. In terms of α-CD/P(PEOMA300), the diffraction patterns were mainly the peaks of free α-CD crystals due to the sample obtained by drying the solution directly; no ICs were detected.

Figure 4 shows the solid-state ^{13}C CP/MAS NMR spectra of the α-CD/P(PEOMA1100) ICs compared with

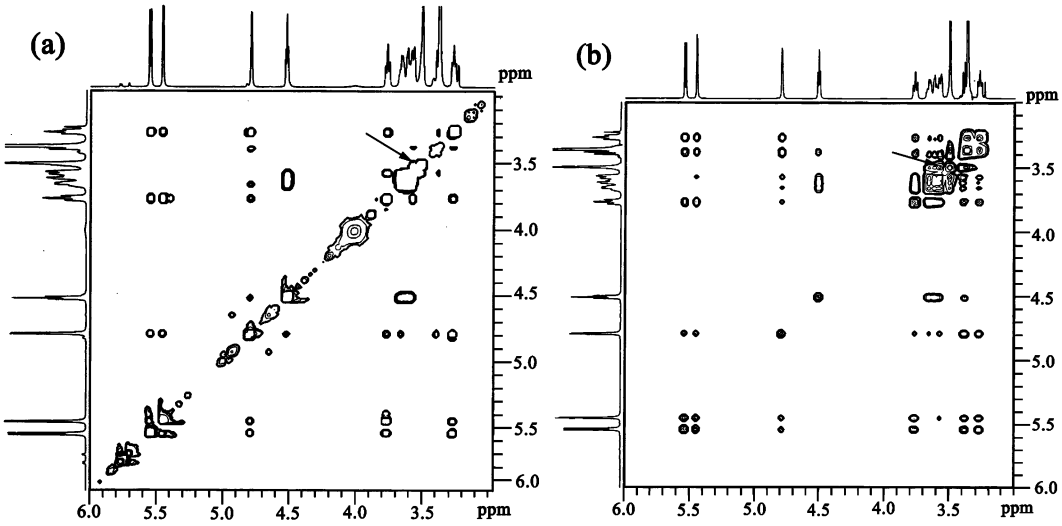


Figure 5. 2D NOESY NMR spectra of (a) α-CD/P(PEOMA475) and (b) α-CD/P(PEOMA1100) in DMSO-d_6.

that of free α-CD. Because of the asymmetrical conformation of the free CDs, each carbon splits into multiple resonances. Moreover, the peaks at $\delta = 82$ and 99.5 ppm were assigned to the conformationally strained glycosidic linkage of free α-CD. However, the threaded CDs adopted column structure of a symmetrical conformation and showed broadened peaks as seen in Figure 4a. The peak at 99.5 ppm disappeared in the spectrum of the ICs. This result further indicates that α-CDs thread onto the PEO side chains in the inclusion complexes.[7,10]

Figure 5 gives the 2D NOESY NMR spectra of ICs for α-CD/P(PEOMA475) and α-CD/P(PEOMA1100) in DMSO-d_6. The two spectra showed that the peaks of the protons located outside of CD cavity, i.e., H-1 ($\delta = 4.79$ ppm), H-2 ($\delta = 3.38$ ppm), and H-4 ($\delta = 3.27$ ppm), have no cross-peaks with the peak of $\delta = 3.48$ ppm, indicating that these three peaks do not correlate with the resonance of the CH_2 in PEO. For the two signals of H-3 ($\delta = 3.76$ ppm) and H-5 ($\delta = 3.58$ ppm) protons that point toward the inside of the cavity, only the H-5 correlates with PEO (the correlation signal is indicated by arrows in Figure 5). In contrast, linear PEO in polyrotaxanes correlates with both H-3 and H-5 in *N*,*N*-dimethylformamide solution and correlation intensity with H-3 is smaller than that with H-5.[9] Therefore, the presence of one correlation demonstrates that the complexation of α-CDs and the grafted PEG chain might be partially destroyed in the DMSO-d_6 solution owing to the incomplete coverage and the correlation between H-3 and EO unit is too weak to find.

The thermal properties of α-CD/polymers complexes were studied by TGA. Figure 6 indicates that the P(PEOMA1100) has similar thermal stability to that of α-CD, and so the initial decomposition temperatures of the comb polymer are almost the same as that of α-CD (ca. 300 °C). After complexation, the thermal stability of ICs has little difference comparing to the two starting materials. Figure 7 gives the DSC thermograms of α-CD, the P(PEOMA1100) and corresponding ICs. For polymer P(PEOMA1100), an endotherm was observed and it corresponds to the melting temperature (T_m) of crystallized PEO segments. However, the ICs showed no melting peak, demonstrating that the PEO side chains are confined in the α-CD channels and their original crystalline properties are lost owing to the formation of inclusion complexation.

