Synthesis, characterization and properties of side-chain pseudopolyrotaxanes consisting of cucurbituril[6] and poly-N1-(4-vinylbenzyl)-1,4-diaminobutane dihydrochloride

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Abstract

Pseudopolyrotaxanes **3** is synthesized from cucurbituril[6] (CB[6]) and polymer **2** (poly-N1-(4-vinylbenzyl)-1,4-diaminobutane dihydrochloride) in water by simple stirring at room temperature. The monomer **1**, polymer **2** and pseudopolyrotaxanes **3** are characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and elemental analysis. In **3**, the CB[6] beads are localized on tetramethylene units in side chains of **2**, and combine N^+ by noncovalent bonds. The degree of threading (number of CB[6] beads per repeat unit) can be controlled from 0 to 1.0 by controlling the amount of CB[6] added. The properties of polymer **2** and pseudopolyrotaxanes **3** are researched by TGA, X-ray powder diffraction (XRD), environment scanning electron microscope (ESEM) and potentiometric titrations. The pseudopolyrotaxanes have higher thermal stability and chain regularity than the parent polymer which are attributed to the bulkiness and the rigidity of the CB[6] threaded. The decomposition temperature and chain regularity of the pseudopolyrotaxanes increase with increasing amount of CB[6] threaded. The effects of salts (NaCl, NaBr or NaI) to pseudopolyrotaxanes are studied by the transmittance with UV–vis, and the results show that NaI is the satisfied precipitant to the pseudopolyrotaxanes. The surface morphologies of pseudopolyrotaxanes **3** observed by ESEM shows a series of spherical particle with different diameter. The results of potentiometric titrations show that the pseudopolyrotaxanes **3** have larger pK_{av} and smaller n than polymer **2**.
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1. Introduction

Polymers in which their components are linked through noncovalent bonds 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 [1]. Such noncovalent bonds linked polymers include (pseudo)polyrotaxanes in which a number of cyclic units are threaded onto a polymer main chain or side chains. Most (pseudo)polyrotaxanes synthesized so far contain cyclodextrins (CDs) or crown ethers threaded on organic polymers. Harada et al. [2] and Wenz et al. [3] reported

main-chain (pseudo)polyrotaxanes containing CDs. Gibson et al. [4] utilized crown ether to synthesize main-chain (pseudo)polyrotaxanes. In addition, side-chain (pseudo)polyrotaxanes have also been synthesized. Ritter et al. [5] synthesized a series of side-chain polyrotaxanes containing CD beads threaded on side chains of various polymer backbones. Takata et al. [6] reported side-chain polyrotaxanes synthesized by polymerization of a semirotaxane monomer containing crown ether threaded on an acrylate derivative. Also, the side-chain polyrotaxanes containing CDs were synthesized by Osakada et al. [7]. 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[6] (CB[6]), which is a macrocycle comprising six glycoluril units interconnected with 12 methylene bridges, has a hydrophobic cavity that is accessible through two identical carbonyl-fringed portals [8]. 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 small molecules such as protonated aminoalkanes diaminoalkanes ($K > 10^5$) [8] through the formation of (pseudo)rotaxane. Taking advantage of this fact, various mechanically interlocked molecules including rotaxanes and (pseudo)polyrotaxanes have been synthesized by Kim et al. [9], Buschmann et al. [10] and Steinke et al. [11]. But side-chain (pseudo)polyrotaxanes containing CB[6] as a molecular bead have been scarcely reported [9d].

We now synthesized a side-chain pseudopolyrotaxanes in which CB[6] beads were threaded on protonated diaminobutane pendant attached to a main polymer chain. A unique feature of the pseudopolyrotaxanes is that the CB[6] bead can be threaded on every diaminobutane unit of the polymer and the degree of threading (number of CB[6] beads per repeat unit) can be controlled by controlling the mount of CB[6] added. Here, we report the synthesis, characterization and properties of the side-chain pseudopolyrotaxanes.

2. Results and discussion

2.1. Preparation of polymer 2 and pseudopolyrotaxanes 3

Monomer **1** (N^1-4-vinylbenzyl-1,4-diaminobutane dihydrochloride) was synthesized according to Scheme 1. Radical polymerization of monomer **1** was carried out in the presence of potassium persulfate (KPS) at 65 °C to give side-chain pendant polymer **2** (poly-N^1-(4-vinylbenzyl)-1,4-diaminobutane dihydrochloride). The intrinsic viscosity [η] of **2** was 0.75 dL/g determined at 25.0 °C in 2.0 mol/L NaCl aqueous solution by Ubblohde viscometer. Side-chain pseudopolyrotaxanes **3** was obtained by mixing **2** and slightly excess CB[6] (∼1.1 equiv per repeating unit of **2**) in water and stirring the mixture at room temperature (rt) (Scheme 2). Pseudopolyrotaxanes with different degree of threading (< 1.0) were prepared by the same procedure as Scheme 2, except that the proper amounts of CB[6] were added to the solution.
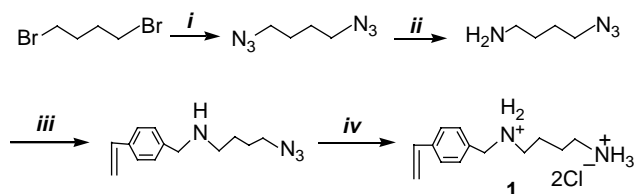
Scheme 1. Synthesis of monomer **1** (i) 2.5 equiv NaN₃, DMF, 80 °C, 24 h; (ii) 0.95 equiv PPh₃, Et₂O/Et₂Ac/5%HCl, rt, 24 h; (iii) 0.9 equiv 4-vinylbenzyl chloride, K₂CO₃, CH₃CN, rt, 24 h; (iv) 1.5 equiv PPh₃, THF, rt, 24 h, then concentrated HCl.
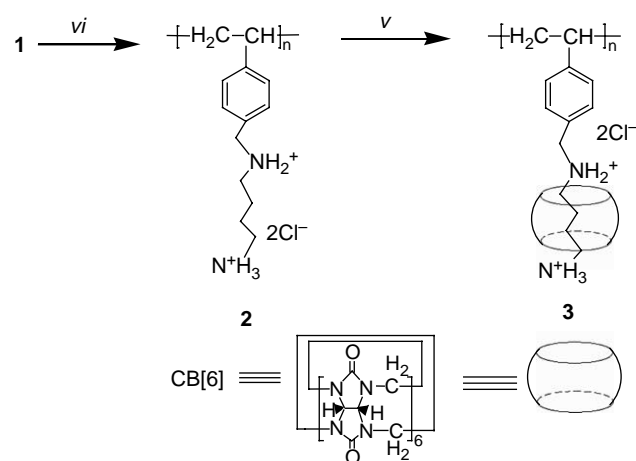
Scheme 2. Synthesis of polymer **2** and pseudopolyrotaxanes **3** (vi) 10^{-2} equiv KPS, H₂O, 65 °C, 24 h; (v) 1.1 equiv. CB[6], H₂O, rt, 24 h.

