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Novel triblock copolymers synthesized via radical telomerization of *N*-isopropylacrylamide in the presence of polypseudorotaxanes made from thiolated PEG and α-CDs

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Abstract

A protocol for the preparation of novel triblock copolymers comprising a polyrotaxane center block and outer blocks of poly(*N*-isopropylacrylamide) (PNIPAAm) as bulky stoppers was developed, in which *N*-isopropylacrylamide was allowed to telomerize in the presence of polypseudorotaxanes made from the self-assembly of thiol end-capped PEG with a varying amount of α-CDs under UV irradiation in aqueous solution. The molecular structure of the resulting copolymers was characterized in detail by ^{1}H NMR, FTIR, XRD, TG and DSC analyses. It was demonstrated that the PNIPAAm blocks are successfully attached to the two terminals of the polypseudorotaxanes and each block having the minimum 7 NIPAAm units seems long and bulky enough to efficiently impede the dethreading of α-CDs from the PEG axle to give rise to the triblock polyrotaxane-containing copolymers.

Keywords: α-Cyclodextrin; Polyrotaxane; Poly(*N*-isopropylacrylamide)

1. Introduction

Polyrotaxanes and polypseudorotaxanes are topological molecules composed of macrocycles threaded onto linear polymer backbones without covalent bonds linking these two species. Their unique molecular architecture related to cyclodextrins (CDs) has drawn extensive interests since the first account reported in the 1990s [1], because of their prospective applications as stimuli-responding systems [2–4], polyrotaxane networks [5,6], biosensors [7,8], tissue engineering scaffolds and carriers for drug controlled release [9,10]. As is well known, the end-capping is a common measure to hold back the dethreading of CDs from polymer axles during the process of polyrotaxane preparation and application. A number of methods have been tried for the rapid and efficient end-capping manipulation [1,11–13]. Recently, a method which involves an initial conversion of a hydroxyl terminated PEG into a ditosylated PEG, threading it into the cavity of a commercially available unprotected cyclodextrin, and then displacement of the tosyl end groups with bulky blocking groups has been disclosed [14]. An effective and convenient method for the end-capping of polypseudorotaxanes using cyclodextrins not only as macrocyclic molecules but also as stoppers has also been reported [15]. Alternatively, we have recently prepared and identified a series of supramolecular structured hydrogel networks based on photocurable polypseudorotaxanes using cross-linking junctions as topological stoppers [16–18].

As well documented, poly(*N*-isopropylacrylamide) (PNIPAAm) is a class of stimuli-sensitive polymers showing a lower critical solution temperature (LCST) around 32 °C in water [19]. Below this temperature, the polymer molecular chains start to unfold, while above that, they collapse. So a phase-transition process occurs within a specific temperature range. Meanwhile, thiols are long known as very important multifunctional reagents in the fields of organic and polymer

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synthetic chemistry [20,21]. In particular, the radical telomerization involving thiol compounds and alkene monomers has been widely used to prepare a great variety of block copolymers or crosslinked networks [22–24]. Our interest, however, lies in taking advantage of this unique radical telomerization technique to attach the temperature-sensitive PNIPAAm block to each terminal of polypseudorotaxanes made from the self-assembly of thiolated PEG with a varying range of α-CDs to synthesize a kind of novel triblock copolymers, PNIPAAm-*b*-polyrotaxane-*b*-PNIPAAm, where polyrotaxane as a center block and outer blocks of PNIPAAm as bulky stoppers to prevent the dethreading of α-CDs from the polymeric axle. Here, it is not necessary to protect α-CDs due to their hydroxyl groups incapable of reacting with vinyl monomers under the reaction conditions. To our best knowledge, polymer blocks have not yet been reportedly used as stoppers in the preparation of polyrotaxanes. On the other hand, incorporating different lengths of stimuli-responsive polymer blocks into polypseudorotaxanes not only yields a kind of novel polyrotaxanes but also endows the triblock copolymers the new properties.

