

SYNTHESIS AND CHARACTERIZATION OF POLYROTAXANES MADE FROM α -CDs THREADED ONTO TRIBLOCK COPOLYMERS WITH PEG AS A CENTRAL AXLE AND FLANKED BY TWO LOW MOLECULAR WEIGHT POLYSTYRENES AS OUTER STOPPERS*

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Abstract A study has been conducted on the synthesis and characterization of a kind of novel polyrotaxanes comprising α -cyclodextrins (α -CDs) threaded on triblock copolymers with poly(ethylene glycol) (PEG) as a central axle and flanked by two low molecular weight polystyrenes as outer stoppers. Styrene was allowed to telomerize with polypseudorotaxanes as chain transfer agents made from the self-assembly of a distal thiol-capped PEG with a varying amount of α -CDs in the presence of a redox initiation system at 40°C in aqueous solutions. The resulting polyrotaxanes were characterized in detail by ¹H-NMR, FTIR, XRD, TG and DSC analyses. The findings from the study demonstrated that the low molecular weight polystyrenes were successfully attached to two axle terminals of polypseudorotaxanes, and the number of α -CDs threaded onto the PEG backbone was tunable by varying its molar feeding ratio to some extent, while the polymerization degree of PS nearly remained constant in this radical telomerization process.

Keywords: Polyrotaxane; α -Cyclodextrin; Polystyrene; Radical telomerization.

INTRODUCTION

Cyclodextrins (CDs) are a series of cyclic oligosaccharides consisting of six to eight glucose units, named α -, β -, and γ -CD, respectively, which possess internal hydrophobic cavities capable of accommodating various organic and polymeric compounds. Since the first report given by Harada and colleagues in the 1990s^[1], CD-based polyrotaxanes (PRs) comprising a linear polymer as an axle and numbers of CDs as wheels trapped by two outer bulky stoppers have attracted tremendous interests, both for their intrinsic scientific importance and potential applications in the area of stimuli-responsive materials^[2, 3], supramolecular structured hydrogels^[4, 5], biosensors^[6], carriers for drug controlled release and scaffolds for tissue engineering^[7–10]. Up to now, a great number of bulky groups and end-capping reactions have been tried and utilized to convert polypseudorotaxanes (PPRs) into the corresponding PRs. Harada *et al.* took advantage of such groups as naphthyl, dinitrobenzoyl, dinitrophenyl, trinitro-phenyl, anthryl, and trityl group as bulky stoppers^[11–13]. Fujita *et al.* used fluorescein-4-isothiocyanate to end-cap PPRs made from the self-assembly of α -CDs with a distal amine-terminated poly(ethylene glycol) (PEG)^[14, 15]. Takata *et al.* described a synthesis of PRs by the end-capping reaction of PPRs comprising permethylated α -CDs and poly(tetrahydrofuran) with electrophiles in the solid state^[16]. In recent years, even more intriguing end-capping procedures have been established. Yui and coworker have disclosed a preparation of PRs from PPRs in high yield by using Huisgen cyclization of azido- and alkynyl-modified precursors in the presence of Cu(I)^[17]. Cyclodextrins used not only as macrocyclic molecules but also as bulky stoppers in the PR preparation have also been presented^[18]. Chiu and colleagues have reported an

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elegant two-component system in which an enyl-2-vinyl-cyclopropane end group of the rod-like molecule “swells” after the macrocycle is threaded^[19]. Our group have disclosed a kind of triblock copolymers composed of a polyrotaxane center block and flanked by poly(*N*-isopropylacrylamide) blocks as bulky stoppers *via* the radical telomerization process of *N*-isopropylacrylamide under UV radiation in aqueous solution^[20, 21].

