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pH-Controllable cyclic threading/dethreading of polypseudorotaxane obtained from cyclodextrins and poly(amino ester)

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Abstract

Cyclic threading/dethreading of novel polypseudorotaxane obtained from β-cyclodextrins and poly(amino ester), poly(BDA–DEEDA), obtained from the Michael addition polymerization of 1,4-butanediol diacrylate (BDA) and *N*, *N*′-diethyl ethylenediamine (DEEDA), was realized by adjusting pH of the aqueous solutions between ca. 9.0 and 3.2 alternatively. ^{1}H NMR, XRD profiles, and ^{13}C CP/MAS NMR verified the formation of polypseudorotaxane, and acid titration induced dethreaded structures were characterized using 2D ROESY NMR, ^{1}H NMR and XRD. The appearance/disappearance of precipitates, the kinetics, and the cyclic performance of pH controllable threading/dethreading processes were monitored by the changes in absorbance or transmittance of the solutions as reflected by UV experiments. Further pH-induced protonated and deprotonated states of poly(BDA–DEEDA) were demonstrated by ^{1}H NMR, which indicated the mechanism of the threading/dethreading processes.

Keywords: Cyclodextrins; Polyrotaxanes; Self-assembly

1. Introduction

Supramolecular complexes formed by molecular self-assembly are one of the promising candidates for future functional molecular devices and nanoscience [1]. However, setting up feasible approaches to manipulating cyclic assembling/disassembling of these supramolecular complexes at will is a prerequisite to realize all their potentials [2]. Polyrotaxanes are typical supramolecular complexes formed by threading cyclic molecules to polymer chains [3]. Cyclodextrins (CDs), a series of cyclic oligosaccharides composed of six, seven and eight D(+)-glucose units named as α-, β-, and γ-cyclodextrins, respectively, can host different polymer guests to form polyrotaxanes [3c,4,5], from which molecular devices and other smart materials with interesting performances such as environmental sensitivity have been obtained [6]. Cyclically assembling/disassembling CD-based polyrotaxanes or polypseudorotaxanes could be realized by thermal treatment [7], using a STM tip to move CD rings along polymer chains directly [8], or deprotonating CDs by adjusting pH to ca. 12 followed by neutralization [9]. Nevertheless, novel feasible approaches are still desirable in order to meet diverse applications requirements and facilitate further understanding of the related systems.

Polypseudorotaxanes have been prepared from several kinds of amine-containing polymers, i.e. protonated poly(iminooligomethylene) [10], viologen polymers [11], and poly(ε-lysine) [12]. The formation of inclusion complexes from some protonated poly(iminooligomethylene) [10] and viologen polymers [11] took hours or even months and the release of cyclodextrins was also slow. Yui et al. reported that pH of the aqueous media affected the yields of inclusion complex (IC) precipitates formed from poly(ε-lysine)/α-CDs [12]. More recently, Yui et al. reported that the formation of polypseudorotaxanes from PEI/α- or γ-CDs was pH dependent similar to that from poly(ε-lysine)/α-CDs [13], and that α-CDs could be threaded/dethreaded along PEI segments as reflected by the pH-dependent changes in stoichiometry of the polypseudorotaxanes precipitates

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obtained from PEI-*b*-PEG-*b*-PEI/α-CDs [14]. So polypseudorotaxanes obtained from CDs and suitable amine-containing polymers have smart pH controllable assembling/disassembling properties, but novel kinds of polypseudorotaxanes, especially from biocompatible polymer guests, are desirable for applications such as pH controllable drug delivery and molecular medical devises. Here we report a new kind of polypseudorotaxane obtained from biodegradable poly(amino ester) [15,16] and β-CD, and the pH controllable cyclic threading/dethreading property of this polypseudorotaxane was clearly demonstrated.

2. Experimental section

2.1. General characterization methods

^{1}H NMR (400 MHz) and 2D ROESY NMR (100 MHz) were recorded on a Bruker DRX-400 spectrometer. Gel permeation chromatography (GPC) measurements were carried out on a Waters 2690 apparatus with two columns in series (Waters Styragel HR 4E and 5E) and a Waters 410 refractive index detector at 40 °C employing 0.1 M piperidine/THF as eluent and polystyrene standards.