2. Experimental section

2.1. Materials

N-Isopropylacrylamide (NIPAAm) (Acros, Belgium) was purified by recrystallization from *n*-hexane. α-CD (Sigma, USA) and 2,2-dimethoxy-2-phenyl acetophenone (DMPA, Fluka, Switzerland) were used as received. PEG (PEG 4k, $M_n = 4000$) was imported from Japan and distributed domestically. *p*-Toluenesulfonic acid and thioglycolic acid were supplied by VAS Chemical Reagents Company, Tianjin, China. Thioglycolic acid was distilled under reduced pressure before using. All other solvents and reagents were of analytical grade.

2.2. Preparation of thiolated PEG

PEG 4k was chain-end thiolated by esterification reaction using thioglycolic acid in the presence of *p*-toluenesufonic acid as a catalyst. Briefly, 10 mg *p*-toluenesufonic acid, 10 g of PEG 4k, and 1.38 g thioglycolic acid were added to 100 ml of toluene preheated to 120 °C. The reaction was allowed to proceed for 10 h under nitrogen atmosphere and driven forward by the continuous removal of water produced. The thiolated polymer was purified by precipitation in anhydrous ether (200 ml) at 5 °C. This sequence was repeated three times using dichloromethane as a solvent. The product was then dried under vacuum at room temperature for 2 days with a yield of 92%. FTIR/cm^{-1}: 2866 (CH_2, CH_3), 1736 (C═O), 1109 (C−O); ^{1}H NMR ($CDCl_3$)/ppm: δ 4.298 (s, 4H, $-CH_2-O-C(=O)-$), 3.645–3.819 (m, 360H, $-OCH_2-CH_2-O-$), 3.298 (s, 4H, $-O-C(=O)-CH_2-$), 2.010–2.050 (t, 2H, −SH). The GPC result showed a unimodal peak with a polydispersity index of 1.02.

2.3. Preparation of polypseudorotaxane

A saturated aqueous solution containing a predetermined amount of α-CDs was added to a certain volume of 20 wt% PEG-thiolated polymer solution in water at room temperature. The resulting mixture was sonicated for 10 min and then allowed to stand for gelation. Gelation took place rapidly to yield a physical hydrogel because of the supramolecular self-assembly between α-CDs and the thiolated PEG 4k. The gel was washed with a small amount of distilled water and then directly freeze-dried to give rise to a polypseudorotaxane.

2.4. Synthesis of triblock polyrotaxane-containing copolymer

Firstly, a physical gel was formed upon mixing a certain volume of 20 wt% thiolated PEG 4k aqueous solution with a predetermined amount of α-CDs in water. Secondly, a calculated volume of 20 wt% NIPAAm aqueous solution together with an appropriate amount of photo initiator solution of 2,2-dimethoxy-2-phenyl acetophenone (DMPA) in *N*-vinylpyrrolidone (10 mg/ml) was directly added to the resultant physical gel, vigorously stirred, and then exposed to 365 nm UV lamp of 20 W (Institute of Electric-Light Resources, Beijing, China) for 30 min. After centrifugation, the precipitate was collected by filtration, washed with deionized water, and freeze-dried at −50 °C to give white powder. The powder product was further purified by the following sequence: 0.5 g crude freeze-dried product was dissolved in 20 ml DMSO and allowed to stand for 12 h at 60 °C. Afterwards, the solution was dropped into 200 ml of acetone to give rise to white precipitate again. The precipitate formed was collected by filtration and washed with 50 ml of cold water three times to yield the target triblock copolymer.

For the sake of expression, the triblock polyrotaxane-containing copolymers were designated as *m*-*x*CD-*m*, where *m* stands for the feeding molar ratio of the monomer NIPAAm to −SH in the thiolated PEG, and *x* for that of α-CDs added to the thiolated PEG. For comparative purposes, PNIPAAm and the corresponding triblock copolymers without α-CDs were prepared in acetone, precipitated in cooled hexane and dried under vacuum at 30 °C until constant weight. These triblock polymers without α-CDs were named as *m*-0CD-*m*, where *m* bears the same meaning as the foregoing.