2.2. ^{1}H NMR spectra

Formations of polymer **2** and pseudopolyrotaxanes **3** were confirmed by ^{1}H NMR spectra as well as elemental analysis. Fig. 1 shows that no peaks corresponding to –CH=CH₂ are observed in the ^{1}H NMR spectrum of **2** (Fig. 1(a)). Upon formation of pseudopolyrotaxanes **3** (Fig. 1(b)), new broad signals appear at 4.42 and 5.77 ppm, which correspond to threaded CB[6]. At the same time, the tetramethylene proton signals (■ and ●) of the pendant diaminobutane unit of **2** are shifted upfield due to the shielding effect of CB[6], while the signals for three protons of the benzylic protons (▲ and ★), which are now located just outside of the CB[6] bead, are shifted downfield. The NMR data support that the CB[6] beads threaded in **3** are localized on the tetramethylene 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] (5.77 ppm) and polymer side-chain peaks (0.60 or 2.33 ppm) in the ^{1}H NMR spectrum (Fig. 1(b)). CB[6] bead can be threaded on every side chain containing a protonated diaminobutane unit in **3**. The high threading efficiency is due to the exceptionally strong interaction of CB[6] and the protonated diaminobutane unit ($K > 10^5$) in neutral or acidic media [8]. Because of the multiple noncovalent interactions between the positively charged nitrogen atoms of **2** and the CB[6] portal oxygen atoms, the resulting pseudopolyrotaxanes **3** is quite stable in solution and solid state.

2.3. Control of the degree of threading

The degree of threading (the number of CB[6] threaded per repeat unit of polymer) of pseudopolyrotaxanes **3** can be controlled. Fig. 2 shows a series of ^{1}H NMR spectra of the pseudopolyrotaxanes taken with different molar of **2** to CB[6]. As the amount of CB[6] added increases from 0 (Fig. 2(b)) equiv to 1.0 (Fig. 2(e)) equiv, the intensity of the signals for CB[6] (4.42 and 5.77 ppm) threaded increases, and a new set of signals for the polymer backbone appear with growing intensities (shown with arrows in Fig. 2). All these data are
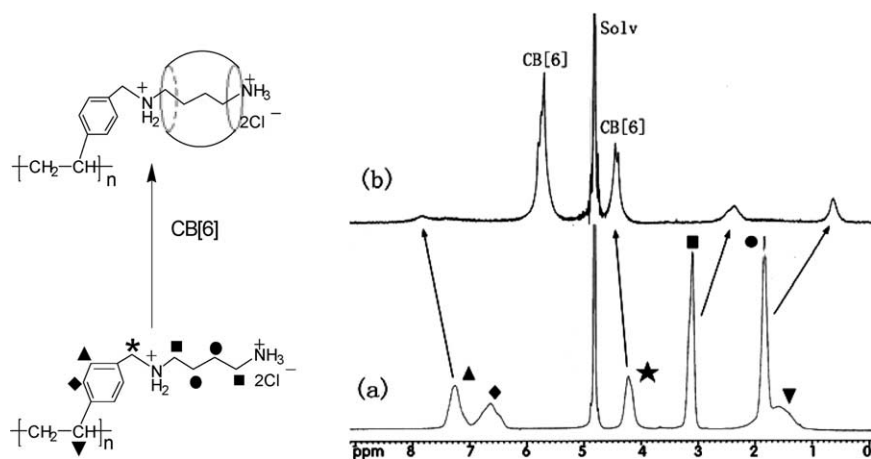
Fig. 1. ^{1}H NMR spectra of (a) polymer **2** and (b) pseudopolyrotaxanes **3** in D$_2$O at room temperature.

consistent with the fact that the CB[6] beads threaded are localized on the tetramethylene units in the side chains of **2**. The number of CB[6] beads threaded in polymer can be determined by comparing the intensity of the CB[6] (5.77 ppm) and the polymer side-chain peaks (0.60 or 2.33 ppm) (Fig. 2(b)–(e)). Fig. 3 shows that the number of CB[6] added and levels off at about 1:1 where all the side-chain tetramethylene units are fully occupied by CB[6]. The linear relationship (Fig. 3) indicates that the degree of threading of pseudopolyrotaxanes **3** can be controlled between 0 and 1.0 simply by adding a desired amount of CB[6] into the solution of **2**. Similar behavior has been observed in main-chain pseudopolyrotaxanes incorporating CB[6] [9e].
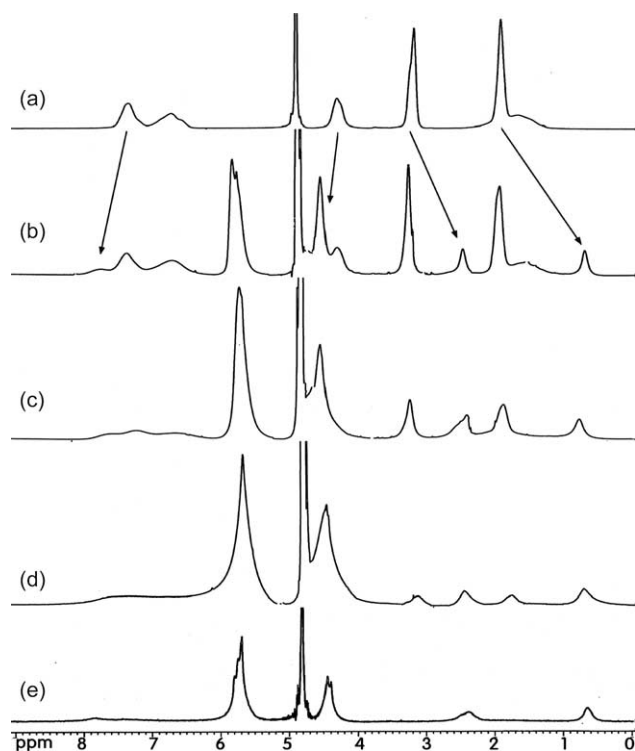
2.4. FT-IR spectra