PEG is perhaps one of the most widely used components for the preparation of di- and tri-block copolymers due to its good solubility in both aqueous and organic solvents. In general, amphiphilic PEG-*b*-PS-*b*-PEG triblock copolymers are synthesized *via* the living anionic polymerization of styrene whereby a living difunctional central PS is extended by the ring-opening polymerization of ethylene oxide^[22]. PS-*b*-PEG diblock copolymers can be prepared by either the nitroxide-mediated radical polymerization (NMRP) or atom transfer radical polymerization (ATRP) protocol^[23]. At the same time, PS-*b*-PEO-*b*-PS triblock copolymers with the relative higher content of hydrophobic end blocks are produced *via* the ATRP by using C—Cl end-capped PEO as macroinitiator, and thereby the multiple morphologies are obtained^[24]. Nowadays, in the field of polymeric science, more and more research interests have been directed towards the self-assembly behavior and aggregate morphologies of PS-*b*-PEG as a model of multiblock copolymers, and a number of hierarchical structures, such as micelles formed in selective solvents^[25], the platelet aggregates in cyclohexane^[26], the vesicles in DMF/water and DMF/acetonitrile, as well as the formation of a highly entangled and interconnected, wormlike-cylinder networks are products of the trend^[27–29]. Nonetheless, until today, only limited research has been given to the CD-derived PRs or copolymers^[30, 31].

As part of the research program of combining PRs with triblock copolymers to impart the resulting copolymers with the extraordinary supramolecular attributes, a study was carried out towards the radical telomerization of styrene with PPRs as chain transfer agents made from the self-assembly of a distal end-thiolated PEG with a varying amount of α -CDs in the presence of a redox initiation system in aqueous solutions.

EXPERIMENTAL

Materials

α -CD (TCI, Japan) was used as received. PEG ($M_n = 4000$, PEG 4K) was imported from Japan and distributed domestically. Styrene, sodium bisulphate (NaHSO₃), potassium persulphate (K₂S₂O₈), *p*-toluenesulfonic acid and thioglycolic acid were supplied by VAS Chemical Reagents Company, Tianjin, China. Styrene was washed using 5 wt% sodium hydroxide solution to remove the inhibitor, stored over CaH₂, and vacuum distilled before polymerization. Thioglycolic acid was vacuum distilled before using. NaHSO₃ and K₂S₂O₈ were purified through recrystallization before use. All other solvents and reagents were of analytical grade.

Preparation of Thiolated PEG

Thiol end-capped PEG 4K was prepared by the methodology as previously reported^[19, 20]. In brief, 10 mg *p*-toluenesulfonic acid, 10 g PEG 4K, and 1.38 g thioglycolic acid were added to 100 mL toluene preheated to 120°C. The reaction was allowed to proceed for 10 h under nitrogen atmosphere and driven forward by continuous removal of water produced. The end-thiolated polymer was purified by precipitation in 200 mL anhydrous ether at 5°C. This sequence was repeated three times using dichloromethane as a solvent. The product was then dried under vacuum for 2 days at room temperature with a yield of 92%. FTIR (cm^{−1}): 2866 (CH₂, CH₃), 1736 (C=O), 1109 (C—O); ¹H-NMR (CDCl₃, δ): 4.298 (s, 4 H, —CH₂—O—C(=O)—), 3.645–3.819 (m, 360 H, —OCH₂—CH₂—O—), 3.298 (s, 4 H, —O—C(=O)—CH₂—), 2.010–2.050 (t, 2 H, —SH).

Preparation of PS-*b*-PEG-*b*-PS Triblock Copolymer

0.16 g styrene was added dropwise into a solution of 0.15 g end-thiolated PEG in 5 mL water with magnetic stirring. An initiator mixture comprising 0.01 g NaHSO₃ and 0.04 g K₂S₂O₈ in 1 mL water was then added. The resulting mixture was deoxygenated by nitrogen bubbling for 5 min at room temperature. The radical telomerization was carried out for 4 h under a nitrogen atmosphere at 40°C. After dialysis by using a cellulose membrane, the whole content was freeze-dried. The product was then dissolved in THF and precipitated in cyclohexane three times in order to leave out polystyrene. The purified product was then dried in vacuum.

Preparation of Polypseudorotaxanes

A saturated aqueous solution containing a predetermined amount of α -CDs was added to a certain volume of a 20 wt% distal thiol end-capped PEG solution, followed by vigorous stirring at room temperature. After standing for 30 min, a white, physical gel was formed as a result of the self-assembly of α -CDs with thiol end-capped PEG. The gel was then washed with a small amount of distilled water. Finally, it was freeze-dried to give the polypseudorotaxane powders.

