Polymer 50 (2009) 4496–4504

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis of polypseudorotaxanes and polyrotaxanes with multiple α- and γ-cyclodextrins co-threaded over poly[(ethylene oxide)-*ran*-(propylene oxide)]

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ARTICLE INFO

Article history:
Received 13 February 2009
Received in revised form
2 June 2009
Accepted 7 June 2009
Available online 12 June 2009

Keywords:
Cyclodextrin
Polyrotaxane
Copolymer

ABSTRACT

A series of novel polypseudorotaxanes, in which multiple α-cyclodextrin (α-CD) and γ-cyclodextrin (γ-CD) rings were randomly co-threaded over a poly[(ethylene oxide)-*ran*-(propylene oxide)] (P(EO-*r*-PO)) copolymer chain, were prepared by reacting the copolymer simultaneously with α-CD and γ-CD in aqueous solution. X-ray diffraction studies demonstrated that both α-CD and γ-CD molecules in the inclusion complexes (ICs) assumed a channel-type structure. ^{1}H NMR spectra revealed that the compositions of the polypseudorotaxanes were strongly dependent on the molar ratio between α-CD and γ-CD in the feed. More interestingly, when we used the moderately bulk 2,4,6-trinitrophenyl (TNP) group, which is larger than the cavity of α-CD but smaller than that of γ-CD, to cap the two ends of the polypseudorotaxanes, we obtained polyrotaxanes with both α-CD and γ-CD randomly co-threaded over the P(EO-*r*-PO) chain, but the compositions of the polyrotaxanes were different from the corresponding polypseudorotaxanes because some γ-CD rings dethreaded since the cavity of γ-CD is larger than TNP. However, some γ-CD rings were sandwiched by α-CD rings, and these γ-CD and α-CD rings were both entrapped over the P(EO-*r*-PO) chain by the TNP ends. Our results revealed that how the compositions of the polypseudorotaxanes and the polyrotaxanes were different, and how their compositions were affected by the feed ratio between α-CD and γ-CD.

1. Introduction

Cyclodextrins (CDs) are a series of cyclic oligosaccharides composed of 6, 7, or 8 D(+)-glucose units linked by α-1,4-linkages, and named α-, β-, and γ-CD, respectively. The torus-like geometry of CDs gives a hydrophobic cavity having a depth of ca. 7.0 Å, and an internal diameter of ca. 4.5, 7.0, and 8.5 Å for α-, β-, and γ-CD, respectively. The hydrophobic cavity of CDs can form inclusion complexes (ICs) with various low molecular weight molecules, which have been extensively studied in the past decades [1–4]. Polyrotaxanes are supramolecular architectures where multiple cyclic molecules are threaded and blocked over the polymer chain. Since the first CD-based polyrotaxanes were synthesized with multiple α-CDs threaded and trapped over a polymer chain [5,6], supramolecular structures formed between CDs and various polymers have gained tremendous interest [7–37], and supramolecular functional materials based on such structures have been explored for applications in electronics [38,39] and biomaterials [19,40–46].

We previously reported that poly[(ethylene oxide)-*ran*-(propylene oxide)] [P(EO-*r*-PO)] can form ICs, i.e., polypseudorotaxanes with α-CD and γ-CD, respectively, in high yields [15]. Although there are propylene oxide (PO) units randomly placed in the polymer backbone, the copolymer still can penetrate the smallest cavity of α-CD to form polypseudorotaxanes. The phenomenon is interesting in light of the fact that poly(propylene oxide) (PPO) homopolymer could not penetrate the small cavity of α-CD to form any polypseudorotaxane. It was concluded that the α-CD molecules can overcome the energy barrier in passing over a PO unit or some short PO segments, and then form a stable IC with the EO units of the copolymer. There was also a report on a computational study on rotaxanes form by α-CD and β-CD with an oligomer of PEO–PPO [47].

P(EO-*r*-PO) can form polypseudorotaxanes with α-CD and γ-CD, respectively, because EO segments selectively complex with α-CD, and PO segments with γ-CD. It may be interesting to allow P(EO-*r*-PO) to react simultaneously with α-CD and γ-CD in aqueous solution. We hypothesize that polypseudorotaxanes with both α-CD and γ-CD randomly co-threaded over the P(EO-*r*-PO) chain can be formed. Particularly, when we use a moderately bulk end group, e.g., 2,4,6-trinitrophenyl (TNP) group which is larger than the cavity of α-CD but

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doi:10.1016/j.polymer.2009.06.019

smaller than that of γ-CD, to cap the two ends of the polypseudorotaxanes, we will obtain polyrotaxanes with both α-CD and γ-CD randomly co-threaded over the P(EO-*r*-PO) chain, but the compositions of the polyrotaxanes may be different from the corresponding polypseudorotaxanes because some γ-CD rings may dethread since the cavity of γ-CD is larger than TNP ends. However, it is interesting that some γ-CD rings may be sandwiched by α-CD rings, and these γ-CD and α-CD rings will be both entrapped over the P(EO-*r*-PO) chain by the TNP ends. In this paper, we report our results on the formation of polypseudorotaxanes between P(EO-*r*-PO) and the mixture of α-CD and γ-CD in aqueous solution in various molar ratios, and the synthesis of polyrotaxanes from the polypseudorotaxanes with both α-CD and γ-CD co-threaded over the P(EO-*r*-PO) chain by capping the ends with TNP groups. We have shown that how the compositions of the polypseudorotaxanes and the corresponding polyrotaxanes are different, and how their compositions are affected by the feed ratio between α-CD and γ-CD in the solution.

2. Experimental section

2.1. Materials

The P(EO_{41}-*r*-PO_{10}) ($M_n = 2370$, $M_w/M_n = 1.06$) and P(EO_{242}-*r*-PO_{67}) ($M_n = 14{,}570$, $M_w/M_n = 1.06$) copolymers were purchased from Aldrich. The molecular characteristics of these random copolymers were confirmed using GPC and ^{1}H NMR spectroscopy, and they were found to be within the specifications of the supplier. 2,4,6-Trinitrobenzenesulfonic acid (TNBS) aqueous solution was obtained from Fluka. 1,1′-Carbonyldiimidazole (CDI), α-CD and γ-CD were purchased from Tokyo Kasei Incorporation. Ethylenediamine and anhydrous DMF were supplied by Aldrich. DMSO-d_6 and D_2O used as solvents in NMR measurements were obtained from Aldrich.

2.2. Measurements

Gel permeation chromatography (GPC) analysis for P(EO-*r*-PO) copolymers was carried out with a Shimadzu SCL-10AVP and LC-10ATVP system equipped with two Phenogel 5 μm, 50 and 1000 Å columns (size: 300 × 4.6 mm) in series and a Shimadzu RID-10A refractive index detector. THF was used as eluent at a flow rate of 0.30 mL/min at 40 °C. Monodispersed poly(ethylene glycol) standards were used to obtain a calibration curve.

