

Side-chain pseudopolyrotaxanes by threading cucurbituril[6] onto quaternized poly-4-vinylpyridine derivative: Synthesis and properties

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Abstract

A novel side-chain pseudopolyrotaxanes **4** is synthesized from cucurbituril (CB[6]) and quaternized poly-4-vinylpyridine derivative **3** in water by simple stirring at room temperature. CB[6] beads are localized on hexamethylene units in side chains of **3** as found by NMR studies, and the hydrophobic and charge-dipole interactions are the driving force. The degree of threading (q/n , the average number of CB[6] beads per repeat recognition unit of **3**) can be controlled from 0.2 to 1.0 by controlling the amount of CB[6] added. The reduced viscosity of pseudopolyrotaxanes in aqueous solution has smaller change with the change of the concentration or temperature, which is consistent with the hydrodynamic radius and more rigid chain conformation because of the threaded CB[6]. DLS results show the average hydrodynamic diameter (D_h) of the pseudopolyrotaxanes in solution increases with the increasing of CB[6] threaded. The pseudopolyrotaxanes have higher thermal stability and intensity of absorption band than the parent polymer **3** as found by TGA and UV–vis studies. The decomposition temperature and intensity of absorption increase with increasing amount of CB[6] threaded. The effect of NaI to pseudopolyrotaxanes is studied by the transmittance with UV–vis, and the result shows that NaI is the satisfied precipitant to the pseudopolyrotaxanes.

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1. Introduction

Supramolecular chemistry [1] has ushered polymer chemistry into a new era. In supramolecular chemistry, (pseudo)polyrotaxanes, in which many cyclic molecular ‘beads’ are threaded by a long ‘string’ have received much attention in recent years not only because of their unique structures but also because of their unusual properties different from those of conventional covalent polymers [2], such as potential use as a material for molecular devices [3] and catalyst [4]. Most main-chain or side-chain (pseudo)polyrotaxanes synthesized contain cyclodextrins (CDs) [5,6] or crown ethers [7,8] threaded on organic polymers. Harada [5] and Wenz [6] reported main-chain (pseudo)polyrotaxanes containing CDs as cyclic units. Gibson [7] utilized crown ethers as cyclic units to synthesize main-chain (pseudo)polyrotaxanes. Side-chain

(pseudo)polyrotaxanes containing rotaxane units on side chains of various polymer backbones have also been synthesized by Yamamoto [8b,d], Ritter [9], and Takata [10] using CDs or crown ethers as cyclic units. However, all of these post-threaded systems in general lack structural regularity as the molecular ‘beads’ are often not threaded in all the available recognition sites of the polymer chains. It is mainly due to the fact that affinity of the ring components (CDs or crown ethers) towards the recognition sites in the polymers is not high enough to ensure complete threading. The requirement for a molecular ‘bead’ seems to be met with cucurbituril.

Cucurbituril (CB[6]), a large-cage compound composed of six glycoluril units, has a hydrophobic cavity that is accessible through two identical carbonyl-fringed portals [11]. CB[6] has been attracting much attention not only because of easy synthesis, highly symmetric structure and high chemical and thermal stability, but also because of the polar carbonyl groups at the portals and a hydrophobic cavity allow it to form stable host–guest complexes with protonated aminoalkanes, diaminoalkanes ($K > 10^5$) or with alkanes having two bipyridinium terminals ($K = 10^2$ – 10^4) through the formation of (pseudo) rotaxane [11]. Taking advantage of this fact, various

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mechanically interlocked molecules including rotaxanes and (pseudo)polyrotaxanes have been synthesized by Kim [12] and others [4,13]. But side-chain (pseudo)polyrotaxanes containing CB[6] as a molecular bead have been scarcely reported other than Kim [12g] and we [14].

We now synthesized a novel water-soluble side-chain pseudopolyrotaxanes containing CB[6] threaded on quaternized diaminohexane pendants attached to a main polymer chain. A unique feature of the pseudopolyrotaxanes is that the CB[6] can threaded in all the available recognition sites of the polymer chains and the degree of threading (number of CB[6] beads per repeat recognition unit) can be controlled by controlling the amount of CB[6] added [12h]. Our work can provide the new method of the interaction between polyelectrolyte and cucurbituril and be used as the separation of polyelectrolyte. Here, we report the synthesis, characterization and properties of the novel pseudopolyrotaxanes.