Synthesis of Polyrotaxane-Based Copolymers

0.16 g styrene was dropped into the suspension of PPR formed from 1.46 g α -CD and 0.15 g distal end-thiolated PEG in water with magnetic stirring. An initiation system consisting of 0.01 g NaHSO_3 and 0.04 g $\text{K}_2\text{S}_2\text{O}_8$ in 1 mL water was then added. The resulting mixture was transferred into the reactor, and deoxygenation was performed for 5 min at room temperature by nitrogen bubbling. The radical telomerization was allowed to proceed for 4 h under a nitrogen atmosphere at 40°C. After centrifugation, the precipitate was freeze-dried and then washed with THF to remove the PS homopolymer. To further remove unthreaded α -CDs and PS homopolymer, the copolymers were again incubated in DMSO for 12 h at 60°C. Then, they were precipitated again into acetone, washed with water several times, and dried in vacuum.

For the convenience of expression, the as-prepared polyrotaxane-based copolymers were designated as PEG- n CD- m , where n stands for the feeding molar ratio of α -CDs and m for that of styrene to thiol end-capped PEG, respectively. The average number of in-chained α -CDs in the PRs could be calculated from the integration ratio of the proton resonance peak area of α -CD (H-1) to that of the methylene protons in PEG, and the number of incorporated styrene monomers could be obtained by calculating the integration area ratio of the proton resonance peaks in phenyl group to that of the corresponding protons in PEG.

Measurements

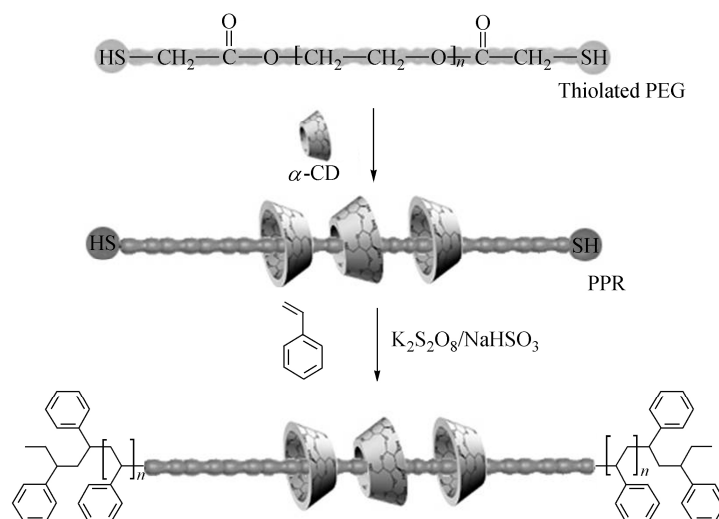
The molecular weight and polydispersity of the distal end-thiolated PEG and the PS-*b*-PEG-*b*-PS triblock copolymer were determined with a gel permeation chromatography (GPC, Waters 2410) using THF as the eluent (1.0 mL/min) at 35°C. The calibration curve was established using a set of narrow molecular weight distribution PS as the standard. ^1H -NMR spectra were obtained on a Bruker ARX 400 NMR instrument at room temperature with DMSO- d_6 as solvent and tetramethylsilane (TMS) as internal standard. FTIR spectra were measured using a Shimadzu IR Prestige-21 FTIR spectrometer at room temperature in the range between 4000 cm^{-1} and 500 cm^{-1} with a resolution of 2 cm^{-1} and 20 scans. Powder samples were prepared by dispersing the samples in KBr and compressing the mixture to form disks. Wide-angle X-ray diffraction (WXR) measurements were performed with powder samples using a Panaltic X'pert PRO X-ray Diffractometer. The radiation source used was Ni-filtered, Cu K α 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 10° to 50° in 2θ at a speed of 5 (°)/min. Thermogravimetric analysis (TGA) of samples was made using a NETZSCH TG 209 thermogravimetric analyzer at a heating rate of 10 K/min with nitrogen used as purge gas. Differential scanning calorimetry (DSC) measurements were carried out using a NETZSCH DSC 204 differential scanning calorimeter. The DSC thermograms covered a temperature range of -30–150°C at a scanning rate of 10 K/min.