2.5. Measurements

^{1}H NMR (400 MHz) spectra was recorded as solutions using 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 Shimadzu IR Prestige-21 FTIR spectrometer at room temperature in the range between 4000 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.

Gel permeation chromatography (GPC) analysis was carried out with a chromatographic system equipped with a Waters 1515 isocratic HPLC pump and a Waters 2414 refractive index detector. Three columns were in series (Waters styragel HT3, HT4, and HT5, 7.8 × 300 mm). THF was used as eluent at a flow rate of 1.0 ml/min. Monodispersed polystyrene standards were used to obtain a calibration curve.

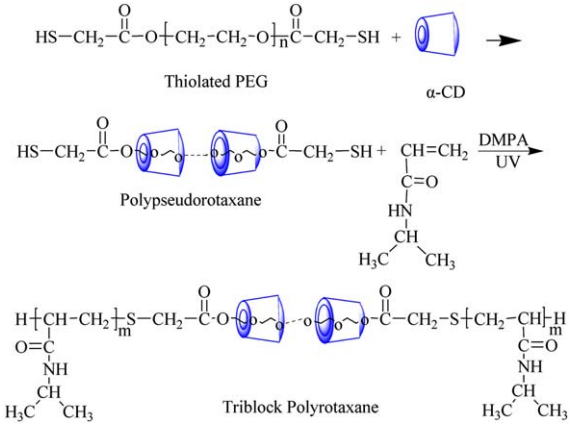
Wide-angle X-ray diffraction (WAXRD) measurements were performed on powder samples using Panaltic X'pert PRO X-ray Diffractometer. The radiation source used was Ni-filtered, Cu Kα radiation with a wavelength of 0.154 nm. The voltage was set to be 40 KV and the current 40 mA. Samples were placed on a sample holder and scanned from 4.5 to 60° in 2θ at a speed of 0.0017°/s.

Thermogravimetric analysis (TGA) of samples was made using TA Instrument 2000 thermogravimetric analyzer at a heating rate of 20 °C/min with nitrogen used as purge gas. Differential scanning calorimetry (DSC) measurements were carried out using a TA Instrument 2910 differential scanning calorimeter. The DSC thermograms covered a temperature range of −100 to 150 °C at a scanning rate of 10 °C/min.

3. Results and discussion

3.1. Preparation

Upon mixing a thiolated PEG 4k aqueous solution with a predetermined amount of α-CD in water, a physical gelation was observed to occur rapidly. The formed physical gel was thixotropic and reversible, and the sol−gel transition process was easily controlled by stirring and standing manipulation [18]. After adding the NIPAAm monomer and an appropriate amount of photo initiator to the physical gel, the resultant mixture was allowed to telomerize for a certain time under UV irradiation to produce the triblock copolymers comprising a polyrotaxane center block and PNIPAAm outer blocks, PNIPAAm-*b*-polyrotaxane-*b*-PNIPAAm. As illustrated in Scheme 1, polypseudorotaxanes holding thiol end groups at the two terminals of the polymer axle not only regulate the polymerization degree or length of the NIPAAm blocks via the photoinitiated radical telomerization but also attach these blocks to themselves as bulky stoppers by the formation of C−S bonds to give rise to the triblock polyrotaxane-containing copolymers.



Scheme 1. Preparation route for triblock polyrotaxane-containing copolymers.

It is easily understood that a shorter PNIPAAm molecular chain could not effectively hold back the dethreading of CDs from the polymer axle owing to its smaller size compared with cavities in CDs, but a longer PNIPAAm block would work well. In order to decide the minimum number of enchained NIPAAm units which makes the PNIPAAm blocks to be as efficient blocking groups, the resulting triblock copolymers were again incubated in DMSO at 60 °C for 12 h. Then, they were precipitated in acetone, washed with water several times, and dried at reduced pressure for the following structure characterization. This process ensured those triblock copolymers incorporated a fewer NIPAAm units which were fully decomplexed into the corresponding free α-CDs and telomers, and then were eliminated with the filtrate after the purification steps. As a result, the precipitation products should be the triblock copolymers whose outer PNIPAAm blocks contain the minimum number of enchained NIPAAm units long and bulky enough to impede the dethreading of α-CDs from thiolated PEG backbone.