2. Results and discussion

2.1. Synthesis of polymer **3** and pseudopolyrotaxanes **4**

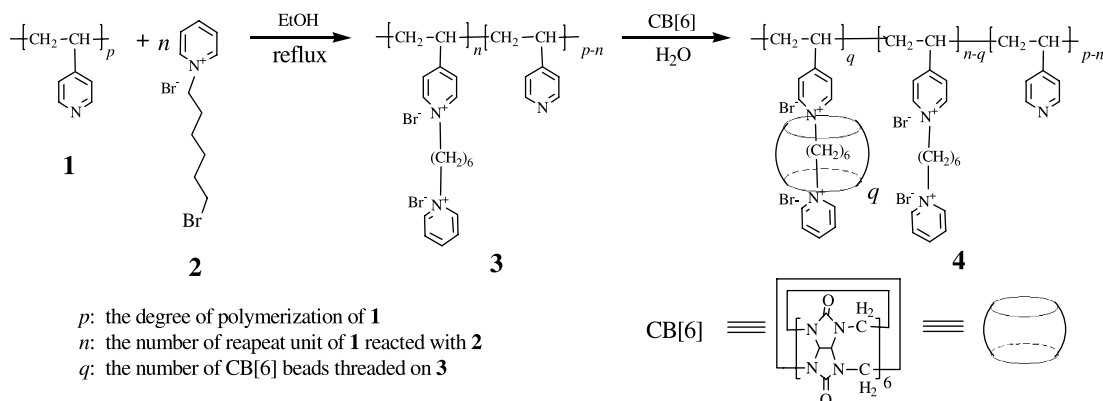
Pseudopolyrotaxanes **4** was prepared according to Scheme 1. Polymerization of 4-vinylpyridine by bulk polymerization using 2,2'-azobis(isobutyronitrile) (AIBN) as the initiator produced polymer **1**. The intrinsic viscosity $[\eta]$ of **1** was 2.00 dL/g measured with an Ubbelohde viscometer in ethanol at 25.0 °C. According to the equation [15] $[\eta] = 25 \times 10^{-5} M^{0.68}$, we can calculate the average molecular weight $M = 5.50 \times 10^5$. **2** was prepared by refluxing the mixture of 1,6-dibromohexane and pyridine, 1,6-dibromohexane was larger excess so that only one bromine group reacted with pyridine. Compound **2** was characterized by ^1H NMR spectrum and elemental analysis. Polymer **3** was given by refluxing the mixture of **1** and large excess of **2**, and purified through a dialytic membrane against water. **3** has been characterized by the ^1H NMR spectrum, which show that part repeat units react with **2**, and the elemental analysis of **3** give $C/N = 7.046$, according, which we can calculated $n/p \% = 43.9\%$ (n, p shown

in Scheme 2), so the average molecular weight of **3** is about 1.3×10^6 . Synthesis of side-chain pseudopolyrotaxanes **4** was easily achieved by self-assembly of **3** with a slight excess of CB[6] in water at room temperature for 24 h. Although CB[6] itself is sparingly soluble in water, it slowly dissolves into the solution as the threading proceeds. Pseudopolyrotaxanes with different degree of CB[6] threaded (< 1.0) were prepared by the same procedure as Scheme 2, except that the proper amount of CB[6] were added to the solution.

2.2. ^1H NMR spectra

Fig. 1 compares the 400 MHz ^1H NMR spectra of polymer **3** and pseudopolyrotaxanes **4**. Upon formation of pseudopolyrotaxanes **4**, new broad signals appear at 4.37, 5.63, and 5.77 ppm, which correspond to threaded CB[6]. At the same time, significant changes in chemical shift for polymer **3** are observed in the ^1H NMR spectrum of pseudopolyrotaxanes **4**, the methylene proton signals (d, e, f and g) of the hexamethylene units of the polymer are shifted upfield due to the shielding effect of CB[6], while the signals (c, h) for the pyridinium protons, which are located just outside of the CB[6], are shifted downfield. The other protons (a, b, j, i), which are located far from the CB[6], remain unchanged or have a little change. The NMR data support that the CB[6] beads threaded in **4** are localized on the hexamethylene units.

The amount of CB[6] threaded onto the side chains of the polymer can be estimated by comparing the intensities of the CB[6] (5.63 and 5.77 ppm) and polymer side-chain methylene peaks (0.57 ppm) in the ^1H NMR spectra. Within experimental error, a CB[6] bead is threaded on every side chain containing a hexamethylene unit in **4**. The high driving force for the threading appears to be the hydrophobic interaction between hexamethylene unit and the interior of CB[6] cavity and the charge-dipole interaction between pyridinium units and the CB[6] portal oxygen atoms [11]. Because of the multiple noncovalent interactions, the resulting pseudopolyrotaxanes **4** is quite stable in solution and solid state; no appreciable dethreading is observed after long standing in solution.



Scheme 1. Synthesis of polymer **3** and pseudopolyrotaxanes **4**.