Fig. 4 shows FT-IR spectra of polymer **2** and pseudopolyr-otaxanes **3** with different degree of CB[6] threaded. The extremely bands at 1732 cm^{-1} (Fig. 4(a)) and 1616 cm^{-1} (Fig. 4(b)) are the characteristic absorption peaks of C=O of CB[6] and ammonium salt of polymer **2**, respectively. In pseudopolyrotaxanes, the band at 1634 cm^{-1} is blue shifted from the band at 1616 cm^{-1}, which dues to the noncovalent bonds of C=O$\cdots$N$^+$, and the band at 1732 cm^{-1} is also observed (Fig. 4(c)–(f)). The ratio of intensity of the peaks at the 1732 and 1634 cm^{-1} increases gradually with increasing amount of CB[6] threaded (shown with arrows in Fig. 4). It is the indirect proof for the existence of pseudopolyrotaxanes.

2.5. Thermal properties

Side-chain pseudopolyrotaxanes are more thermally stable than the parent polymer (Figs. 5 and 6). The small weight loss of polymer **2**, pseudopolyrotaxanes **3** and CB[6] at about

Fig. 2. ^{1}H NMR spectra of (a) polymer **2** and pseudopolyrotaxanes **3** with different degree of CB[6] threaded (molar ratio of **2** to CB[6]: (b) 1:0.25, (c) 1:0.5, (d) 1:0.75, (e) 1:1).
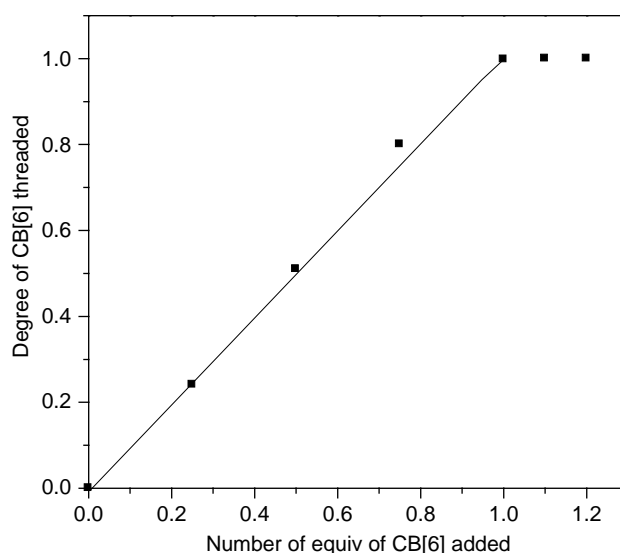

Fig. 3. Relationship of the degree of CB[6] threaded vs the number of CB[6] added (molar ratio of **2** to CB[6]: 1:0, 1:0.25, 1:0.5, 1:0.75, 1:1, 1:1.1, 1:1.2).
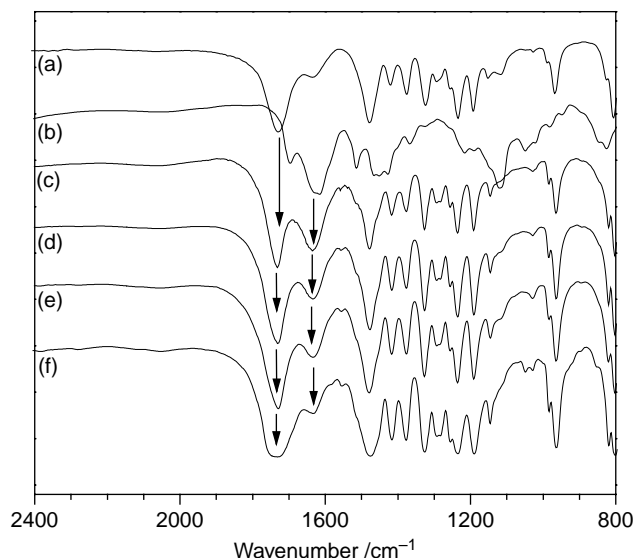
Fig. 4. FT-IR spectra of (a) CB[6], (b) polymer **2** and pseudopolyrotaxanes **3** with different degree of CB[6] threaded (molar ratio of **2** to CB[6]: (c) 1:0.25, (d) 1:0.5, (e) 1:0.75, (f) 1:1).

100 °C is attributed to dehydration. The TGA analysis shows that the decomposition of parent polymer **2** occurs in two steps (first step: main chain; second step: side chain) starting at ∼260 °C (Fig. 5(a)) and losses most of its weight (75%) at ∼480 °C. However, pseudopolyrotaxanes **3** (Fig. 4(e)) is stable up to ∼340 °C. The pseudopolyrotaxanes (Fig. 5(b)–(e)) exhibit small initial weight loss corresponding to parent polymer, followed by large weight loss corresponding to CB[6] (Fig. 5(f)). The TGA curves of the pseudopolyrotaxanes are different from that of the physical mixture of CB[6] and polymer **2** (Fig. 5(g)) which has two 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
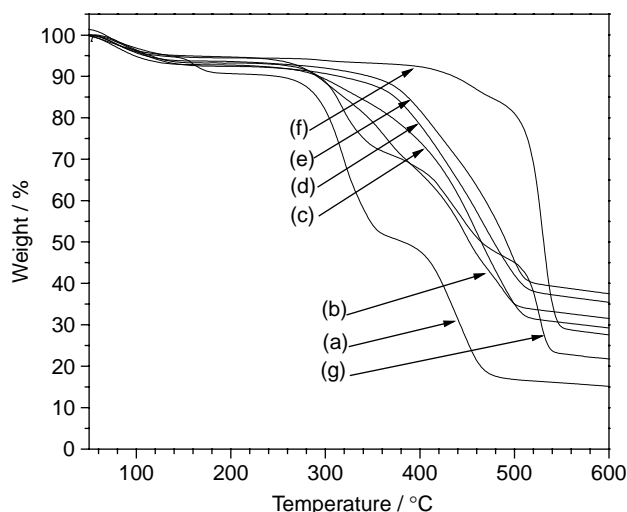