Summarized in Table 1 are the found molar composition and percent α-CD coverage as well as yields of both the triblock polyrotaxane-containing copolymers and their counterpart without α-CDs. It can be seen that when the theoretical feed molar ratio was kept below 20, the number of α-CDs threaded onto thiolated PEG backbone after the photoinitiated radical telomerization was ranged from 17 to 28, much higher than the original feed value. In contrast, however, this number was only 28 while the theoretical feed molar ratio was designed to be 45. Although the changing discipline of the NIPAAm monomers incorporated into the triblock copolymers with the adding amounts was complicated, the results clearly demonstrated that a higher α-CDs or lower NIPAAm feed molar ratio certainly depresses the enchained number of the NIPAAm monomers.

Regarding yields of samples 50-5CD-50, 50-10CD-50, 50-20CD-50 and 50-45CD-50, it was found that 50-20CD-50 had

Table 1
Found molar composition and coverage as well as yield of triblock copolymers with and without α-CDs

Name	Found molar composition		Coverage[c] (%)	Yield[d] (%)
	CD/PEG[a] (mol/mol)	NIPAAm/2PEG[b] (mol/mol)		
50-5CD-50	18	36	40	10.6
50-10CD-50	17	42	37.8	31.5
50-20CD-50	24	36	53.3	38.2
25-20CD-25	23	28	51.1	41.4
10-20CD-10	26	7	57.8	18.9
50-45CD-50	28	16	62.2	27.3
25-0CD-25	0	61	0	81.2

[a] The average number of α-CDs per PEG chain calculated from ^{1}H NMR.
[b] Half of the average number of NIPAAm repeat units per triblock copolymer calculated by ^{1}H NMR.
[c] Coverage = 2(CD/PEG (mol/mol))/(PEG repeat units), assuming 2 PEG repeat units per CD.
[d] Yield based on final product to total feed masses.

the highest yield among them, about 41.4%. This was presumably due to the fact that when too many α-CDs were added and threaded on the polymer axle, such as in the case of 50-45CD-50, they would inhibit the thiol group mobility and diminish its chain transfer reactivity towards the radical telomerization of NIPAAm leading to the polyrotaxane with very shorter PNIPAAm end blocks, which was easily decomplexed into its precursors and eliminated during the DMSO incubation and purification steps. On the other hand, when a fewer α-CDs were used, such as in the samples of 50-5CD-50 and 50-10CD-50, they would lead to a better solubility of the prepared triblock copolymers and, consequently, a great amount of soluble products was held in the filtrate after centrifugation and filtering processes when the radical telomerization was completed. These soluble products in the filtrate after freeze-drying have been collected and characterized in our separate article, which exhibit a lower critical solution temperature (LCST) at around 38 °C, close to the human body temperature [25].

Furthermore, in comparison with yields of samples 50-20CD-50, 25-20CD-25 and 10-20CD-10, 10-20CD-10 was found to have the lowest yield, only around 18.9%. Meanwhile, Table 1 presents that each outer block of 10-20CD-10 comprising 7 NIPAAm units appears long and bulky enough to effectively impede the dethreading of α-CDs from the thiolated PEG axle. This implied that most copolymers formed in this case held the number of enchained NIPAAm units for each block much lower than 7, which were easily decomplexed and eliminated after incubation in DMSO and following purification steps. Hence, 7 is most likely the minimum value for each PNIPAAm block containing NIPAAm units to be as efficient blocking groups for all triblock polyrotaxane-containing copolymers studied in the present work.