RESULTS AND DISCUSSION

Preparation

The preparation strategy of polyrotaxane-based copolymers is shown in Scheme 1. When an aqueous solution of α -CDs was added to a solution of end-thiolated PEG in water, the resultant mixture quickly became turbid, and PPR was formed as the result of the self-assembly of α -CDs with the distal thiol-capped PEG to give an opaque physical gel. This gel is thixotropic and reversible, and the sol-gel transition is easily switched on and off by stirring and standing operations as previously reported^[32, 33]. In fact, after adding styrene to these PPRs under stirring, its radical telomerization with the PPRs containing a distal thiol-capped PEG as a chain transfer agent was carried out in the heterogeneous phase. Here use of $\text{K}_2\text{S}_2\text{O}_8$ and NaHSO_3 as a redox initiation mixture was due to the fact that this redox initiation system usually works perfectly at a relatively lower temperature, highly

desirable for the end-capping reaction of PPRs, otherwise a higher temperature would cause the remarkable dethreading of α -CDs off the PEG axle^[31].



Scheme 1 Preparation strategy of polyrotaxane-based copolymers

The theoretical and found feed compositions and yields of the polyrotaxane-based copolymers are summarized in Table 1. Regarding PEG-50CD-40, PEG-40CD-40, PEG-30CD-40 and PEG-10CD-40, the sample PEG-50CD-40 clearly held the highest number of threaded α -CDs onto its polymeric axle. As can be seen, this value varies from 17 to 38 with the feed ratio changing from 10 to 50. The higher the feed ratio, the higher is the in-chained number of α -CDs. It appears that the in-chained α -CD number is adjustable to some extent by changing the feed ratio. Taking into account one α -CD including two PEG repeating units, the maximum threaded number of α -CDs onto the PEG 4K backbone is around 45. Evidently, an excess amount of α -CDs added cannot ensure them to reach this maximum feed ratio, just as in PEG-50CD-40. This is most likely due to the fact that there is the equilibrium between the threading and dethreading process of α -CDs onto the polymeric axle. When excess α -CDs are intended to be threaded onto the central polymeric axle, they would have a tendency to dethread off the axle chain at the same time leading to the in-chained number of α -CDs lower than that expected. However, when a smaller amount of α -CDs is added, besides the lowest yield, their found feed composition is notably higher than the theoretical ones, just as in PEG-10CD-40.

Table 1. Compositions and yields of PR-based copolymers with α -CDs

Entry	Name	Molar composition (Thiolated PEG: α -CD:styrene)		Yield ^b (%)
		Feed ratio	Found ratio ^a	
1	PEG-0CD-40	1:0:40	1:0:17	57.8
2	PEG-50CD-40	1:50:40	1:38:20	42.3
3	PEG-40CD-40	1:40:40	1:36:24	45.2
4	PEG-30CD-40	1:30:40	1:32:20	48.9
5	PEG-10CD-40	1:10:40	1:17:15	31.2
6	PEG-20CD-80	1:20:80	1:28:21	48.2
7	PEG-20CD-20	1:20:20	1:26:17	35.1
8	PEG-20CD-10	1:20:10	1:27:17	38.3

^aDetermined by ¹H-NMR analysis; ^bAfter incubation in DMSO for 12 h at 60°C

Moreover, the threading and dethreading processes for the added α -CDs might shield the thiol end group in PPRs from contacting with PS propagating radicals and depress its reactivity as a chain transfer agent.

Alternatively, unlike those typical emulsion and suspension polymerizations, a heterogeneous radical telomerization was performed in the present study. Consequently, the in-chained number of styrene became unadjusted by simply changing the monomer to chain transfer agent feeding ratio, always keeping at around 20 with the feed ratio shifting from 10 to 80. However, with regard to the blank sample PEG-0CD-40 prepared under the same conditions but without adding α -CDs, its in-chained number of styrene was nearly in the same range. It seemed that the shielding effect arising from the threading and dethreading of α -CDs as well as the heterogeneous polymerization process are not the reasons for the PD of PS blocks unadjusted. To search more effective initiation systems for the radical telomerization as well as polymerization procedures to make the in-chained number of styrene tunable are our ongoing study.