Size exclusion chromatography (SEC) for polyrotaxanes was carried out with a Sephadex G-50 column (size: 2 cm × 26 cm) using DMSO as eluent. Fractions were collected per 2 mL, and their optical rotation and UV absorption were recorded with a HORIBA SEPA-300 high speed accurate polarimeter at a wavelength of 589 nm with cell length 5 cm and response 2 s, and a Shimadzu UV-2501 UV–vis recording spectrophotometer at a wavelength of 418.5 nm, respectively.

The ^{1}H NMR spectra were recorded on a Bruker AV-400 NMR spectrometer at 400 MHz at room temperature. The ^{1}H NMR measurements were carried out with an acquisition time of 3.2 s, a pulse repetition time of 2.0 s, a pulse width of 30°, a spectral width of 5208 Hz, and 32 K data points. Chemical shifts were referred to the solvent peaks ($\delta = 2.50$ and 4.7 ppm for DMSO-d_6 and D_2O, respectively).

The ^{13}C NMR spectra were recorded on a Bruker AV-400 NMR spectrometer at 100 MHz at room temperature. The ^{13}C NMR measurements were carried out using composite pulse decoupling with an acquisition time of 0.82 s, a pulse repetition time of 5.0 s, a pulse width of 30°, a spectral width of 20,080 Hz, and 32 K data points. Chemical shifts were referred to the solvent peaks ($\delta = 39.43$ ppm for DMSO-d_6).

Wide-angle X-ray diffraction (XRD) measurements were carried out using a Siemens D5005 diffractometer using Ni-filtered Cu KR (1.542 Å) radiation (40 kV, 40 mA). Powder samples were mounted on a sample holder and scanned from 5° to 30° in 2θ at a speed of 0.6° per minute.

2.3. Preparation of P(EO-*r*-PO)-bis(amine) (copolymers **2** and **2′**)

The details of the procedures for preparation of **2** are given below as a typical example (Scheme 1). P(EO_{41}-*r*-PO_{10}) copolymer **1** ($M_n = 2370$, 1.90 g, 0.80 mmol) was heated in a flask at 80 °C in vacuum overnight. When the flask cooled, 15 mL of anhydrous DMF was injected under nitrogen. After all **1** was dissolved, the DMF solution of **1** was added dropwise over 6 h under nitrogen to 15 mL of anhydrous DMF solution in which CDI (1.30 g, 8.0 mmol) was dissolved. The mixture was stirred overnight under nitrogen at room temperature. Then, the resulting solution was slowly added dropwise over 3 hours into 4.8 g (80 mmol) of ethylenediamine which was dissolved in 15 mL of anhydrous DMF under stirring at room temperature. The reaction mixture was stirred overnight. Excess ethylenediamine and DMF was removed by vacuum evaporation. The resulting viscous solution was purified by size exclusion chromatography (SEC) on a Sephadex LH-20 column using methanol as eluent. Finally, 1.42 g of viscous liquid **2** was obtained (yield, 70%).

2.4. Preparation of polypseudorotaxanes (***3a***, ***3b***, ***3c***, ***3d***, ***3e***, ***3′a***, ***3′b***, ***3′c***, ***3′d***, and ***3′e***)

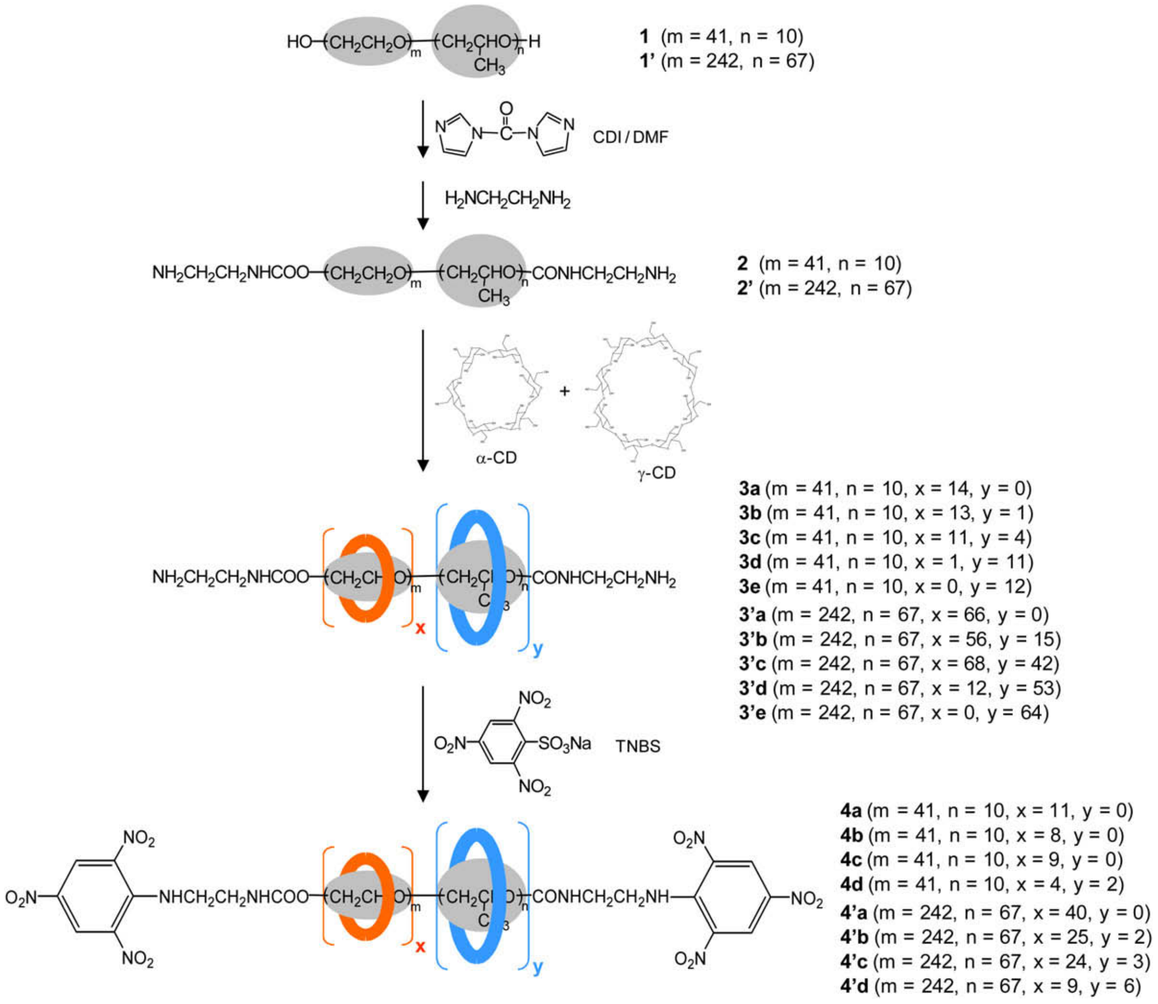
The details of the procedures for preparation of **3c** are given below as a typical example. P(EO_{41}-*r*-PO_{10})-bis(amine) **2** (0.10 g) was added to 10 mL of α-CD and γ-CD mixture aqueous solution, in which the concentrations of α-CD and γ-CD were 0.145 g/mL and 0.193 g/mL, respectively. The solution was ultrasonicated for 20 min and gradually became turbid, producing the IC as precipitate. The reaction mixture was further stirred overnight at 4 °C. The precipitated IC was isolated by centrifugation and washed twice with water, and then freeze-dried in vacuum. Finally, 1.80 g of white powder **3c** was obtained (yield, 91%).