3.2. Characterization

DMSO is a good solvent for polypseudorotaxanes made from the self-assembly of PEG and α-CDs, but the corresponding dissolution will result in the dethreading of α-CDs substantially from PEG molecular backbone. In general, the ^{1}H NMR spectra of the polypseudorotaxanes in DMSO appear to be identical to that of a physical blend of their two components, indicating that they actually exist as a dynamical mixture of threaded and unthreaded species. In contrast, the formation of polyrotaxanes will broaden the resonance peaks of α-CDs attributing to the decrease in conformational flexibility caused by blocking the dethreading of α-CDs from PEG axle [14]. Furthermore, slight changes in the chemical shifts of α-CDs can be observed due to the change of chemical environments as a consequence of host–guest interaction or inclusion complex. ^{1}H NMR spectra of pure α-CD (a) and a triblock copolymer 25-20CD-25 (b) are given in Fig. 1. It showed that the peaks of α-CD in this triblock copolymer were indeed broadened with respect to pure α-CD. In addition, the most notably downfield shifts for the peaks of the secondary hydroxyl groups (O_2H, O_3H) and the upfield shift for the primary hydroxyl peak (O_6H) were also evidenced in the spectra. This is a powerful proof to support the argument that the

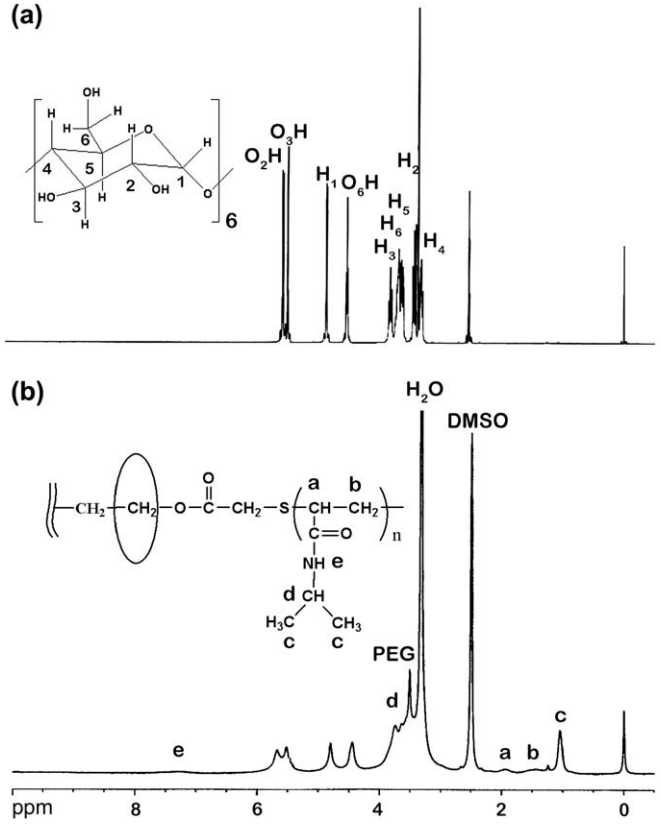


Fig. 1. ^{1}H NMR spectra of pure α-CD (a) and triblock polyrotaxane-containing copolymer 25-20CD-25 (b).

PNIPAAm blocks were successfully attached to the two ends of the corresponding polypseudorotaxane and they were long or bulky enough to efficiently hold back the dethreading of α-CDs from the thiolated PEG axle. Other peaks were assigned as follows: O_2H at δ 5.669, O_3H at 5.511–5.526, H_1 at 4.798, and O_6H at 4.444 ppm, respectively. Multiple resonances appeared at δ 3.709–3.745 are the chemical shift of H_3, H_6, H_5 protons and PEG, and at 3.327–3.450 ppm those of H_2O, H_2, and H_4. Moreover, the peaks attributed to PNIPAAm blocks were definitely observed in this triblock copolymer.