Fig. 5. TGA curves of (f) CB[6], (a) polymer **2**, pseudopolyrotaxanes **3** with different of threading CB[6] (molar rations of **2** to CB[6]: (b) 1:0.25, (c) 1:0.5, (d) 1:0.75, (e) 1:1) and (g) physical mixture of CB[6] and polymer **2** (quality ratio 1:1).
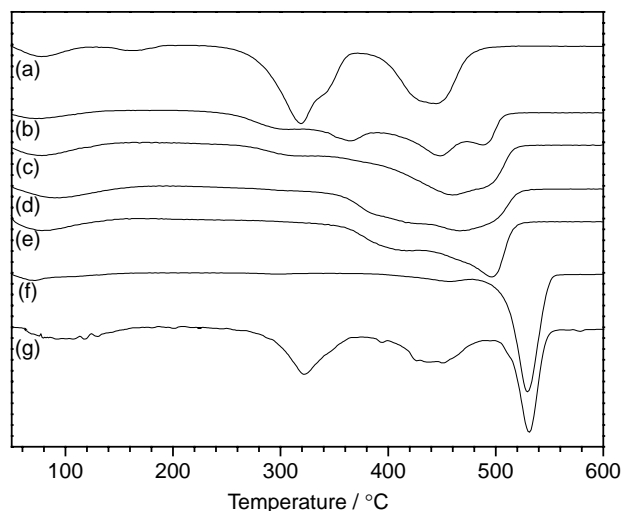

Fig. 6. DTGA curves of (f) CB[6], (a) polymer **2**, pseudopolyrotaxanes **3** with different of threading CB[6] (molar rations of **2** to CB[6]: (b) 1:0.25, (c) 1:0.5, (d) 1:0.75, (e) 1:1) and (g) physical mixture of CB[6] and polymer **2** (quality ratio 1:1).

pure CB[6] which can be seen clearly from the DTGA analysis (Fig. 6). The decomposition temperature of the pseudopolyrotaxanes increases with increasing amount of CB[6] threaded (Fig. 6(b)–(e)). The higher thermal stability of the pseudopolyrotaxanes is due to threading of CB[6] beads 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 **2** (Fig. 6(g)) attributing to the decomposition of free CB[6], while this peak is not observed in the DTGA curves of pseudopolyrotaxanes **3**, 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 tetramethylene units in side chains with the rigid shell. A similar result in thermal stability was observed in main-chain pseudopolyrotaxanes incorporating CB[6] [9e].

2.6. X-ray powder diffraction (XRD)

Fig. 7 shows the XRD patterns of polymer **2**, CB[6] and pseudopolyrotaxanes **3** with different degree of CB[6] threaded. No sharp peaks reflected in the pattern of polymer **2** show that it is a typical non-crystalline polymer (Fig. 7(a)), while CB[6], comparing with **2**, has crystal composition because there are three sharper peaks ($2\theta = 14.8, 23.2, 31.2°$) in the XRD pattern (Fig. 7(f)). As the amount of CB[6] threaded increases from 0.25 to 1.0 (Fig. 7(b)–(e)), a new set of peaks appears ($2\theta = 14.8, 31.2°$). The intensity of the peaks ($2\theta = 14.8, 23.2, 31.2°$) increases with increasing amount of CB[6] threaded and approaches that of pure CB[6] (shown with arrows in Fig. 7). The increasing intensity suggests that the threading of CB[6] causes chain conformational changes of the polymer. Compared with the parent polymer, the pseudopolyrotaxanes have more regular chain conformation because of the bulkiness of the threaded CB[6] beads (as shown in Scheme 1), and the regularity of the chain conformation increases with
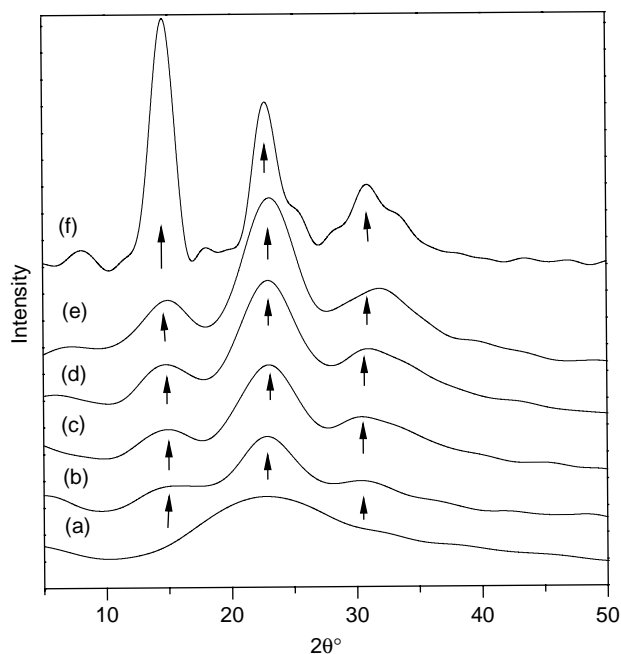
Fig. 7. XRD results of (a) polymer **2**, (f) CB[6] and pseudopolyrotaxanes **3** with different degree of CB[6] threaded (molar ratio of **2** to CB[6]: (b) 1:0.25, (c) 1: 0.5, (d) 1:0.75, (e) 1:1).

increasing amount of CB[6] threaded. Similar changes have been observed in polyrotaxanes incorporating CDs [12].

2.7. Morphology observations

Fig. 8 shows the ESEM micrographs of polymer **2** and pseudopolyrotaxanes **3** (molar ratio of **2** to CB[6] is 1:1). The surface of polymer **2** (Fig. 8(a)) is random block structure, as the most of conventional polymer, while the surface of pseudopolyrotaxanes **3** (Fig. 8(b)) shows a series of spherical particle with different diameter. With the threading of CB[6], the random chain of polymer **2** are taken on a structure of a nearly circle with the beads of CB[6] lies out the circle, as shown in Scheme 3, which are attributed to the bulky steric hindrance of CB[6], so the pseudopolyrotaxanes have more regular chain conformation than the polymer **2** as the result of the XRD. And the degree of polymerization of the polymer is different, so the diameter of the spherical partical is different. The results of ESEM research shows that the threading of CB[6] on the side chain of the polymer can cause chain conformational changes.