Furthermore, styrene was reported to form 1:1 inclusion complex with CDs and the corresponding association constant with α -CD is 7.22×10^3 L/mol^[34, 35]. However, the association constant for PEG and α -CD is only about 21.6 L/mol, substantially lower than that for styrene with α -CD^[36]. At first glance, the α -CD-styrene complex seems to be formed more favorably than the α -CD-PEG system. However, the stability of CD complexes with low molecular weight guests is related to the hydrophobic interaction of the host-guest complexes, and this interaction is probably not comparable directly to that for the inclusion complex of α -CD with PEG. Here, hydrogen bonding between adjacent threaded α -CD molecules is expected to become an important "driving force" in the formation of α -CD-PEG inclusion complexes. Meanwhile, this no-covalent interaction between α -CD molecules which are threaded onto different polymer axes is so strong that it leads to the physical gelation or formation of the precipitation/crystallization of inclusion complexes^[31, 35]. As a heterogeneous polymerization system, it is most likely that the process of α -CDs sliding from polymeric axle and then going to include the styrene monomer into their cavities is remarkably slow because of the strong no-covalent interaction in α -CD-PEG complexes. As a result, a kind of novel PR-based copolymers comprising α -CDs threaded PEG as a central axle and flanked by two PS oligomers was obtained. This presumption is evidently supported by a comparison between the theoretical and found feed compositions of copolymers as summarized in Table 1.

The nearly unalterable and relatively short polystyrene blocks in the resulting PR-derived copolymers would restrict their self-assembly capability to give rise to hierarchical structures, such as micelle and vesicles. However, these short PS blocks are indeed bulky enough to be used as efficient end-cappers to block the α -CDs to slide off the PEG axle. Consequently, a new synthetic strategy for intriguing polyrotaxane-based copolymers was established in the present study by using the radical telomerization.

Characterization

Figure 1 depicts the GPC traces of a distal end-thiolated PEG and PEG-0CD-40. Both of them exhibit a unimodal peak with narrow molecular weight distribution, indicating that the triblock copolymer was formed rather than a mixture of the PEG and PS in the radical telomerization process. The number average molecular weight of PEG-0CD-40 was determined to be 5244, well in agreement with that determined by ¹H-NMR analysis. However, its polydispersity index, 1.13 was slightly higher than its precursor, 1.02.

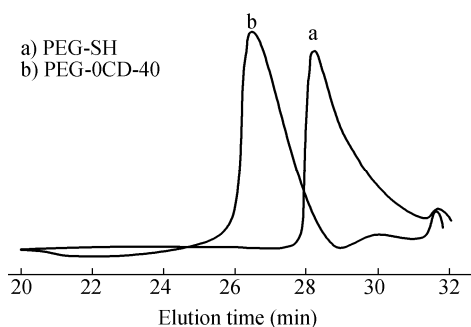


Fig. 1 GPC traces of a distal end-thiolated PEG and PEG-0CD-40

In general, both PPR and PR are insoluble in water and most organic solvents, even in DMF, but are well soluble in DMSO. Although PEG can be included into the cavity of α -CDs to form the inclusion complexes through the non-covalent interactions, α -CDs can also be slid off the PEG backbone in the absence of bulky stoppers^[32]. If the axle chain has not been effectively end-capped, the corresponding dissolution would lead to the dethreading of α -CDs substantially from PEG backbone. Thereby the ^1H -NMR spectrum of PPR in DMSO appears to be a physical blend of the two components. Moreover, upon immobilizing onto the polymeric axle by bulky stoppers, α -CDs become unable to slide off freely unless the chemical bondings between the axle chain and stopper are broken. As reported previously, once a PR obtained, its ^1H -NMR spectrum is characteristic of the broadened resonance peaks, due to the decrease in the conformational flexibility caused by rotaxation^[37]. In addition, slight different chemical shifts between α -CDs with and without accommodating PEG could be discerned, because the chemical environments change before and after the formation of the inclusion complex.