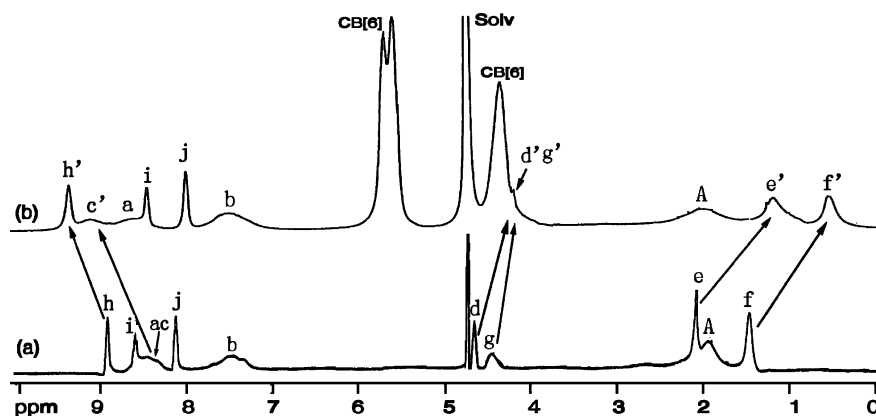


Fig. 1. 400 MHz proton NMR spectra of (a) polymer **3** and (b) pseudopolyrotaxanes **4** in D_2O at room temperature.

2.3. Control of the degree of threading

The degree of threading (q/n , the average number of CB[6] per repeat recognition unit in **3**) of pseudopolyrotaxanes **4** can be controlled. Fig. 2 shows a series of 1H NMR spectra of the pseudopolyrotaxanes taken with different molar ratio of **3** to CB[6]. As the amount of CB[6] added increases from 0.20 (a) equiv. to 1.0 (e) equiv., the intensity of the signals for CB[6] threaded increases (4.37, 5.63, 5.77 ppm), and a new set of signals for the polymer backbone appear with growing intensities (shown with arrows in Fig. 2). All these data are consistent with the fact that the CB[6] beads threaded are localized on the hexamethylene units of the side chains of the polymer. The number of CB[6] beads threaded in polymer can be calculated by comparing the intensity of the CB[6] (5.63 and 5.77 ppm) and the polymer side-chain peaks (0.57 ppm) (b–e). Fig. 3 shows that the number of CB[6] added and levels off at nearly 1:1 where all the internal hexamethylene units are fully occupied by CB[6]. The linear relationship indicates that the q/n value in pseudopolyrotaxanes **4** can be controlled simply by adding a desired amount of CB[6] into the solution of **3**. Similar behavior has been observed in main-chain pseudopolyrotaxanes incorporating CB[6] [12h].

2.4. FT-IR spectra

Fig. 4 shows FT-IR spectra of polymer **3** and pseudopolyrotaxanes **4** with different degree of threading. The extremely bands at 1732 cm^{-1} (Fig. 4(a)) and 1638 cm^{-1} (Fig. 4(b)) are the characteristic absorption peak of C=O of CB[6] [13a] and pyridinium salt of polymer **3**, respectively. Also, the band at 1732 and 1638 cm^{-1} are observed in pseudopolyrotaxanes (Fig. 4(c)–(f)), and the ratio of intensity of the peaks at the 1732 and 1630 cm^{-1} increases gradually with increasing amount of CB[6] threaded (shown with arrows in Fig. 4). The IR data are indirect proof for the existence of pseudopolyrotaxanes.

2.5. Viscosity

The reduced viscosity (η_{sp}/C) of polymer **3** and pseudopolyrotaxanes **4** with different degree of CB[6] threaded

changing with concentration ($25.0\text{ }^\circ\text{C}$) (Fig. 5) or temperature (0.3 g dL^{-1}) (Fig. 6) were also measured using Ubbelohde viscometer in H_2O . The η_{sp}/C of the polymer **3** increases quickly with the concentration decreasing ($C=0.10\text{--}0.20\text{ g dL}^{-1}$), which is the typical character of the dilute solution of a polyelectrolyte, while the η_{sp}/C of the pseudopolyrotaxanes **4** increases slowly and the decreasing rate of η_{sp}/C declines gradually with increasing amount of CB[6] threaded, the reason is due to the shield effect of the polar carbonyl groups of CB[6] to the pyridinium ion, which shows these pseudopolyrotaxanes are different from conventional polyelectrolyte. With increasing CB[6], the reduced viscosity decreases, which maybe due to the decrease of charge density and the interaction between the molecules. The increase of rigidity of the pseudopolyrotaxanes leads to chain extension, but the molecular weight of the pseudopolyrotaxanes increases without the increase of the repeat units of the