2.8. Effect of salts

Fig. 9 shows that the transmittance of the pseudopolyrotaxanes **3** decreases quickly with increasing concentration of 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. 9(a)–(d)). The salting-out of the pseudopolyrotaxanes from the solution dues to the shielding of I^- to pendant ammonium ion, but the oxygen atoms of the CB[6] can also shield the pendant
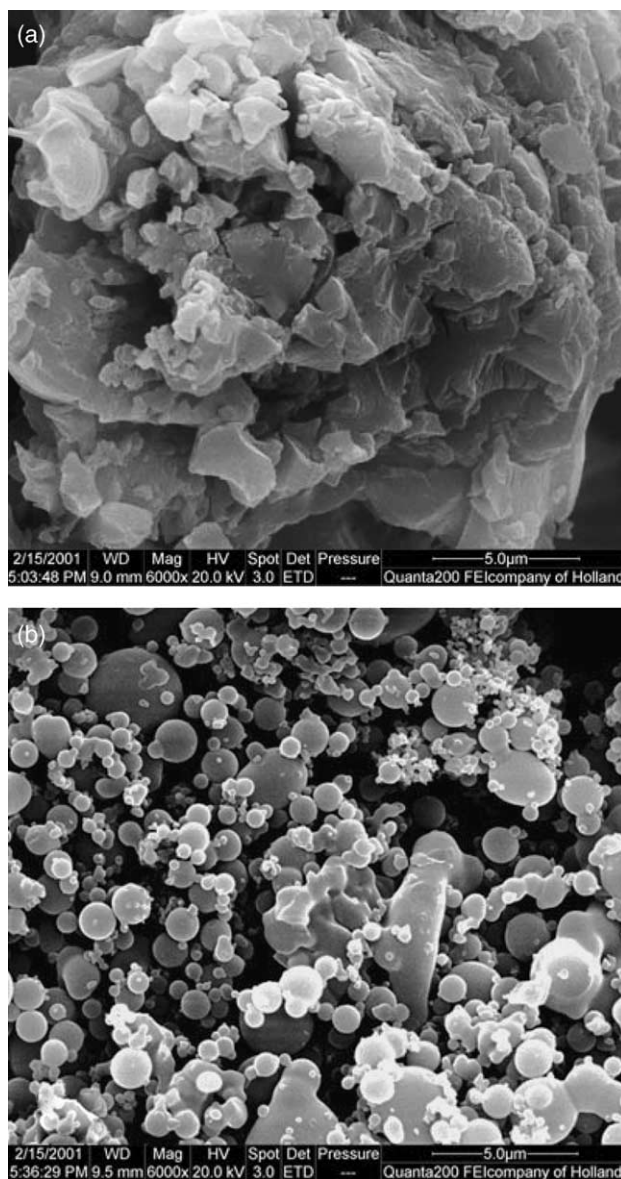

Fig. 8. ESEM photos of (a) polymer **2** and (b) pseudopolyrotaxanes **3** (molar ratio of **2** to CB[6] is 1:1).

ammonium ion, so with increasing amount of CB[6] threaded, the CSC of I^- decreases. Fig. 10 shows the effect of different salts to the transmittance of the pseudopolyrotaxanes (molar ratio of **2** to CB[6] is 1:1). The CSC of the salt (NaCl, NaBr or NaI) increases with the increasing hydrated radius of the negative ion of the salts (hydrated radius: $Cl^- > Br^- > I^-$). The smaller hydrated radius of the negative ion, the more
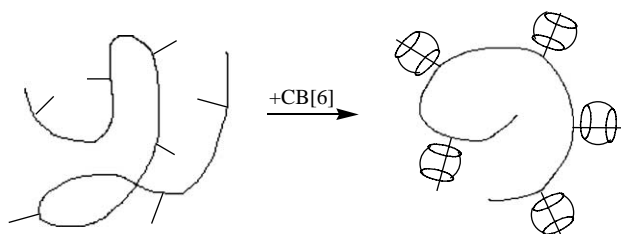
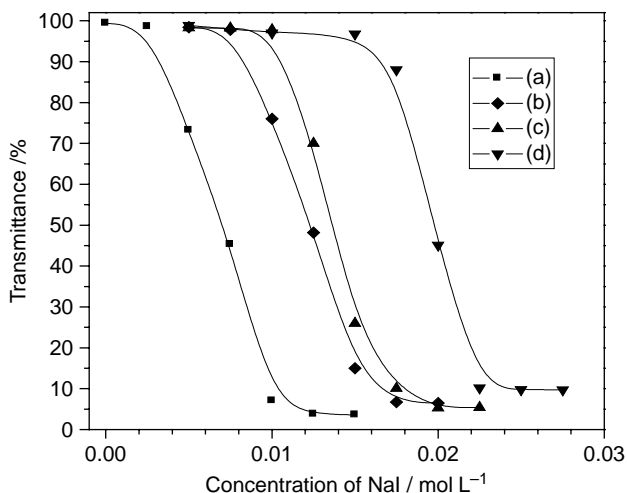Scheme 3. Conformational changes of the chain with CB[6] threaded.

Fig. 9. Transmittance of the pseudopolyrotaxanes **3** with different degree of CB[6] threaded against the concentration of NaI (molar ratio of **2** to CB[6]: (b) 1:0.25, (c) 1:0.5, (d) 1:0.75, (e) 1:1.): [diamine salts]=1.0×10^{-3} mol L^{-1}, taken in water at 25 °C.

effective shielding to the positive ion of pendent ammonium, because of the larger steric hindrance of the CB[6]. From Figs. 9 and 10, NaI is the satisfied precipitant to the pseudopolyrotaxanes.