Wide-angle X-ray diffraction (XRD) measurements were performed using a Bruker general area detector diffraction system with advanced X-ray Solutions (Cu K_α, $\lambda = 1.542$ Å, 40 kV, 40 mA). Powder samples were mounted on a sample holder and scanned from $2\theta = 2.5$ to 65.4° with a step size of 0.02°. UV–vis spectra were obtained on a Shimadzu 2501PC spectrometer at room temperature. The reference samples were pure deionized water. Metrohm 744 pH meter were used for measuring pH values.

2.2. Materials

Poly(BDA–DEEDA) was prepared by the Michael addition polymerization of 1,4-butanediol diacrylate (BDA) and *N*, *N*′-diethyl ethylenediamine (DEEDA) [15]. In a typical experiment, 9 mmol of DEEDA was added dropwise into 10 ml of chloroform solution of equimolar BDA, and the reaction was performed at 50 °C for 3 weeks. Then poly(BDA–DEEDA) was obtained by precipitating the solution into hexanes followed by drying in vacuum at 50 °C. The molecular weight was measured by GPC to be M_n (g mol^{-1}), 5.6 K; M_w/M_n: 1.89.

2.3. Preparation of polypseudorotaxane

Polypseudorotaxane was prepared by adding poly(BDA–DEEDA) into a saturated aqueous solution of β-CD with a 1: 2 molar ratio of the repeating unit to β-CD. The solution was stirred overnight. Then the solution was centrifugated and the precipitate was washed with water for two times followed by drying at 60 °C under vacuum for 48 h. Yield: 74%; ^{1}H NMR (DMSO-d_6 400 Hz): 5.73–5.693 (d, ca. 100H), 4.83 (s, ca. 50H), 4.46 (s, ca. 50H), 4.01 (m, ca. 21H), 3.66–3.54 (m, ca. 220H), 3.37–3.33(m, ca. 264 H), 2.66 (ca. 27H), 2.51 (s, ca. 20H), 2.44–2.37 (m, ca. 62H), 1.62 (m, ca. 23H), 0.936–0.902 (t, ca. 35H).

2.4. Dethreading polypseudorotaxane by acid titration

3.2 ml of the aqueous suspension solution of polypseudorotaxane was transferred to a 4 ml quartz cuvette. Several micro litres of 4.0 M hydrochloric acid aqueous solution was added into the cuvette and the solution was mixed quickly for the recording of UV–vis spectrum. After recording the pH value was measured. For XRD experiments, the titrated aqueous solutions at designed pH values were dried by lyophilization, and the solid obtained was further dried in vacuum at 50 °C.

2.5. Rethreading of CD back to poly(BDA–DEEDA)

A stock solution of dethreaded polypseudorotaxane at pH 3.2 was prepared as described above. Then 3.2 ml of the stock solution was transferred to a 4 ml quartz cuvette. Several micro litres 4.0 M sodium hydroxide aqueous solution was added into the cuvette and the solution was mixed quickly for recording UV–vis spectrum. After the recording, pH was measured. Also the reproduced polypseudorotaxane precipitate was collected by centrifugation and washing with water for two times followed by drying in vacuum at 50 °C.

2.6. Cyclic threading/dethreading of polypseudorotaxane by alternative titration between pH 3.2 and 9.0

For the first dethreading, ca. 10 μl of 4.0 M hydrochloric acid aqueous solution was added into a 4 ml quartz cuvette containing 3.2 ml of suspension aqueous solution of polypseudorotaxane (pH 7.0) as prepared above. The solution was mixed quickly for the recording of UV–vis spectrum. The pH of solution would be ca. 3.2. Then 13 μl of 4.0 M sodium hydroxide aqueous solution was added into the cuvette to realize the first rethreading and the solution was mixed quickly for the recording of UV–vis spectrum again, and the pH of the solution was ca. 9.0. For the second cycle, ca. 13 μl of 4.0 M hydrochloric acid aqueous solution was consumed to adjust the pH to ca. 3.2. Then the following steps were almost the same as above. At a certain cycle, polypseudorotaxane precipitate was collected.