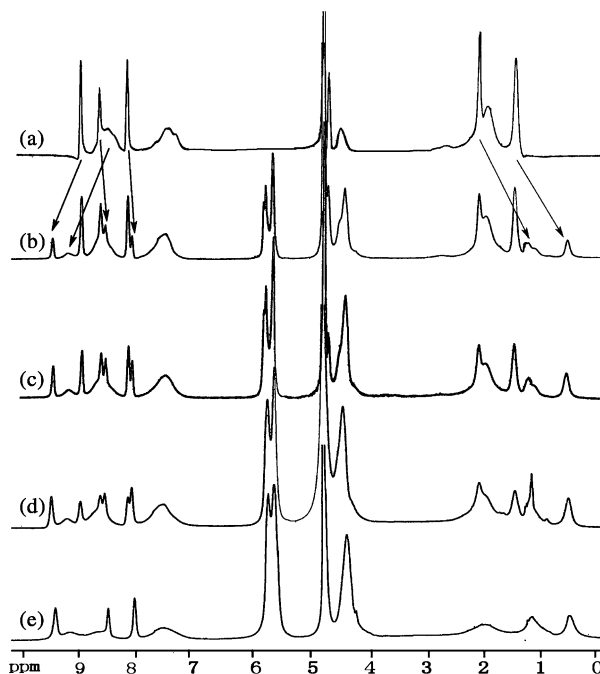


Fig. 2. 1H NMR spectra of (a) polymer **3** and pseudopolyrotaxanes **4** with different degree of CB[6] threaded (q/n : (b) 0.20, (c) 0.40, (d) 0.60, (e) 1.0).

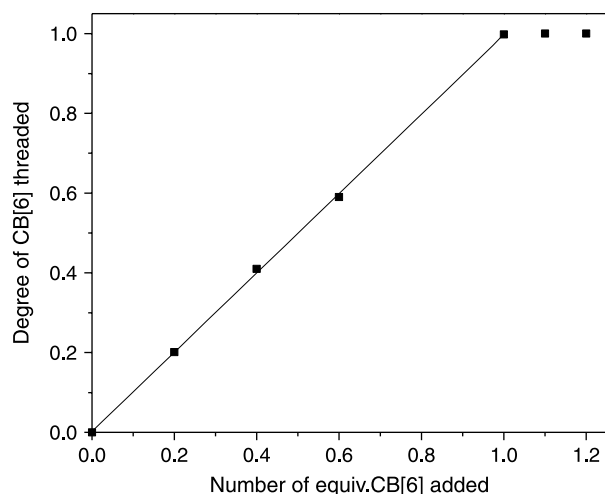


Fig. 3. Relationship of the degree of CB[6] threaded vs the number of CB[6] added.

backbone. With the temperature increasing, the η_{sp}/C of polymer **3** decrease quickly while that of the pseudopolyrotaxanes **4** is nearly unchanged, which suggests that the regularity of the chain conformation increases because of the rigidity of the threaded CB[6] beads. With increasing amount of CB[6] threaded, the pseudopolyrotaxanes become more and more rigidity, so the dependence of chain conformation on temperature is less.

2.6. DLS

Fig. 7 shows that the average hydrodynamic diameter (D_h) of the pseudopolyrotaxanes (q/n : 0.2, 0.4, 0.6, 1.0; D_h : 60.3, 126.5, 224.4, 384.8 nm) measured with dynamic light scattering (DSL) increases with the increasing of CB[6] threaded. These results also show that the regularity of the chain conformation increase with increasing amount of CB[6] threaded as showed Fig. 8. These structure of polymer maybe similar with the side chain liquid crystal polymer.

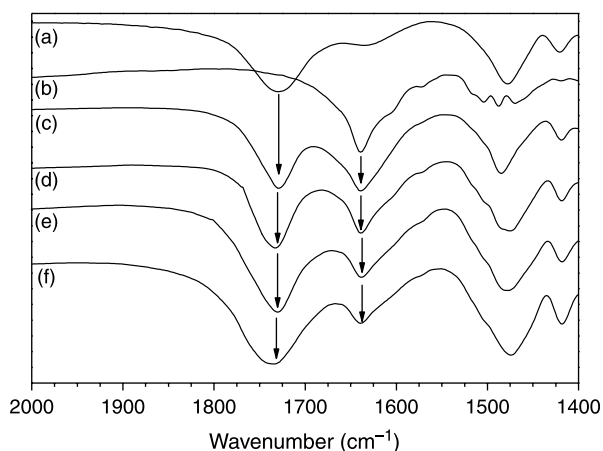


Fig. 4. FT-IR spectra of (a) CB[6], (b) polymer **3** and pseudopolyrotaxanes **4** with different degree of CB[6] threaded (q/n : (c) 0.20, (d) 0.40, (e) 0.60, (f) 1.0).

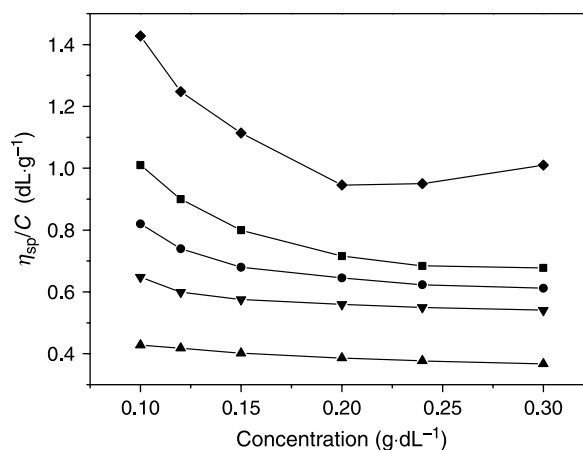


Fig. 5. Relationship of η_{sp}/C vs concentration of (\blacklozenge) polymer **3** and pseudopolyrotaxanes **4** with different degree of CB[6] threaded (q/n : (\blacksquare) 0.20, (\bullet) 0.40, (\blacktriangledown) 0.60, (\blacktriangle) 1.0): taken in H_2O at $25^\circ C$.