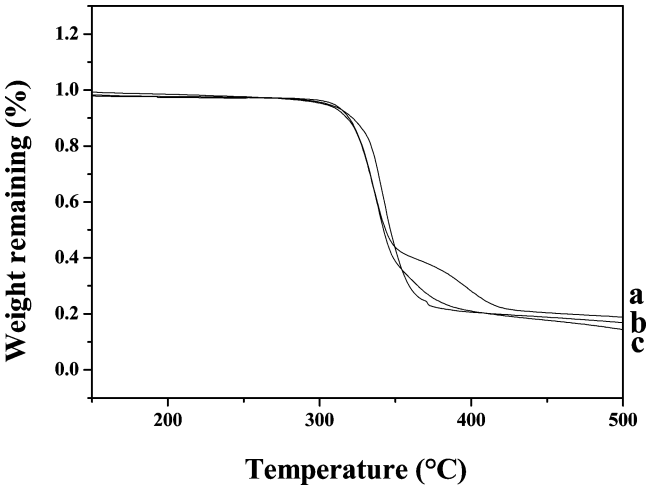


Figure 6. TGA curves of (a) α-CD/P(PEOMA1100), (b) α-CD, and (c) P(PEOMA1100).

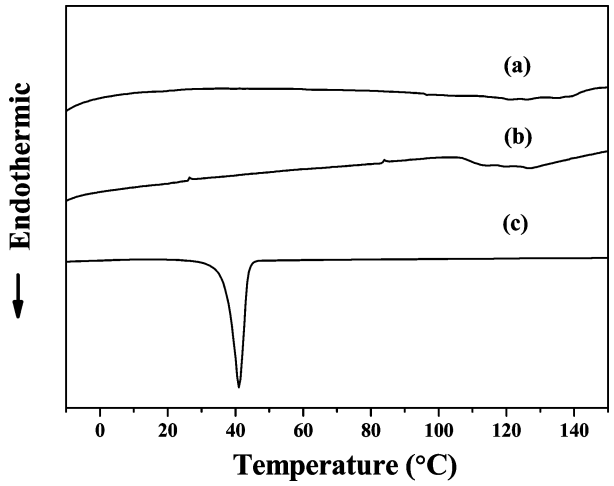


Figure 7. DSC thermograms of (a) α-CD, (b) α-CD/P(PEOMA1100), and (c) P(PEOMA1100).

Above results show that the PEO side chains being densely grafted along polymer backbone can be threaded by α-CDs but it becomes difficult when the length of PEO segments decreases. According to the stoichiometry and XRD results a proposed structure for α-CD/P(PEOMA) is given in Figure 1b. Because of the densely

grafted structure, there are repulsions from inter-side chains, the side chains and the backbones, and the threaded side chains and unthreaded chains. Therefore, not all side chains could be threaded. The reasonable structure is partially threading onto side chains, while the EO units near the backbone are unfavorable to be excluded. In addition, some PEO chains might be not threaded when neighboring PEO were already occupied. If the PEO side chains are too short, the number of CDs allowing to be threaded is too small and no ICs can be stabilized. These supramolecular columns, from same polymer and different polymer, tend to stack into crystalline structure that is as same as that of linear PEO and α-CDs as indicated by XRD patterns. Since partial branches are threaded by α-CDs, comblike polymer structure does not have great influence to the crystalline structure. In another research, PEO grafted dextrins formed hydrogels with α-CDs through the inclusion complexation, which was explained that the IC column assemblies acted as physical cross-linking while the dextrin backbones were hydrated. In comparison, for the comblike PEO grafted polymers used in this study, no formation of hydrogels were observed. From the stoichiometry values obtained in Table 1, the coverage of PEO branches is higher than what was expected. Therefore, hydration of those free EOs is not high enough to give the hydrogels.

Conclusion

A series of densely grafted polymer P(PEOMA)s with three different side-chain lengths were synthesized by the ATRP approach. The inclusion complexes between α-CD and the grafted polymers, P(PEOMA475) and P(PEOMA1100), were successfully prepared and characterized with XRD, ^{13}C CP/MAS NMR, 2D NOESY NMR, TGA, and DSC measurements. XRD measurements indicate that all ICs with α-CD have channel-type crystalline structure. The polymers with longer PEO side chains formed crystalline ICs more easily than those with shorter PEO. The stoichiometry of EO unit to CD ring for the ICs of P(PEOMA475) and P(PEOMA1100) given by ^{1}H NMR spectra indicates that the PEO branches were not completely covered by CDs. This can be explained that the steric hindrance between the backbone and side chains and/or the side chains themselves prevented them to be fully covered. To the best of our knowledge, this is the first report that investigated the inclusion complexation of cyclodextrins with the well-defined polymers of such a high grafting density. When the length ratio of the backbone to side chains is much larger that reported herein, these polymers, i.e., polymer brushes, will adopt a wormlike conformation. The complexation of CDs with such kind of densely grafted polymers is highly interesting and is the focus of our ongoing investigations.

Acknowledgment. Financial support from NSF China (No. 20404014), Bairen Project and Directional Innovation Project of The CAS (KJCX2-SW-H07), and SKLPPC is greatly acknowledged.

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MA047748C