3. Results and discussion

3.1. Formation of polypseudorotaxane

Threading of β-CD to poly(BDA–DEEDA) happened and formed precipitate when poly(BDA–DEEDA) was mixed with a saturated aqueous solution of β-CD

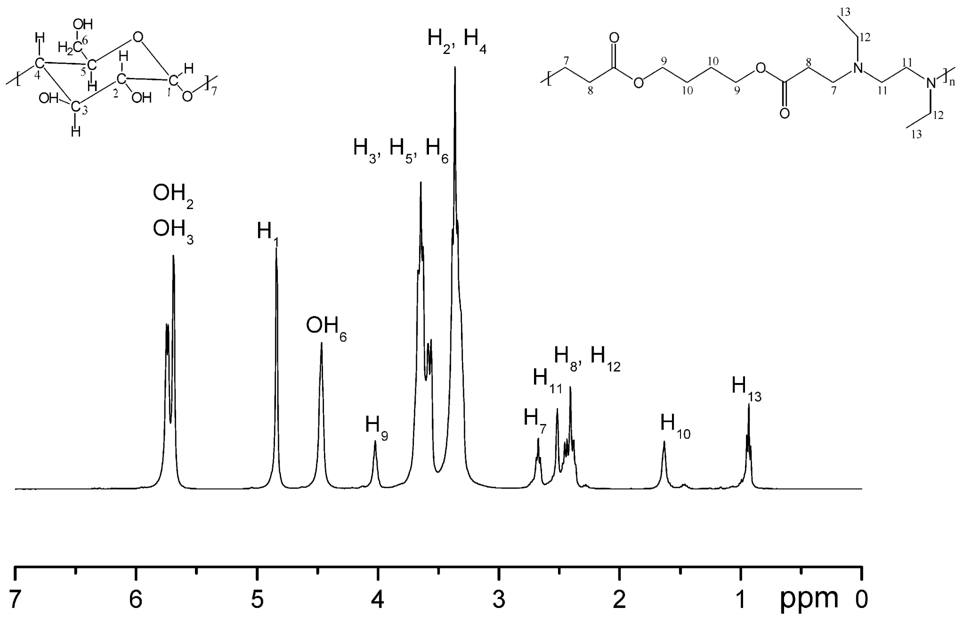


Fig. 1. ^{1}H NMR spectrum of polypseudorotaxane obtained from β-CDs and poly(BDA–DEEDA) in DMSO-d_6.

(0.0178 g/ml) with a 1:2 molar ratio of the repeating unit to β-CD. Fig. 1 shows ^{1}H NMR spectrum of polypseudorotaxane dissolved in DMSO-d_6. The stoichiometry of polypseudorotaxane was calculated based on the ratio of the integral peak area of CD (H_1) and poly(BDA–DEEDA) (H_9) at 4.83 and 4.02 ppm, respectively, and the results showed that the molar ratio of the repeating unit of poly(BDA–DEEDA) to β-CD in polypseudorotaxane was ca. 1:1.9, closing to the feeding compositions. A higher feed ratio of β-CD led to no more β-CD introduced into polypseudorotaxane.

Polypseudorotaxanes from β-CD and different polymers have a channel type crystalline structure with polymer chains being included in the cavities of β-CDs, which is different from the cage type structure [17]. In XRD patterns, the indication of the channel type crystalline structures of β-CD based polypseudorotaxanes is the presence of a characteristic peak at ca. $2\theta = 11.7°$ in comparison with that of β-CD [17]. The appearance of the peak at $2\theta = 11.7°$ in Fig. 2(b) reflects that polypseudorotaxane obtained from β-CDs and poly(BDA–DEEDA) possess a channel type crystalline structure.

The formation of polypseudorotaxane was further supported by the results obtained from ^{13}C CP/MAS NMR. Fig. 3 compares the ^{13}C CP/MAS NMR of β-CD and polypseudorotaxane obtained. The spectrum of β-CD

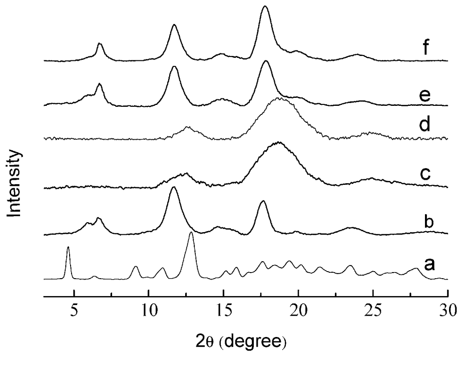


Fig. 2. X-ray powder diffraction patterns for (a) β-CD, (b) polypseudorotaxane from β-CD/poly(BDA–DEEDA) formed for the first time, (c) dethreaded polypseudorotaxane formed at pH ca. 3.2, (d) a milled mixture of solid protonated poly(BDA–DEEDA) and β-CD (both were obtained by lyophilization of the corresponding pH 3.2 aqueous solutions) with the same composition as in (c). (e) Reproduced polypseudorotaxane from β-CD/poly(BDA–DEEDA) formed at pH ca. 9.0, (f) polypseudorotaxane from β-CD/poly(BDA–DEEDA) formed in the eighth cycle of adjusting pH from 3.2 to 9.0 alternatively.