2.7. Thermal properties

Side-chain pseudopolyrotaxanes are more thermally stable than the parent polymer (Figs. 9 and 10). The small weight loss of polymer **3**, pseudopolyrotaxanes **4** and CB[6] at about $100^\circ C$ is attributed to dehydration. The TGA analysis shows that the decomposition of pseudopolyrotaxanes (Fig. 9(b)–(e)) exhibits small initial weight loss corresponding to that of parent polymer **3** (Fig. 9(a)), followed by large weight loss corresponding to that of CB[6] (Fig. 9(f)). The TGA curves of the pseudopolyrotaxane are different from that of the physical mixture of CB[6] and polymer **3** (Fig. 9(g)), which has a obvious flat. This is an indirect proof for the existence of polyrotaxanes. The decomposition temperature of the pseudopolyrotaxanes are higher than that of the parent polymer, and lower than that of pure CB[6], which can be seen clearly from the DTGA analysis (Fig. 10). The decomposition temperature of the pseudopolyrotaxanes increases with increasing amount of CB[6] threaded (Fig. 10(b)–(e)). The higher thermal stability of the pseudopolyrotaxanes is due to threading of CB[6] beads

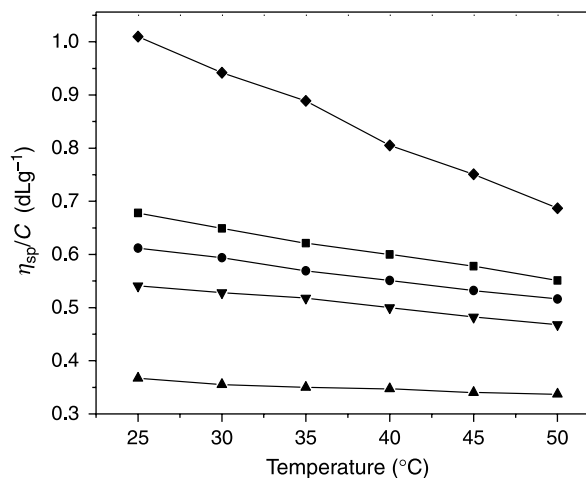


Fig. 6. Relationship of η_{sp}/C vs temperature of (\blacklozenge) polymer **3** and pseudopolyrotaxanes **4** with different degree of CB[6] threaded (q/n : (\blacksquare) 0.20, (\bullet) 0.40, (\blacktriangledown) 0.60, (\blacktriangle) 1.0): taken in H_2O , [3] or [4]= 0.3 g dL^{-1} .

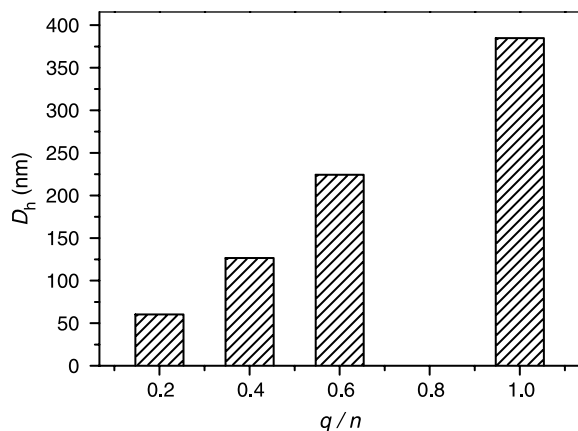


Fig. 7. The average hydrodynamic diameter (D_h) of the pseudopolyrotaxanes with different degree of CB[6] threaded (q/n : 0.2, 0.4, 0.6, 1.0) determined by DLS: taken in 1.0 mol L^{-1} NaCl aqueous solution at 30.0°C .

on the side chains. There is a peak at about 530°C in the DTGA curve of the physical mixture of CB[6] and polymer **3** (Fig. 10(g)) attributing to the decomposition of free CB[6], while this peak is not observed in the DTGA curves of pseudopolyrotaxanes **4**, which supports that there are no free CB[6] in these pseudopolyrotaxanes. This thermal behavior suggests that the threading of CB[6] increases the polymer stability at least in part by protecting the hexamethylene units in side chains with the rigid shell. A similar result in thermal stability was observed in main-chain pseudopolyrotaxanes incorporating CB[6] [12h].