2.5. Preparation of polyrotaxanes (***4a***, ***4b***, ***4c***, ***4d***, ***4′a***, ***4′b***, ***4′c***, and ***4′d***)

The details of the procedures for preparation of **4c** are given below as a typical example. P(EO-*r*-PO)-bis(amine) **2** (0.20 g) was added to 10 mL of α-CD and γ-CD aqueous solution, in which the concentrations of α-CD and γ-CD were 0.0725 g/mL and 0.193 g/mL, respectively. 0.12 g of $NaHCO_3$ was also added to adjust the pH of the solution to 8. The reaction mixture was ultrasonicated for 20 min and stirred at 4 °C overnight. Then, 0.84 g of sodium salt of 2,4,6-trinitrobenzenesulfonic acid solution was added and stirred at room temperature overnight. Finally, the reaction mixture was freeze-dried in vacuum and purified by size exclusion chromatography (SEC) on a Sephadex G-50 column using DMSO as eluent. The polyrotaxane fraction was collected and concentrated, and then precipitated from water. The precipitate was washed for three times with water, and then centrifuged and freeze-dried in vacuum to give 0.169 g of **4c** in brownish yellow powder (yield, 19%).

3. Results and discussion

Scheme 1 shows the procedures for the synthesis of the polypseudorotaxanes **3a**–**3e** and **3′a**–**3′e** and polyrotaxanes **4a**–**4d** and **4′a**–**4′d**. First, P(EO-*r*-PO)-bis(amine) **2** or **2′** was prepared from the corresponding P(EO-*r*-PO) copolymer **1** or **1′**: both hydroxyl end



Scheme 1. Synthesis procedures and structures of polypseudorotaxanes (**3a**–**3e** and **3′a**–**3′e**) and polyrotaxanes (**4a**–**4d** and **4′a**–**4′d**).

groups of the random copolymer were activated with 1,1′-carbonyldiimidazole (CDI), followed by reaction with excessive ethylenediamine. Then, polypseudorotaxanes **3a**–**3e** and **3′a**–**3′e** were formed between the P(EO-*r*-PO)-bis(amine) and α-CD, γ-CD or the mixtures of α-CD and γ-CD at various molar ratios in aqueous solution. Subsequently, polyrotaxanes **4a**–**4d** and **4′a**–**4′d** were synthesized by adding sodium 2,4,6-trinitrobenzenesulfonate (TNBS) to the reaction mixture of the corresponding polypseudorotaxanes **3a**–**3e** and **3′a**–**3′e**, by attaching two bulky stoppers to block both ends of the polymer chain. These polyrotaxanes were purified by column chromatography using Sephadex G-50 as stationary phase and DMSO as eluent.

Fig. 1 shows the GPC diagrams of the two P(EO-*r*-PO) copolymers used in this paper. Both of their elution curves showed a single unimodal peak. Their number-average molecular weight was found to be 2370 and 14,570, respectively. Also, both of the copolymers were found to be nearly monodisperse, with the same polydispersity of 1.06. These GPC results, in conjunction with their ^{1}H NMR spectra, determined that the compositions of the two random copolymers were P(EO_{41}-*r*-PO_{10}) and P(EO_{242}-*r*-PO_{67}), respectively.

The X-ray powder diffraction (XRD) patterns of the polypseudorotaxanes **3a**–**3e** and **3′a**–**3′e** are shown in Fig. 2, as compared with those of free α-CD and γ-CD. For polypseudorotaxanes **3a**–**3c** and **3′a**–**3′c**, the prominent peak was observed at 19.7° (2θ), which is well known to be characteristic of α-CD-based IC crystals adopting a channel structure [15]. Meanwhile, for polypseudorotaxanes **3c**–**3e** and **3′c**–**3′e**, the diffraction peak at around 7.5° (2θ) is also present, which is well known to be characteristic of γ-CD-based IC crystals

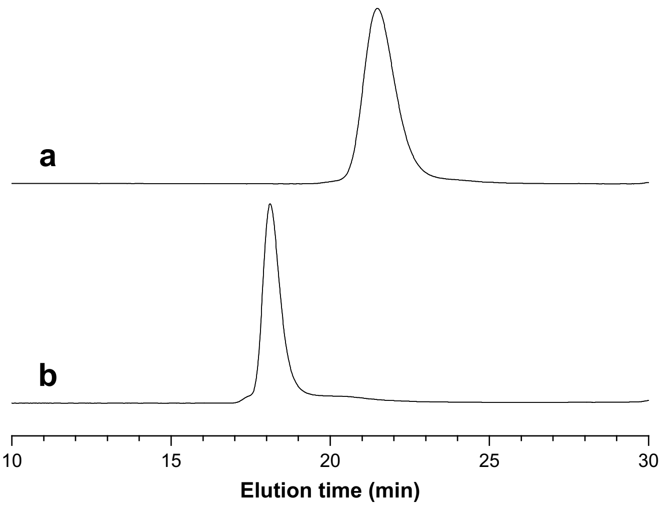


Fig. 1. GPC traces of random copolymers P(EO_{41}-*r*-PO_{10}) ($M_n = 2370$, $M_w/M_n = 1.06$) (a), and P(EO_{242}-*r*-PO_{67}) ($M_n = 14{,}570$, $M_w/M_n = 1.06$) (b).