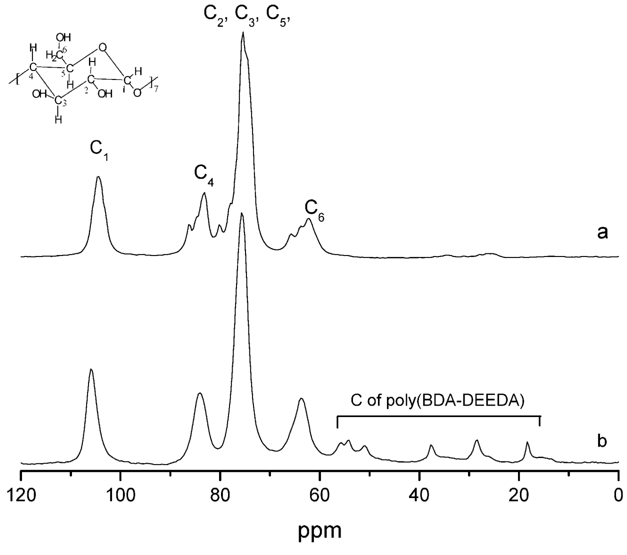


Fig. 3. Comparison of ^{13}C CP/MAS spectrum of (a) β-CD, and (b) polypseudorotaxane from β-CD/poly(BDA–DEEDA).

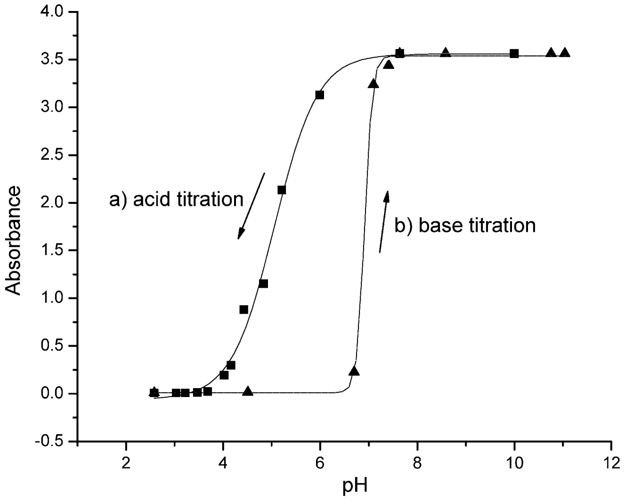


Fig. 4. Effect of pH on the absorbance of the aqueous solution of β-CD/poly(BDA–DEEDA) complex in the process of (a) acid titration, and (b) base titration.

shows a higher resolved resonance than that of the polypseudorotaxane, illustrating that β-CDs in the complexes adopt a symmetrical conformation and each glucose unit has a similar environment as compared with pure β-CDs.

3.2. pH-Induced dethreading of polypseudorotaxane

Dethreading polypseudorotaxane was realized by acid titration of the aqueous suspension solution of polypseudorotaxane. A visible phenomenon was that the dethreading leading to water-soluble β-CD and protonated poly(BDA–DEEDA) resulted in a lower turbidity of the solution, as reflected by a decreased absorbance of the solution at 550 nm. Fig. 4(a) depicts the change in the absorbance of aqueous solution of polypseudorotaxane with pH values in the acid titration processes. The absorbance started to decrease when pH was reduced to ca. 6.7, and reached the lowest value at pH ca. 3.5. Meanwhile, Fig. 5 reflects the kinetics of the dethreading processes at different titration pH values. A lower pH value led to a faster dethreading process and a higher dethreading degree as illuminated by a faster increase in the transmittance and a higher final transmittance degree of the solution, respectively.