2.8. UV-vis spectra

Fig. 11 shows UV-vis spectra of polymer **3** and pseudopolyrotaxanes **4** with different degree of CB[6] threaded. The parent polymer **3** exhibits a weaker absorption band centered around 258 nm , which is characteristic absorption peak of pyridinium chromophore ($\pi \rightarrow \pi^*$). Upon threading of CB[6], the intensity of the band increases with increasing amount of CB[6] threaded. Obviously, the pyridinium chromophore is indirectly affected by the threading of CB[6] on the hexamethylene units of the polymer, it maybe form a hyperconjugation system between the $\text{C}=\text{O}$ of CB[6] and the N^+ of pyridinium salt.

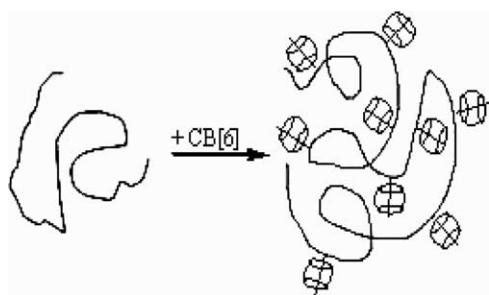


Fig. 8. The model of conformational changes of the chain with CB[6] threaded.

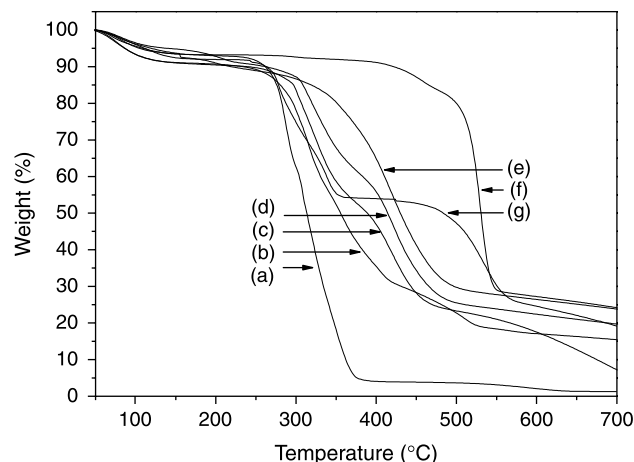


Fig. 9. TGA curves of (f) CB[6], (a) polymer **3**, pseudopolyrotaxanes **4** with different degree of CB[6] threaded (q/n : (b) 0.20, (c) 0.40, (d) 0.60, (e) 1.0) and (g) physical mixture of CB[6] and polymer **3** (quality ratio 1:1).

2.9. Effect of salts

Fig. 12 shows that the transmittance of the pseudopolyrotaxanes **4** with different degree of CB[6] threaded decreases quickly with increasing concentration of the NaI, and the critical salt concentration (CSC: concentration of the salt in the minimum transmittance) of NaI decreases with increasing amount of CB[6] threaded (Fig. 12(a)–(d)). The salting-out of the pseudopolyrotaxanes from the solution due to the shielding of I^- to pendant pyridinium ion, at the same time, the oxygen atoms of the CB[6] can also shield the pendant pyridinium ion, so with increasing amount of CB[6] threaded, the CSC of I^- decreases. The pseudopolyrotaxanes precipitated from NaI solution can be dissolved in distilled water. Their ^1H NMR spectra show the same result as Fig. 2.

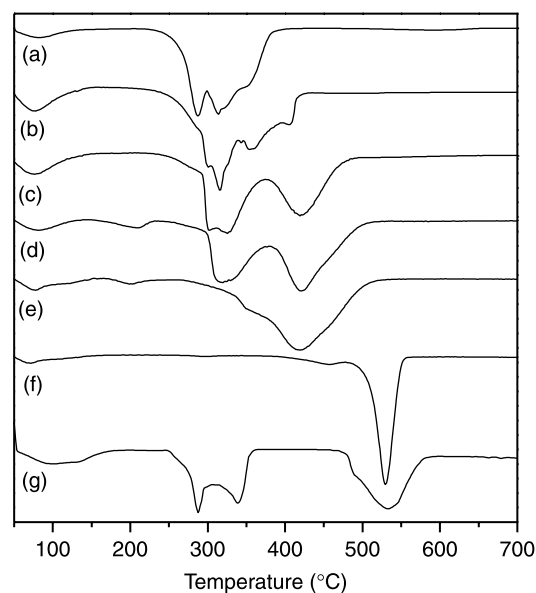


Fig. 10. DTGA curves of (f) CB[6], (a) polymer **3**, pseudopolyrotaxanes **4** with different degree of CB[6] threaded (q/n : (b) 0.20, (c) 0.40, (d) 0.60, (e) 1.0) and (g) physical mixture of CB[6] and polymer **3** (quality ratio 1:1).