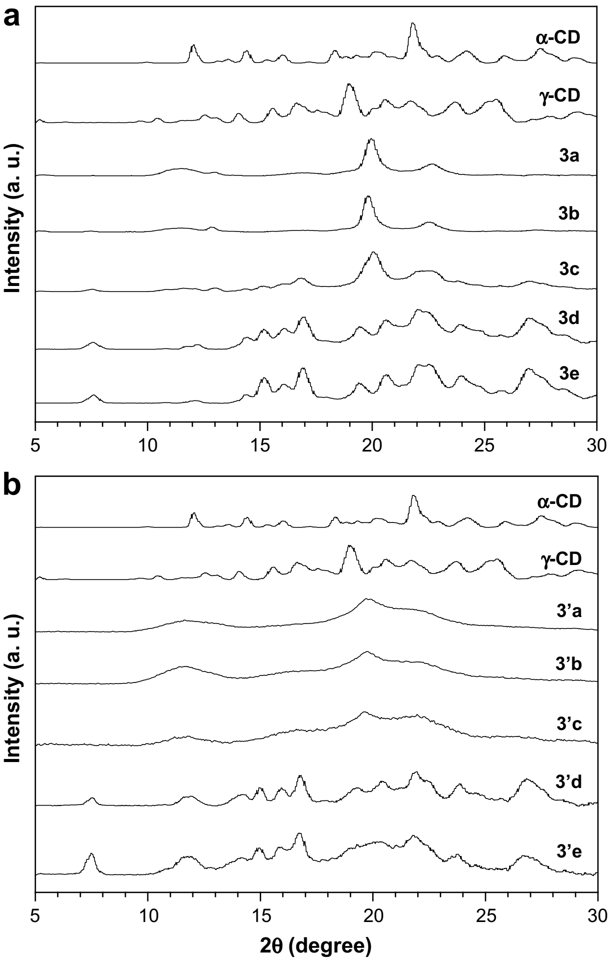


Fig. 2. X-ray powder diffraction diagrams of polypseudorotaxanes **3a**–**3e** (a) and **3′a**–**3′e** (b), in comparison with those of α-CD and γ-CD.

adopting a channel structure [15]. These results indicate that both α-CD and γ-CD molecules in the polypseudorotaxanes adopt a channel structure.

The compositions of the polypseudorotaxanes were quantitatively studied using ^{1}H NMR spectroscopy. Figs. 3 and 4 show the ^{1}H NMR spectra of polypseudorotaxanes **3a**–**3e** and **3′a**–**3′e** in DMSO-d_6, respectively. For polypseudorotaxanes **3b**–**3d** and **3′b**–**3′d**, it is clearly observed that, with a decrease in molar ratio of α-CD to γ-CD in the feed, the integral intensity of H-1 peak of γ-CD increased, and that of α-CD decreased significantly. A comparison between the integral intensity of H-1 peak for α-CD (and/or γ-CD) and that of methyl proton peak of the P(EO-*r*-PO) copolymer gives the composition of the polypseudorotaxanes **3a**–**3e** and **3′a**–**3′e**. Table 1 lists the measured numbers of α-CD (x) and γ-CD (y) in a single polypseudorotaxane chain. As shown in Table 1, the α-CD and γ-CD molecules threaded in the polypseudorotaxanes **3b**–**3d** are strongly dependent on the molar ratio of α-CD to γ-CD in the feed: decreasing the molar ratio enables less α-CD and more γ-CD molecules to reside on a random copolymer chain, and vice versa. A similar trend was also observed in the polypseudorotaxanes **3′b**–**3′d** obtained. These results indicate that the molar ratio between various cyclodextrin molecules in the feed has a great influence on the composition of the polypseudorotaxane formed.

During the formation of polypseudorotaxanes **3a**–**3e** and **3′a**–**3′e**, both α-CD and γ-CD rings could pass over and respectively reside at the EO and PO segments of the random copolymer chain, leading to two distinctly different and mutually independent complexation processes. For the polypseudorotaxanes **3b**–**3d** and **3′b**–**3′d**, the coexisting α-CD and γ-CD molecules in the feed competitively slide onto the random copolymer chain and produced the polypseudorotaxanes with both α-CD and γ-CD threaded over P(EO-*r*-PO). Hence, changing the molar ratio of α-CD to γ-CD in the feed resulted in the variation of the numbers of α-CD and γ-CD molecules threaded, giving rise to polypseudorotaxanes with variable compositions.

The above polypseudorotaxanes could be further converted to corresponding polyrotaxanes by attaching TNP groups to both ends of the random copolymer to stop CDs from dethreading. Fig. 5 shows the size exclusion chromatography (SEC) profiles of the reaction mixtures for syntheses of polyrotaxanes **4a**, **4b**, **4c**, and **4d**, with reference to the reaction mixture of P(EO_{41}-*r*-PO_{10})-bis(amine) **2**, γ-CD, and TNBS. All the samples for the SEC were obtained by freeze drying the reaction mixtures after the reaction completed between polypseudorotaxanes **3a**–**3e** with TNBS. The elution curves were recorded against UV–vis absorption (Abs) at 418.5 nm and optical rotation (OR). As shown in Fig. 5, a–d, for the reaction mixture of each polyrotaxane, the fraction for the first peak (P1) was eluted after the void volume of the column in both UV and OR diagrams, indicating that it has large molecular size and comprises both CD and TNP end group in a single species. Therefore, P1 represents the target polyrotaxane products. Similarly, the fractions for P2, P3 and P4 can be attributed to the byproducts and/or unreacted reactants P(EO_{41}-*r*-PO_{10})-TNP_2, TNBS, and free CDs, respectively. In contrast, there is no P1 peak found in Fig. 5e, indicating that the polyrotaxane with pure γ-CD could not be formed in the reaction. In other words, the TNP group is too small to block γ-CD molecules to dethread from P(EO_{41}-*r*-PO_{10})-TNP_2 copolymer chain: the polypseudorotaxane **3e** with TNP ends decomposed during passing through the column.

Fig. 6 shows the SEC profiles of the reaction mixtures for syntheses of polyrotaxanes **4′a**, **4′b**, **4′c**, and **4′d**, with reference to the reaction mixture of P(EO_{242}-*r*-PO_{67})-bis(amine) **2′**, γ-CD, and TNBS. The only difference from Fig. 5 is that, in each UV diagram of Fig. 6, the peak for the polyrotaxane (P1) and that for P(EO_{242}-*r*-PO_{61})-TNP_2 (P2) overlap entirely due to the high molecular size of P(EO_{242}-*r*-PO_{61})-TNP_2. The fractions for P3 and P4 represent TNBS and free CDs, respectively. Similar to Fig. 5e, there is no polyrotaxane (P1) peak found in the OR diagram in Fig. 6e, indicating that the polyrotaxane composed of pure γ-CD molecules threaded over P(EO_{242}-*r*-PO_{67})-TNP_2 could not be formed due to the small size of TNP ends.