2.9. Potentiometric titrations

The potentiometric titration curves for polymer **2** with and without added salt are shown in Fig. 11(a) and (b). There is no iso-electric jump (IEJ), called by Katchalsky et al. [13], in Fig. 11(a), while the IEJ (pH=4.19–6.85) can be seen clearly in Fig. 11(b). The reason is that the shield effect of the salt to the aminium ion, so the salt solution of polymer **2** can be titrated accurately. Fig. 11(c) is the potentiometric titration curve for pseudopolyrotaxanes **3** without added salt, in which there is a obvious IEJ (pH=4.28–9.71). This unusual behavior
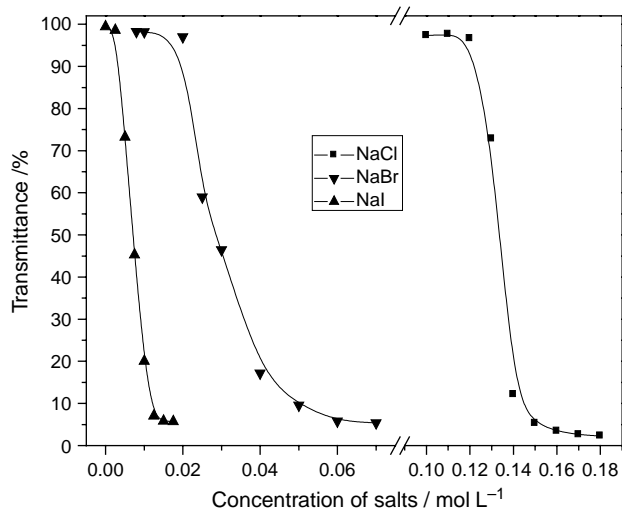

Fig. 10. Transmittance of the pseudopolyrotaxanes **3** (molar ratio of **2** to CB[6] is 1:1) against the concentration of different salts: [diamine salts]= 1.0×10^{-3} mol L^{-1}, taken in water at 25 °C.
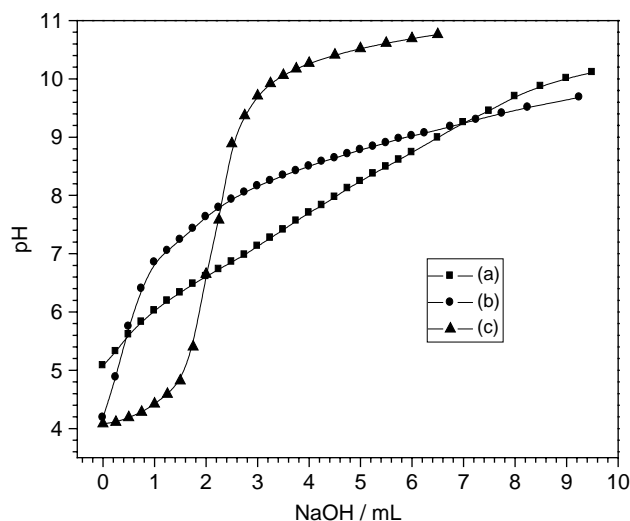

Fig. 11. Potentiometric titration for (a) polymer **2** in salt-free, (b) polymer **2** in 1.0 mol L^{-1} NaCl and (c) pseudopolyrotaxanes **3** (molar ratio of **2** to CB[6] is 1:1) in salt-free: [diamine salts]=0.001 mol L^{-1} (50 mL), [NaOH]= 0.01 mol L^{-1}.

may be caused by conformational changes of the chain upon CB[6] threading, as shown in Chart 1. The chain taken on a structure of a nearly ball (see the result of ESEM) because of the bulky steric hindrance of CB[6], and the aminium ion lies on the exterior of the ball. Also the oxygen atoms of the CB[6] can shield the pendant ammonium ion (see the result of effect of salts), so the IEJ can be seen clearly without added salt.

The protonation constant (K_{av}) of the aminium ion can be calculated according to the modified Henderson–Hasselbalch Equation: $pH = pK_{av} + n \log[(1-\alpha)/\alpha]$, where K_{av} value is average stability constant of the $K^a(NH_2^+ \leftrightarrow NH + H^+)$ and $K^b(NH_3^+ \leftrightarrow NH_2 + H^+)$, n is a constant, α is the degree of protonation which can be calculated using the equation: $\alpha = [A]_{eq}/C_{AH}^+ = (C_{OH} + [H^+] - [OH^-])/C_{AH}^+$, $[A]_{eq}$ is the concentration of the monomer aminium ion of polymer neutralized by strong base (NaOH) at the equilibrium, C_{AH}^+ is the total (analytical) concentration of the monomer aminium ion of polymer, C_{OH} is the concentration of the strong base added for the partial neutralization of the aminium ion at each α value, $[H^+]$ and $[OH^-]$ at equilibrium can be calculated from the pH value. The linear regression fit of pH versus $\log[(1-\alpha)/\alpha]$ ($\alpha = 0.2$–0.8) give pK_{av} and n as the intercept and slope, respectively. The average stability constant of pseudopolyrotaxanes **3** ($pK_{av}=8.52$) is larger than that of polymer **2** ($pK_{av}=7.82$) in 1.0 mol L^{-1} NaCl solution, which indicates the aminium ion in pseudopolyrotaxanes **3** reacted with OH^- is more difficult than that of polymer **2**. We estimate that noncovalent bonds formed between aminium ion and carbonyl groups of CB[6] in pseudopolyrotaxanes **3** makes the ionizing power of aminium ion reduce. While the value of n of pseudopolyrotaxanes **3** ($n=1.24$) is smaller than that of polymer **2** ($n=1.45$). The more compact the polymer coil the smaller the value of n [14]. The smaller n shows that the threaded CB[6] causes the change of the chain conformation. We deduce that the pseudopolyrotaxanes chain tends to shrink

because of the shield effect of the polar carbonyl groups of CB[6] to the aminium ion, and thus they have a smaller hydrodynamic volume and shrinking chain conformation.

3. Conclusions

We have synthesized and characterized a novel side-chain pseudopolyrotaxanes. The degree of CB[6] threaded can be controlled from 0 to 1.0. In these pseudopolyrotaxanes, the CB[6] beads are localized at the tetramethylene sites in side chains of the polymer through noncovalent bonds. The side-chain pseudopolyrotaxanes have higher conformational rigidity and thermal stability than the parent polymer, which are attributed to the bulkiness and the rigidity of the CB[6] threaded. The thermal stability and the chain regularity of the pseudopolyrotaxanes increase with the increasing amount of CB[6] threaded. The effects of salts show that the CSC of the salts increases with the increasing hydrated radius of the negative ion of the salts (hydrated radius: $Cl^- > Br^- > I^-$), and NaI is the satisfied precipitant to the pseudopolyrotaxanes. The surface morphologies of pseudopolyrotaxanes **3** observed by ESEM shows a series of spherical particle with different diameter. The results of potentiometric titrations show that the pseudopolyrotaxanes **3** have larger pK_{av} and smaller n than polymer **2**.