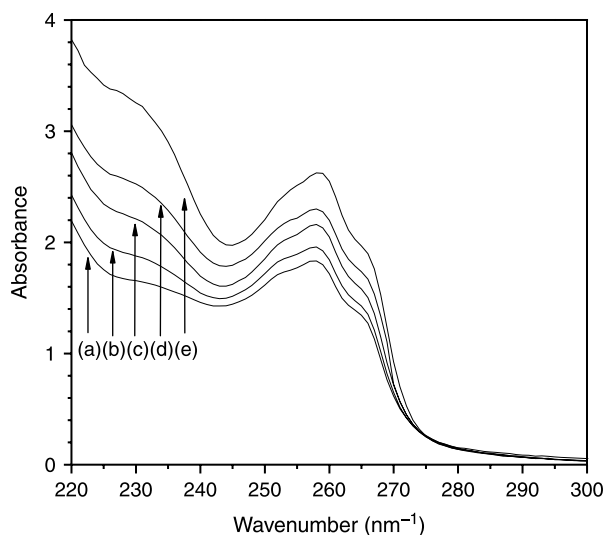


Fig. 11. UV-vis spectra of (a) polymer **3** and pseudopolyrotaxanes **4** with different degree of CB[6] threaded (q/n : (b) 0.20, (c) 0.40, (d) 0.60, (e) 1.0): $[n]=1\times 10^{-4}$ mol L $^{-1}$, taken in water at 25 °C.

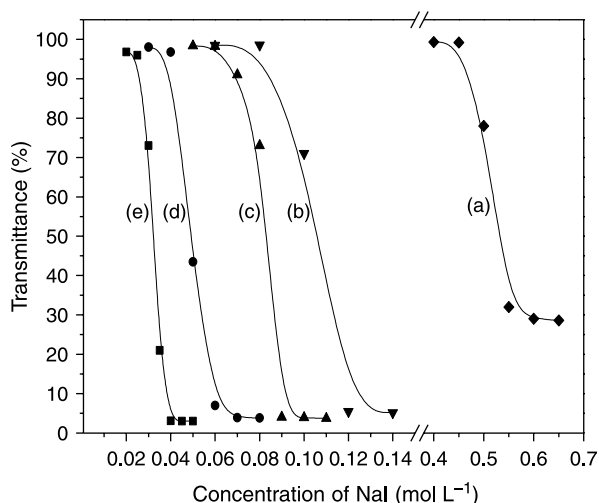


Fig. 12. Transmittance of pseudopolyrotaxanes **4** with different of CB[6] threaded against the concentration of NaI (q/n : (a) 0, (b) 0.20, (c) 0.40, (d) 0.60, (e) 1.0): $[n]=1.5\times 10^{-3}$ mol L $^{-1}$, taken in H $_2$ O at 25 °C.

The results indicate that NaI is the satisfied precipitant to the pseudopolyrotaxanes **4** from Fig. 12.

3. Conclusions

We have synthesized and characterized a novel water-soluble side-chain pseudopolyrotaxanes. In these pseudopolyrotaxanes, CB[6] beads are localized on the hexamethylene units in side chains of the polymer, and the driving force is the hydrophobic and charge-dipole interactions. The degree of CB[6] threaded can be controlled from 0.2 to 1.0. The pseudopolyrotaxanes in aqueous solution have more rigid chain conformation because of the threaded CB[6]. The decomposition temperature and the intensity of UV-vis absorption band of the pseudopolyrotaxanes increases with the

increasing amount of CB[6] threaded. The effect of salts shows that NaI is the satisfied precipitant to the pseudopolyrotaxanes.

4. Experimental section

4.1. Materials and methods

CB[6] was prepared according to the literature [16]. 4-Vinylpyridine (95%, Merck), pyridine (99%, Acros) were redistilled under reduced pressure, and AIBN (99%, Acros) was recrystallized from anhydrous ethanol. 1,6-Dibromohexane (96%, Fluka) and other chemicals were of reagent grade and used as received. All NMR experiments were performed on a Bruker AVANCE400 NMR spectrometer. D $_2$ O was used for field-frequency lock, and the observed 1 H chemical shifts are reported in parts per million (ppm) relative to an internal standard (TMS, 0 ppm). IR spectra were obtained on a Vector-22 spectrometer (Bruker, Switzerland) with sample prepared as KBr pellets. The reduced viscosities were measured with an Ubbelohde viscometer (capillary $\phi=0.6$ mm). Dynamic light scattering (DSL) experiments were carried out using a BI-200SM laser light-scattering spectrometer (Bruker, USA) equipped with a digital correlator (BI-9000AT) at 488 nm. The samples (concentration: $[n]=1.0\times 10^{-4}$ mol L $^{-1}$) in 1.0 mol L $^{-1}$ NaCl aqueous solution were prepared by filtering with a 1 μ m Millipore filter and all light-scattering measurement were performed at 20 °C. TGA analyses were carried out using a Mettler-Toledo SDTA-851TGA system at a rate of 20 °C/min for heating from 50 to 700 °C under a nitrogen atmosphere (flow rate 50 mL/min). Elemental analysis (C, N, and H) was performed on Elementar Vario E1 III elemental analyzer (German). UV spectra were recorded with a spectrophotometer (Hitachi, Japan, UV-4100) and scanned with a step size of 120 nm/min between 200 and 400 nm. The optical transmittance of the aqueous polymer solution was monitored at $\lambda=540$ nm with a spectrophotometer (Hitachi, Japan, UV-4100).