Fig. 7 shows the ^{13}C NMR spectra of polyrotaxanes **4d** and **4′d** with reference to free α-CD and γ-CD. In Fig. 7c and d, all peaks attributed to α-CD, γ-CD, and the threading P(EO-*r*-PO) copolymer were observed, while the peaks of the polyrotaxanes were broader than those of free α-CD because the molecular motion of the components in the polyrotaxane was restricted due to the molecular interlocking.

Figs. 8 and 9 show the ^{1}H NMR spectra of the polyrotaxanes **4a**–**4d** and **4′a**–**4′d** with reference to the pristine α-CD and γ-CD. The ^{1}H NMR spectra show that polyrotaxanes **4a**, **4b**, **4c**, and **4′a** contain only α-CD, and there are no γ-CD threaded and entrapped over the polymer. For polyrotaxanes **4d**, **4′b**, **4′c**, and **4′d**, the signals for α-CD, γ-CD, threading P(EO-*r*-PO) copolymer, and TNP ends were observed, while the peaks were also broadened due to the restriction of the molecular motion by molecular interlocking. A comparison between the integral intensity of H-1 peak for α-CD (and/or γ-CD) and that of methyl proton peak of the P(EO-*r*-PO) copolymer gives the composition of the polyrotaxanes **4a**–**4d** and **4′a**–**4′d**. From the ^{1}H NMR spectra, the numbers of α-CD (x) and γ-CD (y) in a single polyrotaxane molecule are estimated and listed

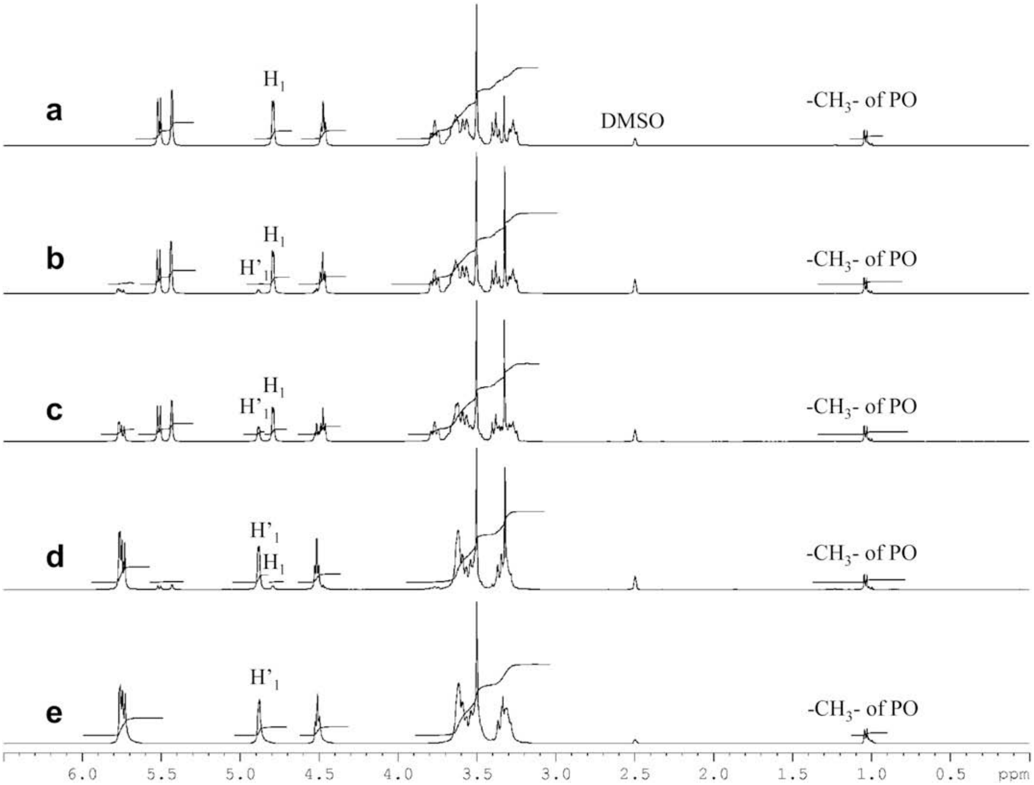


Fig. 3. ^{1}H NMR spectra of polypseudorotaxanes **3a** (a), **3b** (b), **3c** (c), **3d** (d), and **3e** (e) in DMSO-d_6.

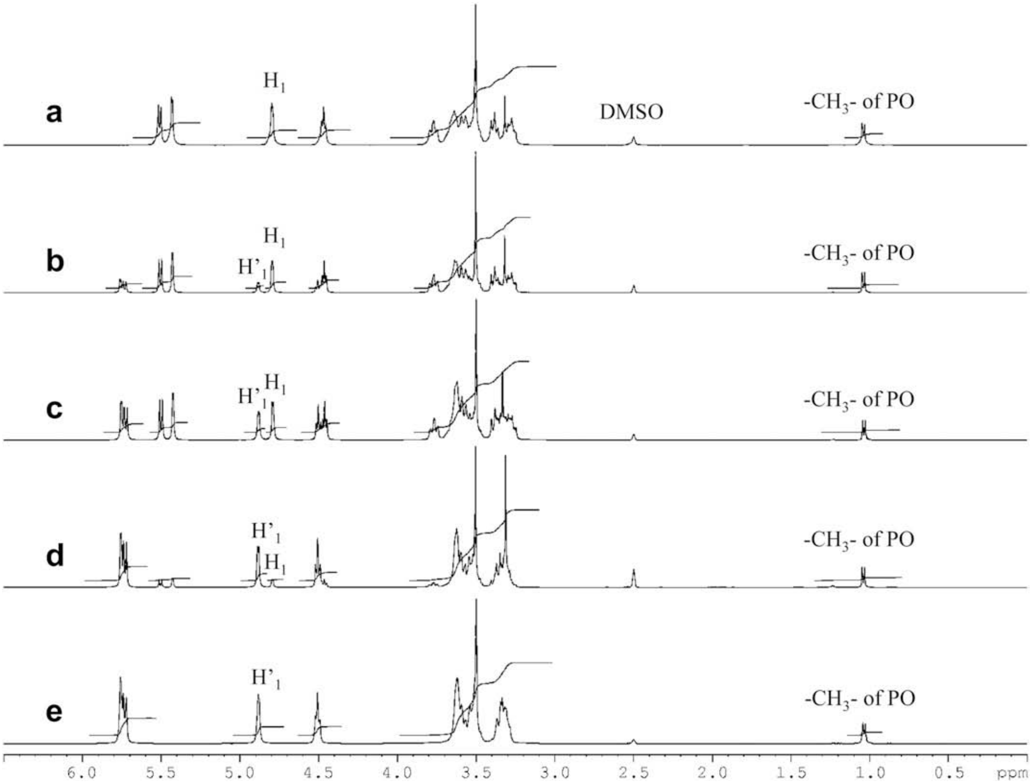


Fig. 4. ^{1}H NMR spectra of polypseudorotaxanes **3′a** (a), **3′b** (b), **3′c** (c), **3′d** (d), and **3′e** (e) in DMSO-d_6.