FTIR spectra of pure α-CD (a), triblock copolymers 25-20CD-25 (b), 25-10CD-25 (c) and 10-20CD-10 (d) as well as a triblock copolymer 25-0CD-25 without α-CD (e) are described in Fig. 2. The spectrum of 25-0CD-25 exhibited bands at 1109 and 1736 cm^{-1}, which are attributed to C–O–C stretching mode and the stretching vibration of carbonyl in ester, respectively. The characteristic absorbance bands of the PNIPAAm blocks were also observed in the spectrum. The amide I band (C=O stretch) emerges at 1643, the amide II band (N–H vibration) at 1547, and the methyl groups (in isopropyl group) at 1362–1386 cm^{-1}. Furthermore, not only the characteristic bands of PNIPAAm but also those of α-CD and thiolated PEG were found in the spectra of 25-20CD-25, 25-10CD-25 and 10-20CD-10, clearly suggesting that α-CD and PNIPAAm were incorporated into the corresponding thiolated PEG to give rise to the triblock polyrotaxane-containing copolymers.

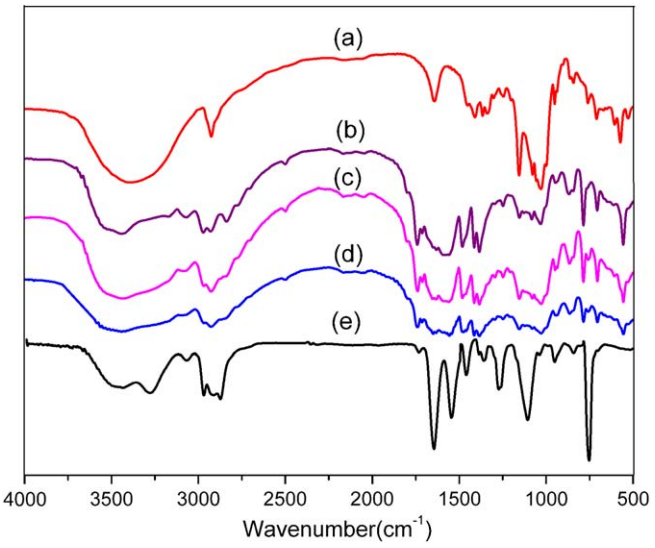


Fig. 2. FTIR spectra of pure α-CD (a), triblock polyrotaxane-containing copolymers 25-20CD-25 (b), 25-10CD-25 (c), and 10-20CD-10 (d) and triblock copolymer 25-0CD-25 without α-CDs (e).

Wide-angle X-ray diffraction (XRD) measurements of the resulting triblock copolymers were performed in the form of powder samples. Their diffraction patterns are shown in Fig. 3. The peaks of pure α-CDs appear at 12.31°, 13.92° and 22.02°, respectively. Meanwhile, thiolated PEG shows two strong peaks at 19.31° and 23.45°. The pattern of the polypseudorotaxane (Fig. 3c) is rather different from that of either α-CDs or thiolated PEG to exhibit a strong peak at $2\theta = 20.11°$ ($d = 4.41$ Å). This is the characteristic diffraction peak to form a channel-type crystalline structure of polypseudorotaxane or inclusion complex [1]. As can be seen, the XRD patterns of all the triblock copolymers 50-5CD-50 (d), 50-10CD-50 (e), 50-20CD-50 (f), 25-20CD-25 (g), 10-20CD-10 (h) and 50-45CD-50 (i) resemble that of their

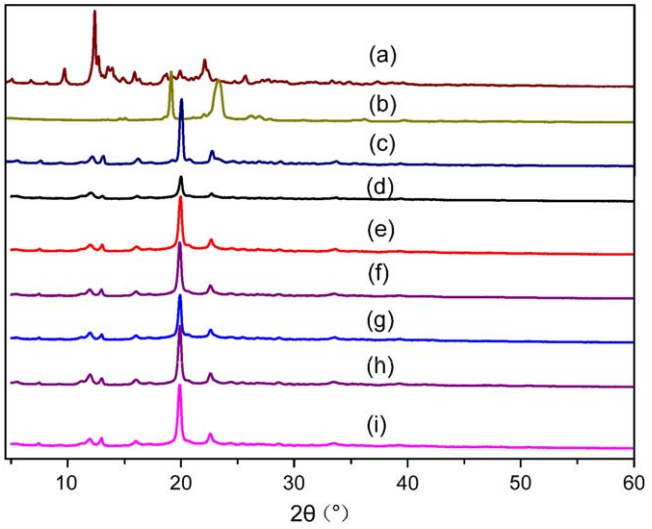


Fig. 3. XRD diffraction patterns of free α-CD (a), thiolated PEG 4k (b), a polypseudorotaxane resulted from them (c) and triblock polyrotaxane-containing copolymers 50-5CD-50 (d), 50-10CD-50 (e), 50-20CD-50 (f), 25-20CD-25 (g), 10-20CD-10 (h) and 50-45CD-50 (i).