^1H -NMR spectra of pure α -CD (A) and a PR-based copolymer PEG-40CD-40 (B) are given in Fig. 2. As can be seen, all the resonance peaks of α -CDs in the copolymer are evidently broadened, and the corresponding resonance peaks of the secondary hydroxyl groups (O_2H , O_3H) are also different from those of the pure α -CDs. This fact clearly indicated that added α -CDs have been successfully held on the PEG chains with the low molecular weight PS as the end stoppers. The peaks at $\delta = 6.540\text{--}7.040$ correspond to the CH of the phenyl groups in PS segments. Though the peaks of the styrene are well discerned, they are not very strong compared to the other components, because a small number of styrene monomers are incorporated into the copolymers as

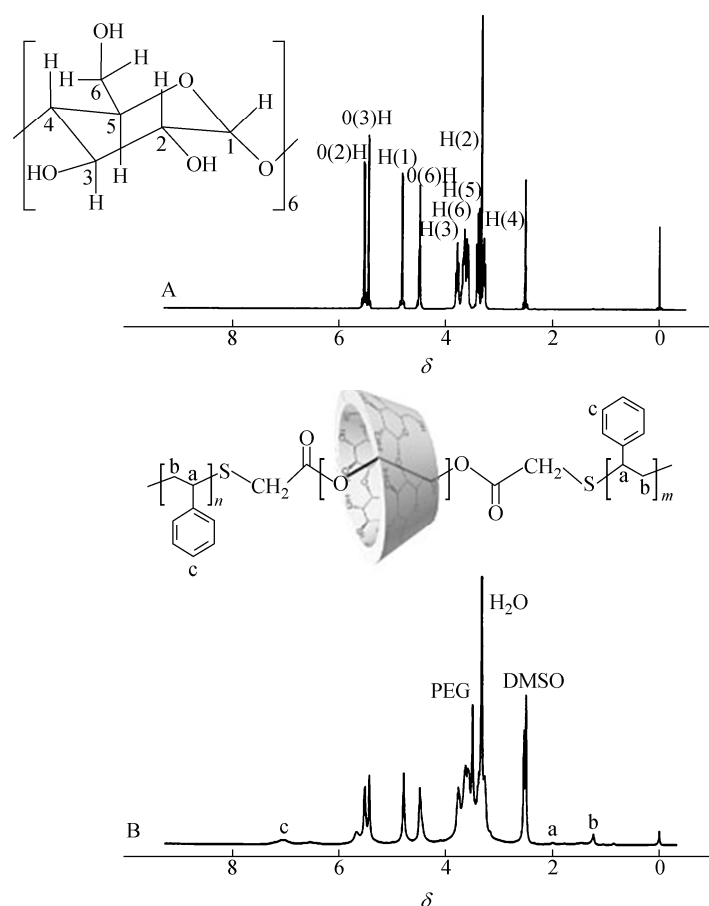


Fig. 2 ^1H -NMR spectra of pure α -CD (A) and polyrotaxane-based copolymer PEG-40CD-40 (B)

discussed above. The other resonance peaks in the PR-based copolymers are assigned as follows: O_2H at $\delta = 5.669$, O_3H at 5.511–5.526, H_1 at 4.798 and O_6H of CD at 4.444, CH at 1.990 and CH_2 of PS at 1.240, respectively. Multiple resonances at $\delta = 3.709$ –3.745 are ascribed to the chemical shifts of H_3 , H_6 , H_5 and PEG protons. As illustrated in Table 1, the average number of in-chained α -CDs in the copolymers was readily calculated from the integration area ratio of the proton resonance peak of α -CD (H-1) to that of the methylene protons in the central PEG axle, while the number of incorporated styrene monomers was easily obtained from the integration area ratio of the proton resonance peaks in phenyl group to that of the corresponding protons in PEG. Because the broadening of resonance peaks of α -CDs led to the superposition of H_3 , H_5 , H_6 of α -CDs and methylene protons of PEG, the integration area of the methylene protons should be calculated by subtracting 3 times integration area of H_1 peak in α -CDs from the summation of all the area of H_3 , H_5 , H_6 peaks and methylene peaks.

FTIR spectra of a distal end-thiolated PEG and PR-based copolymers with and without α -CD addition are shown in Fig. 3. The absorption peaks characteristic of the C—O—C stretching mode and the stretching vibration of carbonyl group in ester linkage appear at 1109 and 1736 cm^{-1} , respectively. The characteristic absorbance bands of the PS are also observed in the spectra. The benzene skeleton vibration emerges at 1600 and 1450 cm^{-1} , and the peaks appear at 757 and 697 cm^{-1} ascribed to the deformation of five adjacent hydrogen atoms in the mono-substituted benzene ring. All of the characteristic peaks of the PS and those of α -CDs were clearly found in the spectra of PEG-20CD-80 (c) and PEG-10CD-40 (d). This is also the direct evidence confirming that the resulting PR-based copolymers are composed of the α -CD threaded PEG central axle and the PS outer bulky stoppers.