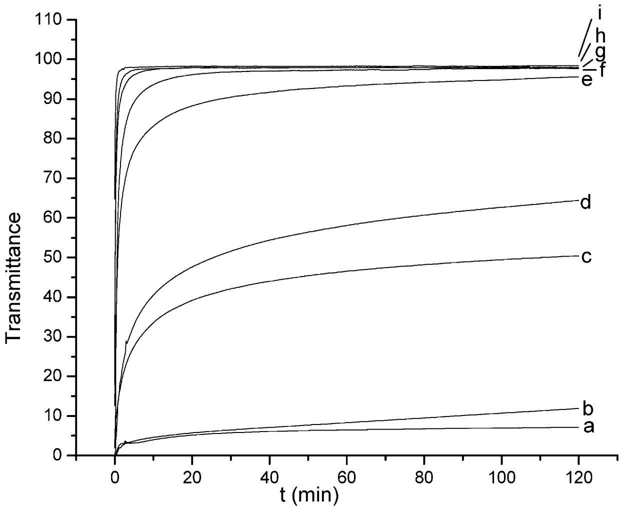


Fig. 5. Time-course profile of transmittance changes at 550 nm for the dethreading process of β-CD/poly(BDA–DEEDA) polypseudorotaxane at pH (a) 4.8, (b) 4.4, (c) 4.2, (d) 4.0, (e) 3.7, (f) 3.5, (g) 3.2, (h) 3.0, (i) 2.6.

In order to verify the dethreaded structure produced by acid titration, pure dethreaded polypseudorotaxae solid was obtained by lyophilization from an pH 3.2 aqueous solution. Figs. 6 and 7 are 2D ROESY NMR and ^{1}H NMR spectrum of the solid dissolved in D_2O, respectively. Both verify that a completely dethreaded structure was obtained at pH ca. 3.2 instead of soluble polypseudorotaxane. If β-CD was still threaded onto protonated poly(BDA–DEEDA) forming soluble protonated polypseudorotaxane, 3,5-protons in CD rings directing into the cavities should correlate with some protons of poly(BDA–DEEDA) in 2D ROESY NMR [7b, 18] and some peaks ascribed to β-CD or protonated poly(BDA–DEEDA) in ^{1}H NMR should shift [11b,19]. However, no such types of cross-peaks appear in Fig. 6 and no peaks in ^{1}H NMR shift in Fig. 7. In Fig. 7, the broader peaks of protonated poly(BDA–DEEDA) indicates that β-CD can form a complex but not a threaded complex with protonated poly(BDA–DEEDA) with a fast exchange between the complex and free species on the NMR time scale [19b]. So β-CD was dethreaded from protonated poly(BDA–DEEDA). The disappearance of the characteristic peaks of polypseudorotaxane at $2\theta = 11.7°$ in the XRD profile for the product obtained at pH ca. 3.2 (Fig. 2(c)) is in agreement with the dethreaded structure, which was further supported by the similarity between the XRD profiles for the dethreaded polypseudorotaxane and the milled mixture of solid protonated poly(BDA–DEEDA) and β-CD (prepared by lyophilization of their pH 3.2 aqueous solutions) with the same composition (as reflected by comparing Fig. 2(c) and (d)).

3.3. pH-Controllable cyclic threading/dethreading of polypseudorotaxane

Feasibly rethreading β-CD back to poly(BDA–DEEDA) was performed by titrating a solution of the dethreaded polypseudorotaxane at pH ca. 3.2 using 4 M sodium hydroxide aqueous solution. The rethreading of β-CD back to polymer chains reproducing polypseudorotaxane led to precipitation again, as reflected by an increased absorbance of the solution as indicated in Fig. 4(b). Fig. 8 depicts the kinetic processes of rethreading as illuminated by the time-course changes in the absorbance of the solution. When pH values increased from 6.7 to 11.0, the rates and the final degree of rethreading increased accordingly, but a further increasing in pH to 11.9 resulted in a decreased rethreading rate and degree.