4. Experimental section

4.1. Materials and measurements

CB[6] was prepared according to the literature [15]. 4-Vinlbenzyl chloride (90%), 1,4-dibromobutane (99%), triphenylphosphine (Ph₃P, 99%), sodium azide (NaN₃, 99%) were received from Acros or Fluka and used as received. Potassium persulfate (KPS, Acros) was recrystallized from deionized water before use. Other chemicals were of reagent grade and used without further purification.

All NMR experiments were performed on a Bruker AVANCE400 NMR spectrometer. D₂O was used for field-frequency lock, and the observed ¹H chemical shifts are reported in parts per million (ppm) relative to an internal standard (TMS, 0 ppm). FT-IR spectra were obtained on a Vector-22 spectrometer (Bruker, Switzerland) with sample prepared as KBr pellets. TGA analyses were carried out using a Mettler-Toledo SDTA-851TGA system at a rate of 20 °C/min for heating from 50 to 600 °C under a nitrogen atmosphere (flow rate 50 mL/min). Elemental analyses (C, N and H) were performed on Elementar Vario E1 III analyzer (German). Data of X-ray powder diffraction (XRD) were collected on a Max 2200PC power X-ray diffractometer (Rigaku, Japan) with Cu Kα (1.54051 Å) radiation (40 kV, 20 mA). Powder samples were mounted on a sample holder and scanned with a step size of $2\theta = 0.02°$ between $2\theta = 5$ and 50°. The morphologies of the surfaces of the samples were observed in an environment scanning electron microscope (ESEM, Quanta200, FEI, Holand). The specimens used for ESEM observations were prepared from the water solution by evaporing the solvent

slowly under reduced pressure. The surfaces of the specimens were coated with a thin layer of gold prior to ESEM examinations. The optical transmittance of the polymer solution was monitored at $\lambda = 540$ nm with a spectrophotometer (Hitachi, Japan, UV-4100). The pH measurements, with and without added salt (NaCl, 99.9% purity), were performed with a potentiometric pHmeter (P^H S-3). A glass electrode (23I) and a calomel electrode (K401) were used. A gentle stream of N₂ was passed through distilled deionized water at 90 °C for 15 min in order to remove dissolved gases. Titrations were performed in a nitrogen atmosphere to maintain a CO₂-free atmosphere and thermostatically controlled at 25 °C. Standardization was carried out with phosphate buffers (pH = 6.864) on the National Bureau of Standards scale.

4.2. Synthesis of monomer 1

4.2.1. 1, 4-Diazobutane

1,4-Dibromobutane (50.0 g, 0.23 mol) and NaN₃ (37.6 g, 0.58 mol) were dissolved in 80 mL of DMF and 8 mL H₂O, and stirred for 20 h at 80 °C. After cooled to room temperature, 160 mL of Et₂O was added to a reaction mixture, then the resulting solution was washed with 4% NaCl solution for four times. The organic layer was dried with magnesium sulfate for 24 h, and concentrated to give 30.8 g (0.22 mol) of 1,4-diazidobutane (yield: 95.1%). ¹H NMR(400 MHz, DCCl₃, ppm): δ 3.30 (t, $J = 5.8$ Hz, 4H, N₃CH_2), δ 1.68 (m, $J = 12.4$ Hz, 4H, CH₂CH_2CH_2CH₂).

4.2.2. 1-Azido-4-aminobutane

1,4-Diazidobutane (23.5 g, 0.168 mol) was dissolved in 100 mL of Et₂O, 100 mL of EtOAC and 160 mL of 5% HCl. To the solution was added PPh₃ (31.9 g, 0.16 mol) portionwise in small portion for about 1 h at 0 °C and stirred for 24 h at room temperature. The organic layer was discarded and the aqueous layer was washed with 75 mL CH₂Cl₂ for two times. The resulting aqueous phase was basified with NaOH carefully (pH ≅ 13) and then extracted with 3×100 mL of CH₂Cl₂. The combined extracts were dried with sodium sulfate for 24 h and concentrated to give 17.08 g (0.15 mol) of pure 1-azido-4-aminobutane (yield: 93.7%). ¹H NMR(400 MHz, DCCl₃, ppm): δ 5.30 (s, 2H, NH_2), δ 3.31(t, $J = 13.5$ Hz, 2H, N₃CH_2), δ 2.72 (m, $J = 13.7$ Hz, 2H, NH₂CH_2), δ 1.67 (m, $J = 13.5$ Hz, 2H, N₃CH₂CH_2), δ 1.56 (m, $J = 22.9$ Hz, 2H, NH₂CH₂CH_2); ¹³C NMR (400 MHz, DCCl₃, ppm): δ 51.68 (N₃CH₂), δ 42.02 (NH₂CH₂), δ 31.15 (NH₂ CH₂CH₂), δ 26.64 (N₃CH₂CH₂).

4.2.3. 1-Azido-4-(4-vinylbenzyl) aminobutane

To a solution of 1-azido-4-aminobutane (7.52 g, 0.066 mol) and K₂CO₃ (10.0 g, 0.072 mol) in 50 mL of CH₃CN was added 4-vinylbenzyl chloride (10.17 g, 0.060 mol) slowly at room temperature and stirred for 24 h at the same temperature. The reaction solution was concentrated and added aqueous solution of NaHCO₃ and CH₂Cl₂. The organic phase was separated, dried with Na₂SO₄, concentrated and then purified by column chromatography using CH₂Cl₂:MeOH (1:2) as an eluent to

give 10.24 g (0.445 mol) of 1-azido-4-(4-vinylbenzyl) amini-butane (yield: 74.2%). ^{1}H NMR (400 MHz, DCCl$_3$, ppm): δ 1.62 (br, 4H, CH$_2$ C*H$_2$C*H$_2$CH$_2$), δ 1.93 (s, br, 1H, N*H*), δ 2.63 (q, $J=13.3$ Hz, 2H, NHC*H$_2$*CH$_2$), δ 3.23 (t, $J=11.8$ Hz, 2H, N$_3$C*H$_2$*), δ 3.76 (d, $J=3.4$ Hz, 2H, PhC*H$_2$*N), δ 5.24 (d, $J=$ 10.9 Hz, 1H, vinyl), δ 5.72 (d, $J=17.6$ Hz, 1H, vinyl), δ 6.68 (dd, $J=28.4$ Hz, 1H, vinyl), δ 7.26–7.37 (m, 4H, 6 aromatic *H* of Ar); ^{13}C NMR (400 MHz, DCCl$_3$, ppm): δ 140.5, 136.7, 128.7, 126.7 (6 aromatic *C* of Ar), δ 137.0 (*C*H$_2$CH), δ 113.9 (*C*H$_2$CH), δ 54.1 (Ph*C*H$_2$NH), δ 51.7 (NH*C*H$_2$CH$_2$), δ 49.1 (N$_3$*C*H$_2$), δ 27.64 (NHCH$_2$*C*H$_2$), δ 27.12 (N$_3$CH$_2$*C*H$_2$).