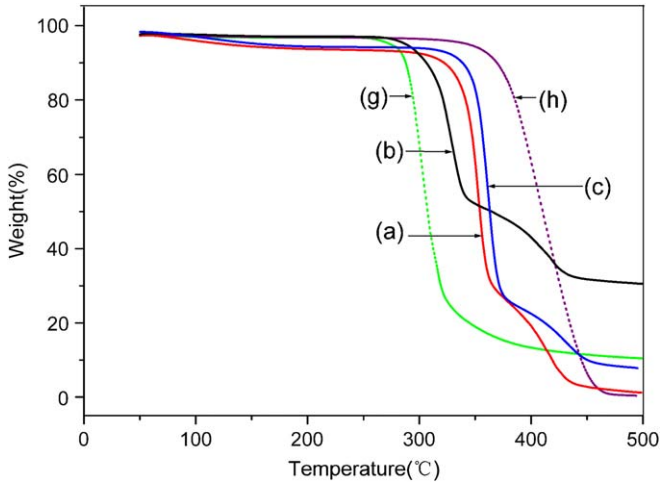


Fig. 4. TGA curves of triblock polyrotaxane-containing copolymers 50-5CD-50 (a), 50-10CD-50 (b), 50-20CD-50 (c) and free α-CD (g) and triblock copolymer 25-0CD-25 without α-CDs (h).

polypseudorotaxane precursor showing a strong diffraction peak at the same position. This clearly demonstrated that these triblock copolymers also possess the characteristic tubular or channel-type crystalline structure. Moreover, although thorough purification steps were intended in this study, small peaks corresponding to α-CDs were always visible in the diffraction patterns. The incomplete removal of free α-CDs is probably due to the presence of relatively stable hydrogen bonded clusters between free and complexed α-CDs which are difficult to be broken down during the purification steps.

Thermogravimetric analysis (TGA) of the resultant triblock copolymers was conducted using TA 2000 thermogravimetric analyzer. The thermal stability of the samples 50-5CD-50 (Fig. 4a), 50-10CD-50 (Fig. 4b), 50-20CD-50 (Fig. 4c), 25-20CD-25 (Fig. 5d), 10-20CD-10 (Fig. 5e) and 50-45CD-50 (Fig. 5f) were assessed and compared with free α-CDs (Figs. 4g and 5g) as well as with a triblock copolymer 25-0CD-25

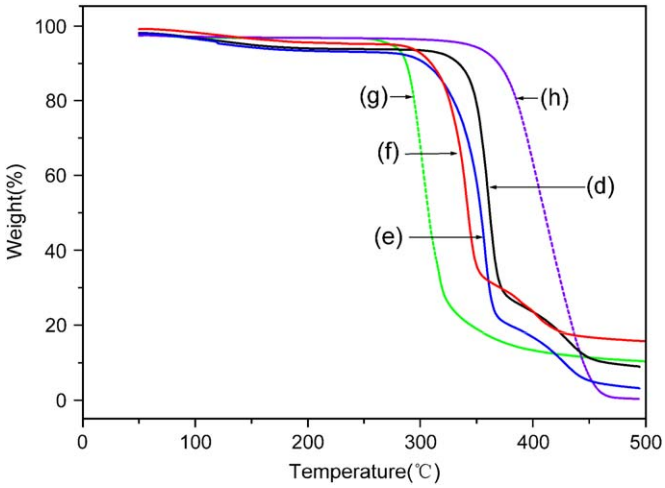


Fig. 5. TGA curves of triblock polyrotaxane-containing copolymers 25-20CD-25 (d), 10-20CD-10 (e) and 50-45CD-50 (f), free α-CD (g) and triblock copolymer 25-0CD-25 without α-CDs (h).