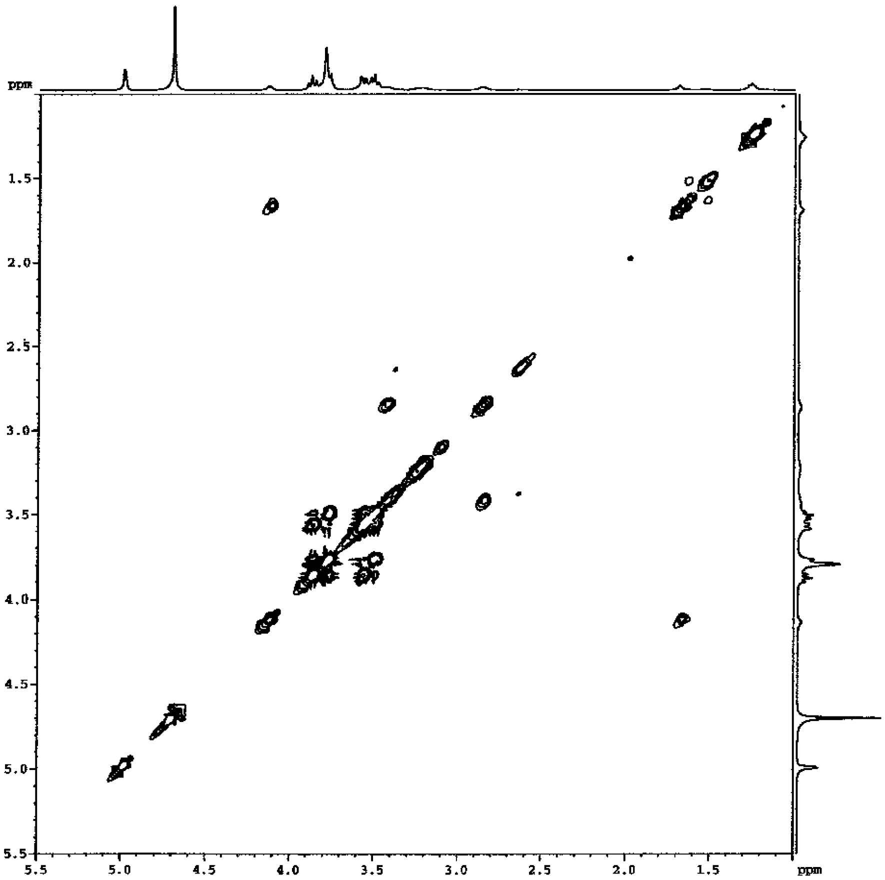


Fig. 6. 2D ROESY NMR spectrum of the acidified complex of β-CD/poly(BDA–DEEDA) obtained at pH ca. 3.2 in D_2O.

^{1}H NMR results showed that the stoichiometry of the newly formed polypseudorotaxane was close to that obtained for the first time, i.e. the molar ratio of the repeating unit of poly(BDA–DEEDA) to β-CD in polypseudorotaxane was ca. 1:1.9. The reappearing characteristic peak at $2\theta = 11.7°$ in the XRD profile for the precipitate reproduced (Fig. 2(e)) verified the reproduced polypseudorotaxane still possess a channel type crystalline structure.

The excellent cyclically threading/dethreading capability

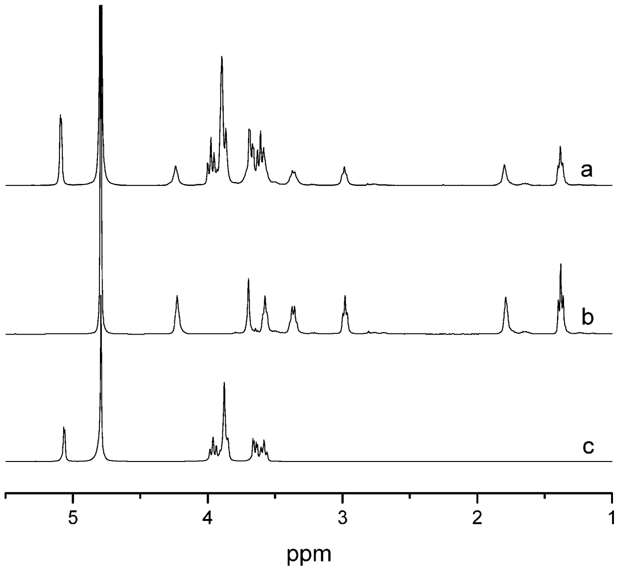


Fig. 7. A Comparison of ^{1}H NMR spectrum of (a) the acidified complex of β-CD/poly(BDA–DEEDA) at pH 3.2, (b) pure protonated poly(BDA–DEEDA) at pH 3.2, (c) β-CD in D_2O.