Table 1
Preparation of polypseudorotaxanes and their compositions.[a]

Polypseudorotaxane		Molar ratio of P(EO-*r*-PO) to α-CD to γ-CD in the feed	Composition		Yield (%)
Code	Constitution		x[b]	y[c]	
3a	α-CD-P(EO_{41}-*r*-PO_{10})	1:38:0	14	0	82
3b	α-CD-γ-CD-P(EO_{41}-*r*-PO_{10})	1:38:19	13	1	68[d]
3c	α-CD-γ-CD-P(EO_{41}-*r*-PO_{10})	1:38:38	11	4	91
3d	α-CD-γ-CD-P(EO_{41}-*r*-PO_{10})	1:19:38	1	11	88
3e	γ-CD-P(EO_{41}-*r*-PO_{10})	1:0:38	0	12	88
3′a	α-CD-P(EO_{242}-*r*-PO_{67})	1:220:0	66	0	93
3′b	α-CD-γ-CD-P(EO_{242}-*r*-PO_{67})	1:220:110	56	15	99
3′c	α-CD-γ-CD-P(EO_{242}-*r*-PO_{67})	1:220:220	68	42	92
3′d	α-CD-γ-CD-P(EO_{242}-*r*-PO_{67})	1:110:220	12	53	91
3′e	γ-CD-P(EO_{242}-*r*-PO_{67})	1:0:220	0	64	98

[a] A comparison between the integral intensity of H-1 peak for α-CD (and/or γ-CD) and that of methyl proton peak of the P(EO-*r*-PO) copolymer gives the composition of the polypseudorotaxanes **3a**–**3e** and **3′a**–**3′e**.

[b] The number of α-CD in a single polypseudorotaxane chain determined by ^{1}H NMR.

[c] The number of γ-CD in a single polypseudorotaxane chain determined by ^{1}H NMR.

[d] Loss of some product by accident.

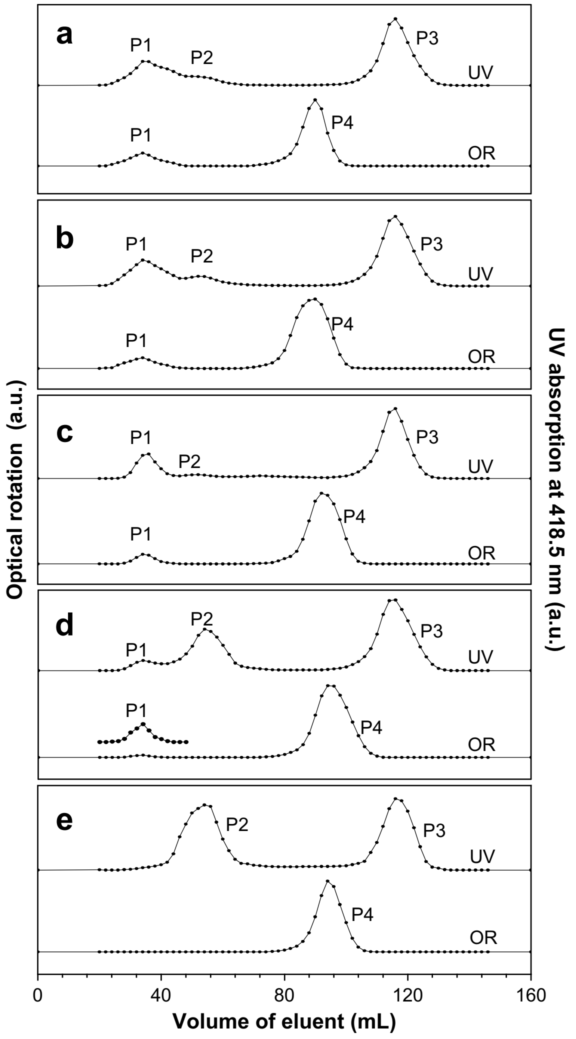


Fig. 5. Size exclusion chromatograms of the reaction mixtures for syntheses of polyrotaxanes **4a** (a), **4b** (b), **4c** (c), **4d** (d), and the reaction mixture of P(EO_{41}-*r*-PO_{10})-bis(amine), γ-CD, and TNBS (e).

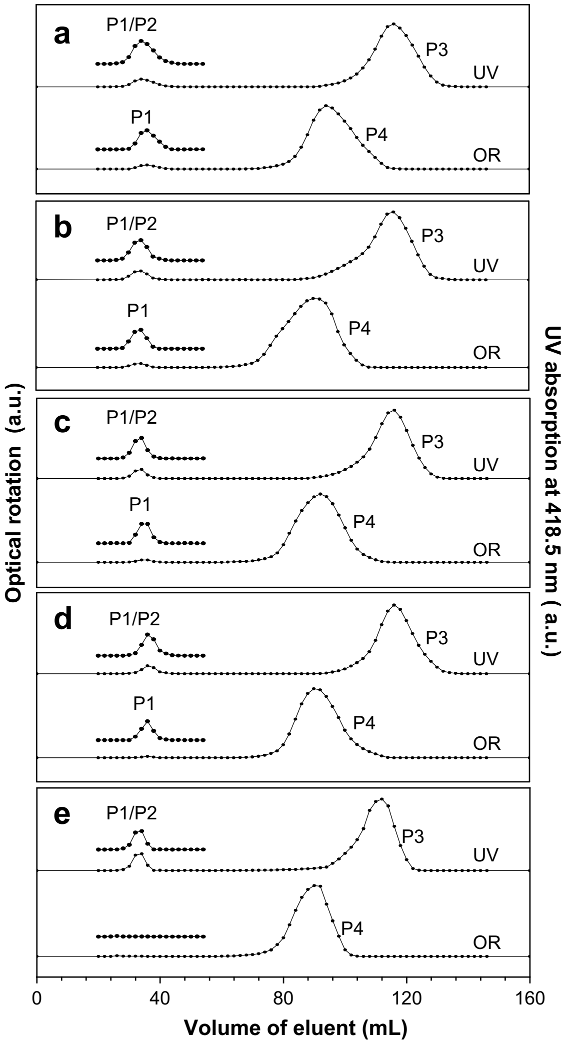


Fig. 6. Size exclusion chromatograms of the reaction mixtures for the syntheses of polyrotaxanes **4′a** (a), **4′b** (b), **4′c** (c), **4′d** (d), and the reaction mixture of P(EO_{242}-*r*-PO_{67})-bis(amine), γ-CD, and TNBS (e).