4.2.4. Monomer 1 (N^1-(4-vinylbenzyl)-1,4-diaminobutane dihydrochloride)

1-Azido-4-(*N*-4-vinylbenzyl) aminobutane (3.0 g, 13 mmol) was dissolved in 15 mL of THF and 0.2 mL of H$_2$O. To the solution was added of PPh$_3$ (4.74 g, 18 mmol) slowly and stirred for 24 h at room temperature. The reaction solution was concentrated to leave half volume and concentrated HCl was added slowly at ice-bath to precipitate as HCl salt, filtered, and washed with THF and ether. The product was dried under reduced pressure to give 2.90 g (10.5 mmol) of monomer **1** (yield: 80.5%). ^{1}H NMR (400 MHz, D$_2$O, ppm): δ 1.78 (s, br, 4H, CH$_2$C*H$_2$C*H$_2$CH$_2$), δ 3.04 (t, $J=13.16$ Hz, 2H, NH$_3^+$C*H$_2$*), δ 3.14 (t, $J=13.5$ Hz, 2H, NH$_2^+$C*H$_2$*CH$_2$), δ 4.26 (s, 2H, PhC*H$_2$*N), δ 5.37 (d, $J=17.9$ Hz, 1H, vinyl), δ 5.92 (d, $J=$ 17.7 Hz, 1H, vinyl), δ 6.83 (dd, $J=28.6$ Hz, 1H, vinyl), δ 7.48 (m, 2 aromatic *H* of Ar, 2H), δ 7.60 (m, 2 aromatic *H* of Ar, 2H); ^{13}C NMR (400 MHz, D$_2$O, ppm): δ 136.2, 130.6, 130.4, 127.2 (6 aromatic *C* of Ar), δ 139.0 (CH$_2$*C*H), δ 115.9 (*C*H$_2$CH), δ 46.7 (Ph*C*H$_2$N), δ 51.1 (NH$_2^+$*C*H$_2$CH$_2$), δ 39.2 (NH$_3^+$*C*H$_2$), δ 24.3 (NH$_3^+$CH$_2$*C*H$_2$), δ 23.1 (NH$_2^+$CH$_2$*C*H$_2$); Anal. Calcd for C$_{13}$H$_{22}$N$_2$Cl$_2$ (%): C, 56.32; H, 7.94; N, 10.11. Found: C, 56.28; H, 8.01; N, 9.93.

4.3. Preparation of polymer 2 (poly-N^1-(4-vinylbenzyl)-1,4-diaminobutane dihydrochloride)

Monomer **1** (2.0 g) was dissolved in 5 mL of H$_2$O and the solution was stirred with a small magnetic stir bar under an inert N$_2$ atmosphere and heated to 65 °C with a oil bath. After thermal equilibrium had been reached and the solution had been bubbled for 0.5 h, KPS (0.02 g, dissolved in 0.5 mL of H$_2$O) was added to the solution. After 24 h, the solution was cooled to room temperature, precipitated with acetone and washed with ether, and dried under reduced pressure to give 1.65 g of polymer **2** (yield: 82.5%). ^{1}H NMR (400 MHz, D$_2$O, ppm): δ 1.55 (br, C*H$_2$* of polymer backbone, 2H), δ 1.80 (s, br, NCH$_2$C*H$_2$C*H$_2$CH$_2$N, 4H), δ 3.08 (s, br, NC*H$_2$*CH$_2$CH$_2$C*H$_2$*N, 4H), δ 4.21 (s, br, PhC*H$_2$*N, 2H), δ 6.64, 7.26 (br, 4 aromatic *H* of Ar, 4H). Anal. Calcd for C$_{13}$H$_{22}$N$_2$Cl$_2$ (%) (repeat unit of **2**): C, 56.32; H, 7.94; N, 10.11. Found: C, 56.29; H, 8.02; N, 9.97.

4.4. Preparation of pseudopolyrotaxanes

Pseudopolyrotaxanes **3** was prepared by stirring a mixture of **2** (0.194 g, [diamine salts]=0.70 mol) and CB[6]·5H$_2$O

(0.76 g, 0.77 mol) in H$_2$O (20 mL) at room temperature for 24 h. Excess CB[6] was filtered off to provide a clear solution which was then concentrated to ~2 mL. Addition of ethanol (50 mL) to the solution produced a precipitant, which was filtered, wash with ethanol, and dried under reduced pressure to produce **3** (0.85 g, 0.67 mol) (yield: 82.5%). ^{1}H NMR (400 MHz, D$_2$O, ppm): δ 0.60 (s, br, NCH$_2$C*H$_2$C*H$_2$CH$_2$N, 4H), δ 2.33 (s, br, NC*H$_2$*CH$_2$CH$_2$C*H$_2$*N, 4H), δ 4.42 (br, PhC*H$_2$*N, 12H from C*H$_2$* of CB[6], 14 H), δ 5.77 (br, 24H from C*H*C*H* and C*H$_2$* of CB[6], 24H), δ 7.21–7.96 (4 aromatic *H* of Ar). Anal. Calcd for C$_{49}$H$_{58}$N$_{26}$O$_{12}$Cl$_2$ (%) (repeat unit of **3**): C, 46.19; H, 4.56; N, 28.59. Found: C, 45.94; H, 4.81; N, 28.43. Pseudopolyrotaxanes with different degree of CB[6] threaded (<1.0) were prepared by the same procedure as described above, except that the proper amounts of CB[6] were added to the solution.

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