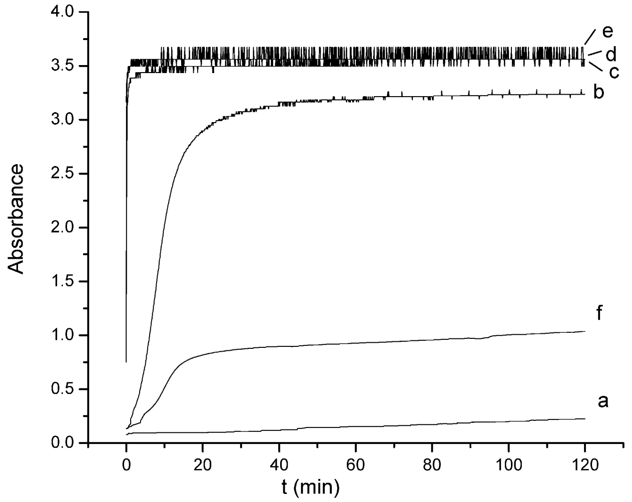


Fig. 8. Time-course profile of absorbance changes at 550 nm for the rethreading process of β-CD/poly(BDA–DEEDA) complex at (a) 6.7, (b) 7.1, (c) 7.6, (d) 8.6, (e) 11.0, (f)11.9.

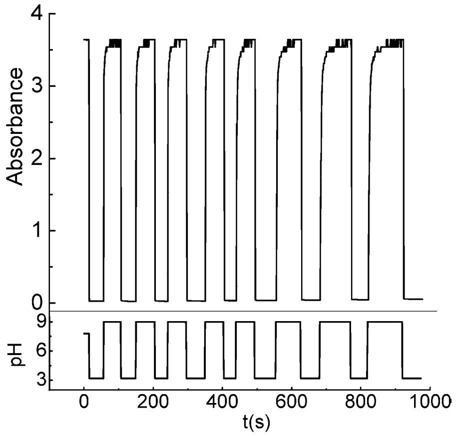
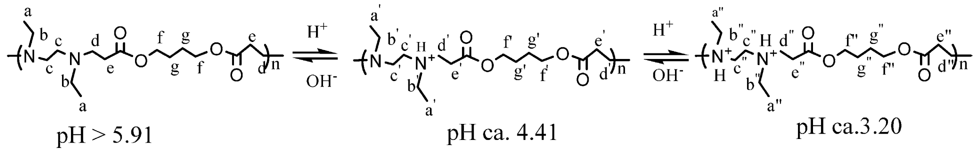


Fig. 9. Plot of the absorbance at 550 nm versus time during titrating the saturated aqueous solution of β-CD/poly(BDA–DEEDA) complex to pH ca. 3.2 and 9.0 alternatively.

of the polypseudorotanxane was well displayed by the cyclic changes in the absorbance of solution when pH was adjusted between 3.2 and 9.0 by using 4.0 M hydrochloric acid or sodium hydroxide aqueous solution alternatively as presented in Fig. 9. The aqueous solution of polypseudorotanxane was obtained in a similar way as described above, i.e. adding poly(BDA–DEEDA) with a 1:2 molar ratio of its repeating units to β-CD to a saturated β-CD aqueous solution. The volume of 4.0 M hydrochloric acid or sodium hydroxide aqueous solution needed was only ca. 4‰ (v/v) of the complex solution for each cycle titration. As shown in Fig. 9, the threading/dethreading degrees in each cycle are almost the same as indicated by the similar changes in the absorbance although the rethreading processes got a little slow gradually. After eight cycles, the precipitate collected still had a channel type crystalline structure and a chemical composition similar to that formed for the first time as illustrated by the XRD profile (Fig. 2(f)) and ^{1}H NMR results, respectively.