in Table 2. Compared to the corresponding polypseudorotaxanes, the number of γ-CD in the polyrotaxanes **4b**–**4d** and **4′b**–**4′d** decrease dramatically, and only **4d**, **4′b**, **4′c**, and **4′d** have a few γ-CD rings threaded. It is clear that many threaded γ-CD molecules in the polypseudorotaxanes could traverse the TNP ends and dethreaded from the random copolymer chain. Because of the restriction and blocking of adjacent threaded α-CD molecules, however, a few γ-CD molecules could be sandwiched and entrapped on the random copolymer chain. And it is obvious that longer copolymer chain is helpful to allow γ-CD molecules to be sandwiched by α-CD molecules on the random copolymer chain. It is also noted that the numbers of α-CD molecules entrapped on the polyrotaxanes are smaller than that in their corresponding polypseudorotaxanes, because they partially dethreaded during the end capping reaction. However, the number of α-CD in polyrotaxane **4d** is larger than that in polypseudorotaxane **4d**. There may be two reasons: (1) The dethreading of γ-CD during the end capping reaction could give more room for more α-CD to rethread, and then the number of α-CD finally entrapped increased; (2) The numbers x and y for **3d** are average values since we deal with polymers. Only those having larger x had better chance to be converted to polyrotaxanes, because there was dethreading of both α-CD and γ-CD during the end capping reaction.

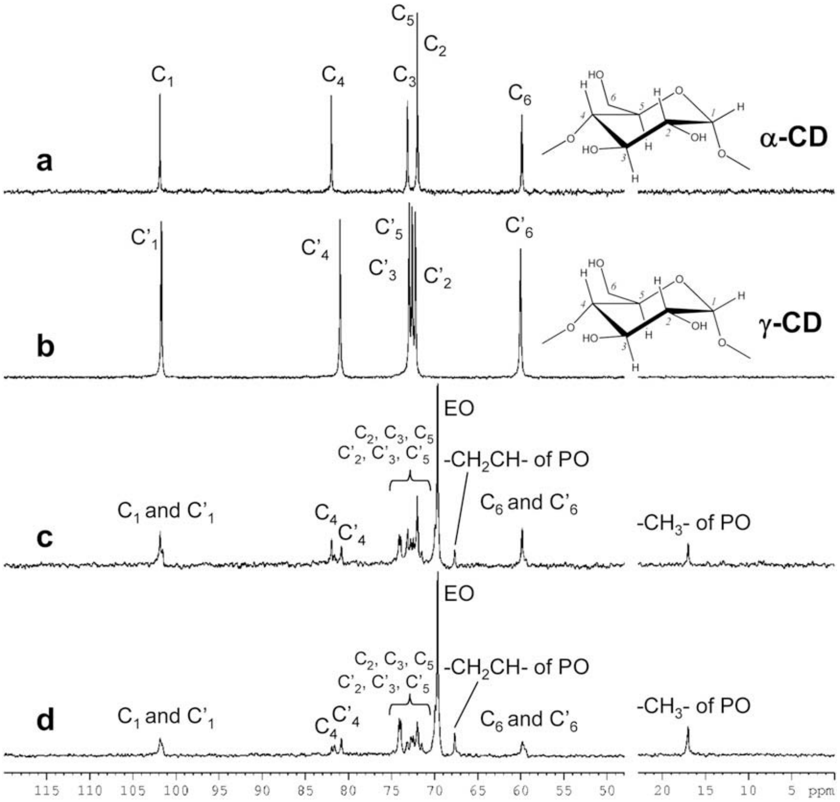


Fig. 7. ^{13}C NMR spectra of α-CD (a); γ-CD (b); and polyrotaxanes **4d** (c) and **4′d** (d) in DMSO-d_6.

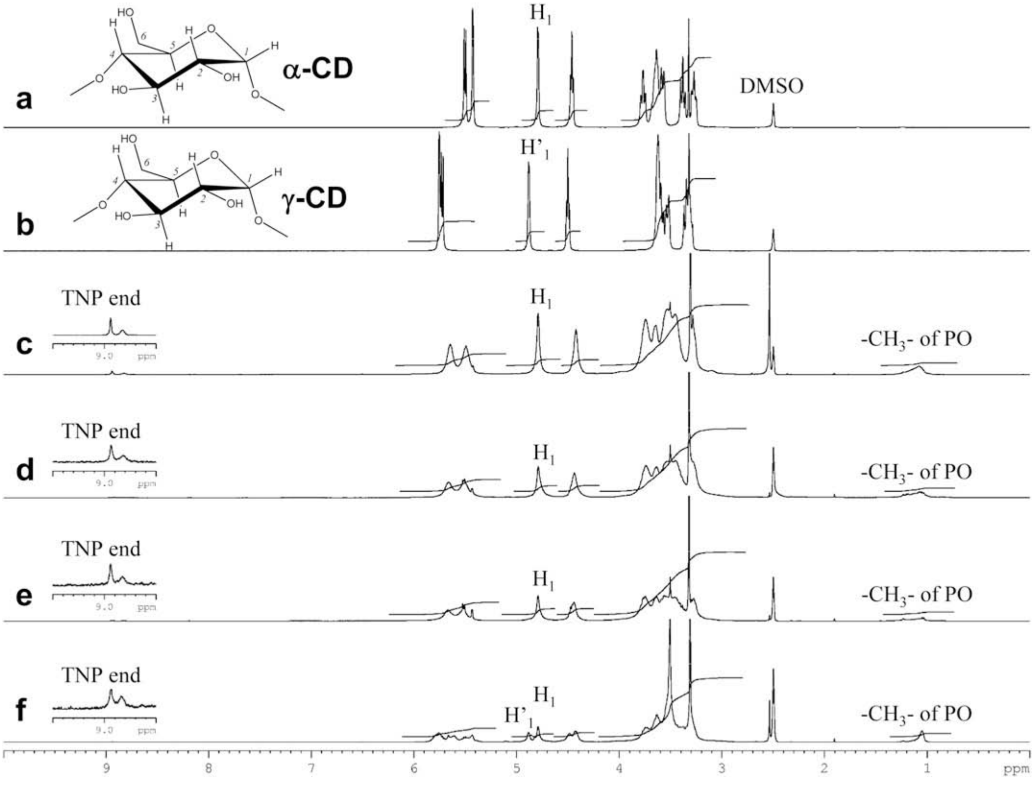


Fig. 8. ^{1}H NMR spectra of α-CD (a); γ-CD (b); and polyrotaxanes **4a** (c), **4b** (d), **4c** (e) and **4d** (f) in DMSO-d_6.