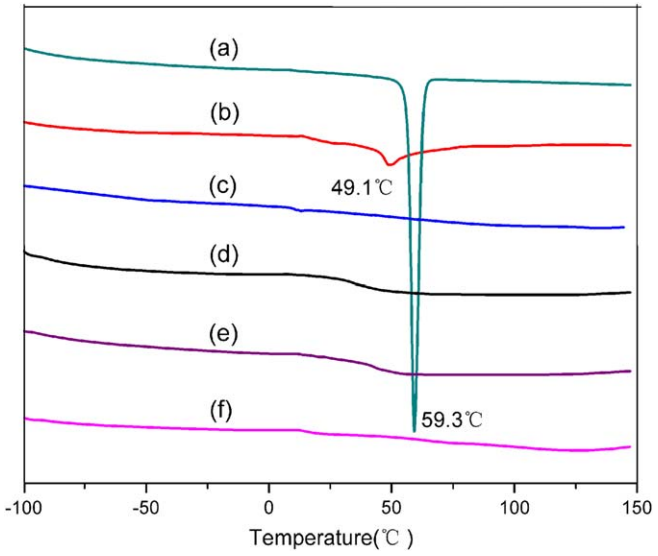


Fig. 6. DSC curves of thiolated PEG (a), 25-0CD-25 (b), PNIPAAm (c), 10-20CD-10 (d) and 50-20CD-50 (e), and pure α-CD (f).

(Figs. 4h and 5h) without α-CDs. As shown in Figs. 4 and 5, respectively, these triblock polyrotaxane-containing copolymers all experienced a two-step thermal degradation. The first step was mainly attributed to the decomposition of α-CDs and the second one to the PEG and PNIPAAm blocks, in which the decomposition of the corresponding free α-CDs did not appear. The temperature at which two tangents intersect is taken as the decomposition temperature of a particular component (T_d) to quantitatively evaluate its thermal stability. The T_d values for α-CD in the triblock copolymers rose by 20–60 °C as compared to its free counterpart. Therefore, the α-CD was significantly stabilized by the formation of the inclusion complexes. This is also a direct proof to indicate that the supramolecular interaction indeed exists between host and guest molecules in the resultant triblock copolymers.

Fig. 6 shows the DSC curves of thiolated PEG 4k (a), 25-0CD-25 (b), PNIPAAm (c), 10-20CD-10 (d), 50-20CD-50 (e) and pure α-CD (f). There was a distinct endothermic peak at 49.1 °C corresponding to the melting point of PEG crystalline phase in the sample 25-0CD-25, while for thiolated PEG it appeared at 59.3 °C. Here, the lower endothermic peak at lower temperature for the former was certainly ascribed to the interference of the PNIPAAm blocks attached at the two terminals of the latter. Upon forming a triblock polyrotaxane-containing copolymer, the corresponding endothermic peak was absent as evidenced in 10-20CD-10 and 50-20CD-50, because the PEG molecular chains were included separately in the channels of the host α-CD lattice, which restricted them from aggregating to form the crystalline phase again.

4. Conclusions

In this work, we present a convenient method for the preparation of triblock copolymers comprising a polyrotaxane center block and outer blocks of PNIPAAm via the radical telomerization of NIPAAm in the presence of polypseudorotaxanes made from the self-assembly of thiol end-capped PEG with varying amounts of α-CDs under UV irradiation in aqueous solution. The study shows that the PNIPAAm blocks are successfully attached to the two terminals of the polypseudorotaxanes and each outer block containing the minimum 7 NIPAAm units seems long and bulky enough to efficiently impede the dethreading of α-CDs from the thiolated PEG axle. This kind of novel triblock polyrotaxane-containing copolymers has the potential to be used in the preparation of supramolecular sliding networks called "sliding ring gels" as well as in drug controlled release.

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