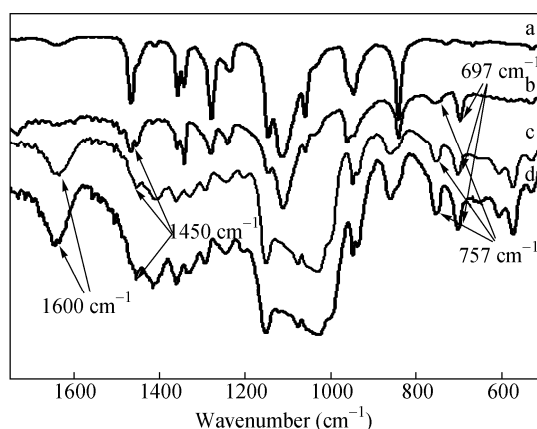


Fig. 3 FTIR spectra of a distal end-thiolated PEG (a), PEG-0CD-40 (b), PEG-20CD-80 (c) and PEG-10CD-40 (d)

Figure 4 shows the X-ray diffraction patterns of the pure α -CDs (a), end-thiolated PEG (b), PEG-0CD-40 (c) and PR-based copolymers (d–i). The major peaks at 12.04°, 14.36°, 18.24° and 21.76° were observed for the pure α -CDs. The pattern of the end-thiolated PEG shows prominent peaks at 19.15° and 23.35°, and that of PEG-0CD-40 looks rather similar to the end-thiolated PEG. However, the patterns of the PR-containing copolymers PEG-20CD-80 (d), PEG-20CD-20 (e), PEG-10CD-40 (f), PEG-30CD-40 (g), PEG-40CD-40 (h) and PEG-50CD-40 (i) are all quite different from that pure α -CDs or end-thiolated PEG and the blank triblock copolymer without addition of α -CD. The peak appeared at $2\theta = 19.69^\circ$ ($d = 0.432$ nm) is the characteristic diffraction peak strongly supporting the channel-type crystalline structure of polyrotaxane or inclusion complex^[1]. Thus, it is demonstrated that these PR-based copolymers also have the characteristic channel-type crystalline structure. Aside from the peak of the tubular crystalline structure, the small peaks corresponding to α -CDs were observed here, which likely result from the relatively stable hydrogen bondings between free and included α -CDs that are not easily broken in the purification processes.

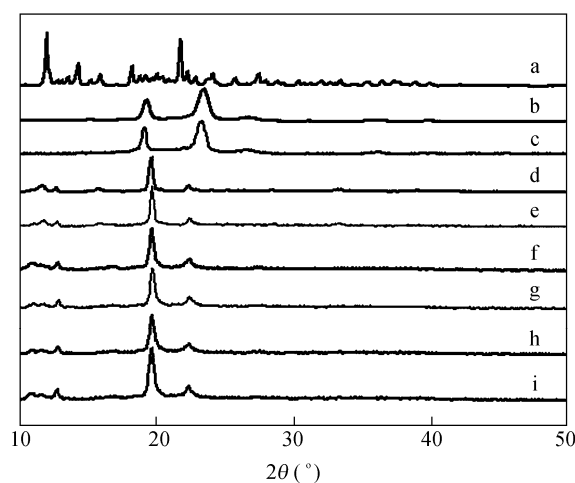


Fig. 4 X-ray diffraction patterns of pure α -CDs (a), a distal end-thiolated PEG (b), PEG-0CD-40 (c) and PR-based copolymers PEG-20CD-80 (d), PEG-20CD-20 (e), PEG-10CD-40 (f), PEG-30CD-40 (g), PEG-40CD-40 (h) and PEG-50CD-40 (i)

Unlike either the pure α -CDs (a) or blank triblock copolymer PEG-0CD-40 without α -CD adding (b), the two-step thermal decomposition processes were clearly discerned from the TGA curves of PR-containing copolymers (c–f) as shown in Fig. 5. These two decomposition processes are explained to be the decomposition of α -CDs and that of the axle chain comprising PEG as a central block and the PS as outer stoppers. The temperature at which two tangents intersected is used as the decomposition temperature (T_d) of a particular component to quantitatively evaluate its thermal stability. The T_d values for α -CDs in the incubated polyrotaxane-based copolymers rise by 29–42°C in comparison with those of their free counterparts. Evidently, the PEG axle chain after fitting into the cavities of α -CDs substantially increases the thermo-stability of the α -CDs-PEG complexes^[38].