In order to get an understanding of the driving force for the threading/dethreading of the polypseudorotaxane, the different protonation states of poly(BDA–DEEDA) were monitored at different pH values by ^{1}H NMR and the results are depicted in Fig. 10. It was found that poly(BDA–DEEDA) was neutral, partially and fully protonated at pH ca. 7.4, 4.4 and 3.2, respectively. Using the change in the absorbance or transmittance of the solution as an indicator of the threading/dethreading degree demonstrated in Figs. 4, 5 and 8, we observed that a partial amine protonation of poly(BDA–DEEDA) led to a partial dethreading of polypseudorotaxane, and a complete dethreading was achieved when all the amines were protonated in the acid titration process and a higher protonation degree resulted in a faster dethreading, whereas in the base titration process, the rethreading only started when almost all the protonated amines were neutralized, therefore, there was a hysteresis of



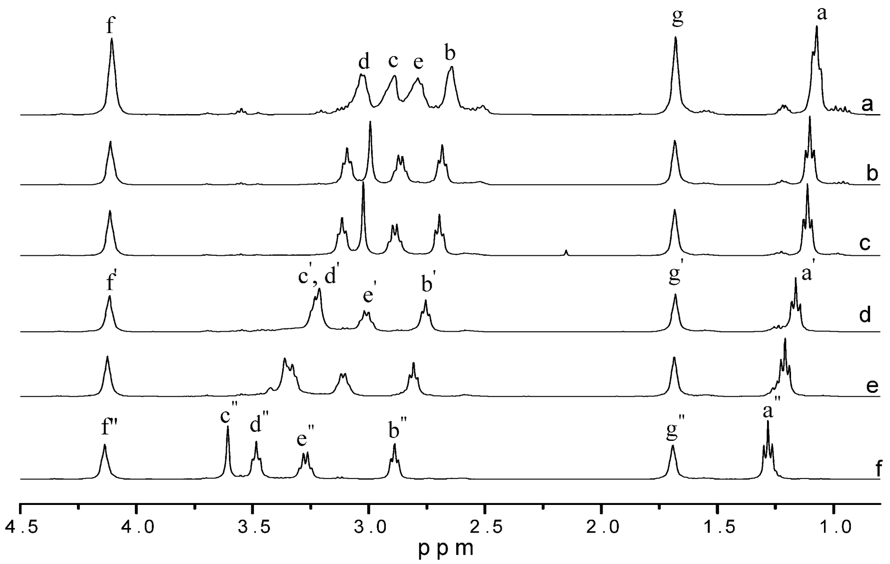
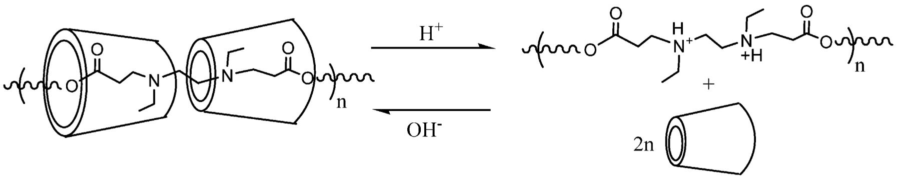


Fig. 10. ^{1}H NMR spectrum of poly(BDA–DEEDA) in D_2O at pH (a) 7.4, (b) 6.7, (c) 5.9, (d) 4.4, (e) 4.1, (f) 3.2.



Scheme 1.

the rethreading in comparison to the dethreading, but a complete rethreading was achieved quickly in terms of pH. A higher neutralization degree induced by a higher pH facilitated a faster rethreading, but a too higher pH (>11.0) would cause ionization of β-CDs rendering their host function [9,12a]. The formation of polypseudorotanxane was promoted by hydrophobic interactions and the mutual size compatibility of CD cavities and polymer chains [20]. The protonation of amines led to the dethreading of β-CDs due to the increased hydrophilicity of protonated poly (BDA–DEEDA), and the deprotonation of amines forming neutralized poly(BDA–DEEDA) resulted in the rethreading of β-CDs. The mechanism of the pH-controllable cyclic threading/dethreading of polypseudorotaxane obtained from cyclodextrins and poly(amino ester) can be described as in Scheme 1. Based on this mechanism, polypseudorotaxane from polymers that cannot be protonated should show no pH sensitivity. This was verified by the behavior of polypseudorotaxane obtained from poly(ethylene oxide) (2000) and α-CD, which was stable at low pH and showed no pH sensitivity.

4. Conclusions

pH-Controllable cyclic threading/dethreading of novel polypseudorotanxane obtained from poly(amino ester) and β-CDs was realized. The changes in the hydrophilic/hydrophobic property of poly(amino ester) main chains caused by the pH-induced protonation/deprotonation of amines were the impetus to the cyclic threading/dethreading of polypseudorotaxane. The effects of chemical structures of poly(amino ester)s on the formation of polypseudorotaxane and pH controllable cyclic threading/dethreading properties were being investigated.

Acknowledgements

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