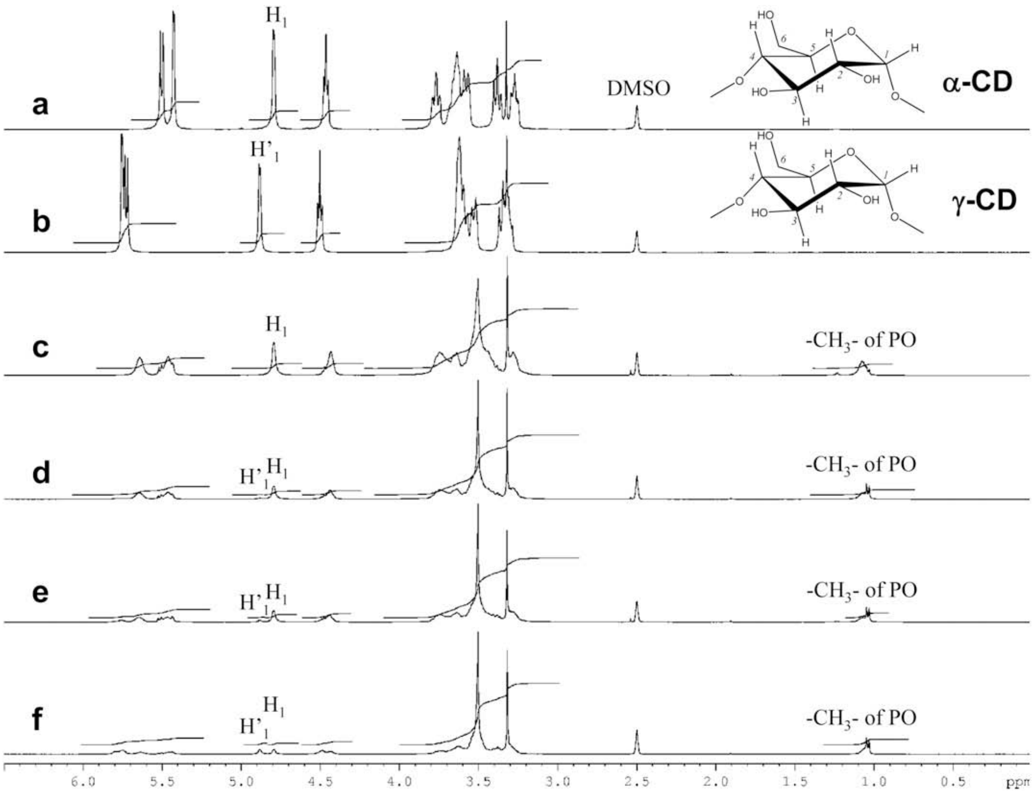


Fig. 9. ^{1}H NMR spectra of α-CD (a); γ-CD (b); and polyrotaxanes **4′a** (c), **4′b** (d), **4′c** (e) and **4′d** (f) in DMSO-d_6.

Table 2
Syntheses of polyrotaxanes and their compositions.[a]

Polyrotaxane		Molar ratio of P(EO-*r*-PO) to α-CD to γ-CD in the feed	Composition		Yield (%)
Code	Constitution		x[b]	y[c]	
4a	α-CD-P(EO_{41}-*r*-PO_{10})-TNB	1:38:0	11	0	54
4b	α-CD-γ-CD-P(EO_{41}-*r*-PO_{10})-TNB	1:38:19	8	0	21
4c	α-CD-γ-CD-P(EO_{41}-*r*-PO_{10})-TNB	1:38:38	9	0	19
4d	α-CD-γ-CD-P(EO_{41}-*r*-PO_{10})-TNB	1:19:38	4	2	2.3
—	—	1:0:38	0	0	0
4′a	α-CD-P(EO_{242}-*r*-PO_{67})-TNB	1:220:0	40	0	10
4′b	α-CD-γ-CD-P(EO_{242}-*r*-PO_{67})-TNB	1:220:110	25	2	12
4′c	α-CD-γ-CD-P(EO_{242}-*r*-PO_{67})-TNB	1:220:220	24	3	10
4′d	α-CD-γ-CD-P(EO_{242}-*r*-PO_{67})-TNB	1:110:220	9	6	4.9
—	—	1:0:220	0	0	0

[a] A comparison between the integral intensity of H-1 peak for α-CD (and/or γ-CD) and that of methyl proton peak of the P(EO-*r*-PO) copolymer gives the composition of the polyrotaxanes **4a**–**4d** and **4′a**–**4′d**.

[b] The number of α-CD in a single polyrotaxane chain determined by ^{1}H NMR.

[c] The number of γ-CD in a single polyrotaxane chain determined by ^{1}H NMR.

4. Conclusions

In this study, we interestingly observed that P(EO-*r*-PO) copolymers could co-threaded multiple α-CD and γ-CD rings to form polypseudorotaxanes by reacting P(EO-*r*-PO) with the mixture of α-CD and γ-CD in aqueous solution. XRD studies indicated that both α-CD and γ-CD molecules in the polypseudorotaxanes assumed a channel-type structure, and the polypseudorotaxanes with both α-CD and γ-CD co-threaded over P(EO-*r*-PO) assumed a structure where α-CD-P(EO-*r*-PO) crystalline phase coexists with γ-CD-P (EO-*r*-PO) crystalline phase. The ^{1}H NMR results revealed that the compositions of the polypseudorotaxanes were strongly dependent on the molar ratio of α-CD to γ-CD in the feed, attributing to the coexistence of the two competitive complexation processes between P(EO-*r*-PO) and α-CD or γ-CD in the reaction.

The successful syntheses of corresponding polyrotaxanes by attaching moderately bulk TNP group, which is larger than the cavity of α-CD but smaller than that of γ-CD, to both ends of the P(EO-*r*-PO) chain in the above polypseudorotaxanes, further confirmed that both α-CD and γ-CD rings could coexist and be entrapped on a P(EO-*r*-PO) chain. Because of the large inner cavity, the threaded γ-CD rings could traverse the TNP ends and dethread from the polymer chain. Hence, polyrotaxanes with pure γ-CD could not be formed. Only polyrotaxanes with α-CD or with α-CD and γ-CD co-threaded on P(EO-*r*-PO) could be formed. In such cases, γ-CD molecules close to the ends dethreaded, only those sandwiched by α-CD molecules could be entrapped over the P(EO-*r*-PO) chain, forming stable polyrotaxanes with both α-CD and γ-CD co-threaded over the P(EO-*r*-PO) chain.

Acknowledgements

We acknowledge the financial support from the Ministry of Education and the Agency for Science, Technology and Research, Singapore.

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