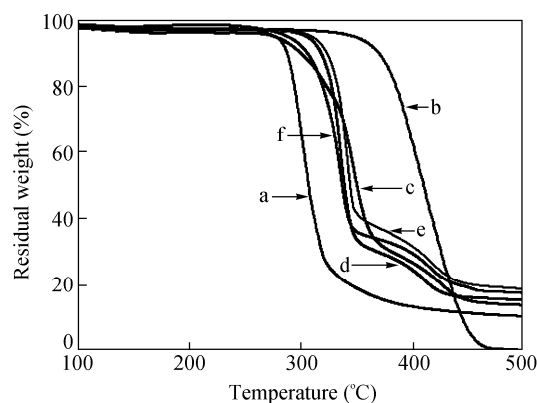


Fig. 5 TGA curves of pure α -CDs (a), PEG-0CD-40 (b) and PR-based copolymers PEG-50CD-40 (c), PEG-30CD-40 (d), PEG-10CD-40 (e) and PEG-20CD-80 (f)

Figure 6 shows the DSC curves of end-thiolated PEG (a), PEG-0CD-40 (b), and PR-based copolymers PEG-50CD-40 (c), PEG-10CD-40 (d), PEG-20CD-80 (e) and pure α -CDs (f). There is a clear endothermic peak appeared at 51.5°C corresponding to the melting point of PEG crystalline phase in the triblock copolymer sample without α -CDs adding, while for end-thiolated PEG it emerges at 59.3°C. The lower temperature of endothermic peak in the former is certainly ascribed to the interference of the PS attached to the two terminals of

the end-thiolated PEG. Upon the formation of PR-based copolymers, the corresponding endothermic peak is completely absent as evidenced in PEG-50CD-40, PEG-10CD-40 and PEG-20CD-80, because the PEG axle chain is included into the channel of the host α -CD lattices, which restrict it from aggregating to form the crystalline phase again.

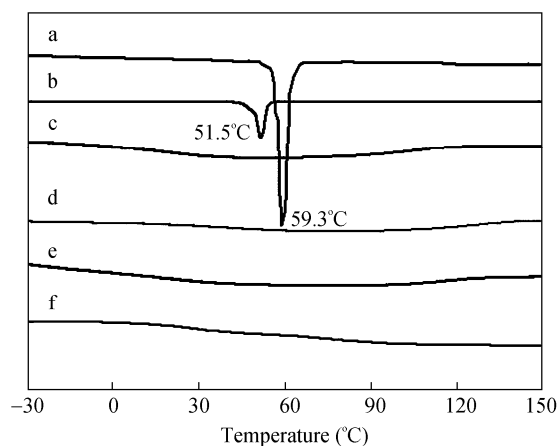


Fig. 6 DSC curves of a distal end thiolated PEG (a), PEG-0CD-40 (b) and PR-based copolymers PEG-50CD-40 (c), PEG-10CD-40 (d), PEG-20CD-80 (e) and pure α -CDs (f)

CONCLUSIONS

A study was carried out on the radical telomerization of styrene with polypseudorotaxanes as chain transfer agents made from the self-assembly of a distal thiol-capped PEG with a varying amount of α -CDs by using a redox initiation system of NaHSO_3 and $\text{K}_2\text{S}_2\text{O}_8$ in aqueous solutions. The resulting polyrotaxanes-based copolymers are shown to be polyrotaxane centered and the hydrophobic low molecular weight PS as bulky stoppers outside. The threaded α -CD number appears adjustable to some extent by changing the feed ratio. However, the in-chained number of styrene always keeps at about 20 per PEG axle chain even the feed ratio shifting from 10 to 80 in the polymerization process. Anyway, a new synthetic strategy for polyrotaxane-based copolymers is established in the present study, and thereby the obtained supramolecular structured copolymers would be promising in the preparation of supramolecular sliding gels, carriers for drug controlled release and scaffolds for tissue engineering.

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