4.2. Polymer 1 (poly-4-vinylpyridine)

4-Vinylpyridine (5.0 g) was added to a round-bottom flask and was stirred with a magnetic stir bar under an inert N $_2$ atmosphere and heated to 60 °C with a oil bath. After thermal equilibrium had been reached and the solution had been bubbled for 0.5 h, AIBN was added and reacted for 6 h at this temperature to give crude product. The crude product was purified with EtOH/Et $_2$ O for three times, and dried under reduced pressure to give polymer **1** (4.2 g, 84%). 1 H NMR (400 MHz, D $_2$ O/DCI): δ 2.04 and 2.70 (br, 3H, $-CH-CH_2-$), 7.50 (br s, 2H, *m*-pyridyl), 8.53 (br s, 2H, *o*-pyridyl). Anal. Calcd for C $_7$ H $_7$ N (repeat unit of **1**) (%): C, 80.00; H, 6.67; N, 13.33. Found: C, 80.09; H, 6.70; N, 13.21.

4.3. Compound 2

To a solution of pyridine (2.37 g, 0.03 mol) in 40 mL of CH $_3$ CN was added 1,6-dibromohexane (29.28 g, 0.12 mol)

slowly at room temperature and stirred for 24 h at 80 °C. The reaction solution was cooled to room temperature, filtered, washed with ether, and recrystallized with CH₃CN for two times. The product was dried under reduced pressure to give compound **2** (7.85 g, 24.3 mmol, 81%). ¹H NMR (400 MHz, D₂O): δ 1.39 (m, *J* = 17.8 Hz, 2H, Br(CH₂)₂CH₂), 1.47 (m, 2H, Br(CH₂)₃CH₂), 1.85 (m, 2H, BrCH₂CH₂), 2.04 (m, 2H, Br(CH₂)₄CH₂), 3.49 (t, *J* = 13.3 Hz, 2H, BrCH₂), 4.64 (t, *J* = 14.6 Hz, 2H, N⁺CH₂), 8.09 (t, *J* = 14.1 Hz, 2H, *m*-pyridyl), 8.56 (m, 1H, *p*-pyridyl), 8.87 (d, *J* = 5.5 Hz, 2H, *o*-pyridyl). IR (KBr): 1632 cm⁻¹ (s, pyridinium), 1165 cm⁻¹ (s, C–Br). Anal. Calcd for C₁₁H₁₇NBr₂·2H₂O (%): C, 37.08; H, 5.90; N, 3.93. Found: C, 36.97; H, 5.92; N, 3.89.

4.4. Polymer 3

1 (0.525 g, 5.0 mmol) and **2** (6.46 g, 20.0 mmol) were dissolved in 80 mL of ethanol and refluxed for 48 h. After cooled to room temperature, the solution was precipitated with acetone to give crude product. The water solution of the crude product was dialyzed through a dialytic membrane for a week against water. The resulting solution was evaporated to leave about 2 mL of solution, 50 mL of acetone was added to the resulting solution to make the precipitate, which was isolated by filtration and dried under reduced pressure to obtain polymer **3** (1.05 g). ¹H NMR (400 MHz, D₂O): δ 1.48 (br s), 2.10 (br s), 1.90 (br), 4.48 (s), 4.62 (br s), 7.45 (br), 8.44 (br), 8.12 (br s), 8.57 (br s), 8.90 (br s). IR (KBr): 1639 cm⁻¹ (s, pyridinium).

4.5. Pseudopolyrotaxanes 4

Pseudopolyrotaxanes **4** was prepared by stirring a mixture of **3** (0.114 g, *n* = 0.2 mmol) and CB[6]·5H₂O (0.24 g, 0.22 mmol) in H₂O (20 mL) at room temperature for 24 h. The solution was filtered to remove the excess CB[6] and give clear solution. The filtrate was evaporated to leave about 2 mL of solution, 50 mL of ethanol was added to the resulting solution to make the precipitate, which was isolated by the filtration and dried under reduced pressure to obtain pseudopolyrotaxanes **4** (0.30 g, 96%). ¹H NMR (400 MHz, D₂O): δ 0.57 (br s, 4H), 1.20 (br s, 4H), 1.92 (br), 4.36 (br, 16H), 5.61, 5.72 (24H), 7.53 (br), 8.60 (br), 9.13 (br), 8.03 (br s), 8.48 (br s), 9.40 (br s, 2H). IR (KBr): 1735 cm⁻¹ (s, C=O), 1639 cm⁻¹ (s, pyridinium). Pseudopolyrotaxanes with different degree of CB[6] threaded were prepared by the same procedure as described above, except that proper amount of CB[6] were added to the solution.

Acknowledgements

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