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Synthesis and Characterization of Novel Side-Chain Pseudopolyrotaxanes Containing Cucurbituril

Yebang Tan,† SooWhan Choi, Jae Wook Lee, Young Ho Ko, and Kimoon Kim*

National Creative Research Initiative Center for Smart Supramolecules and Department of Chemistry, Division of Molecular and Life Sciences, Pohang University of Science and Technology, San 31 Hyojadong, Pohang 790-784, Republic of Korea

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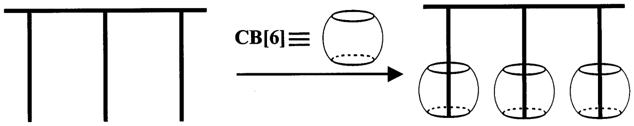
Introduction

Polymers whose components are held together by mechanical bonds have received much attention in recent years not only because of their unique structures but also because of their unusual properties.[1] Such mechanically linked polymers include (pseudo)polyrotaxanes in which a number of cyclic units are threaded onto a polymer main chain or side chains.[1,2] While main-chain (pseudo)polyrotaxanes have been studied quite extensively, studies on side-chain (pseudo)polyrotaxanes are limited.[3−8] Ritter[3] synthesized a series of side-chain polyrotaxanes containing cyclodextrin (CD) beads threaded on side chains of various polymer backbones. Osakada and Yamamoto[4] also prepared side-chain polyrotaxanes in which CD containing semirotaxane units are attached to a poly(bezimidazole) backbone. More recently, Takata[5] reported side-chain polyrotaxanes synthesized by polymerization of a semirotaxane monomer containing crown ether threaded on an acrylate derivative.

Cucurbituril (CB[6]) is a macrocycle comprising six glycoluril units with a hydrophobic cavity that is accessible through two identical carbonyl-fringed portals.[9] The polar carbonyl groups at the portals and the hydrophobic cavity allow CB[6] to form stable host−guest complexes with small molecules such as protonated aminoalkanes. In particular, it forms very stable complexes ($K > 10^5$) with protonated diaminoalkanes such as diaminobutane.[9] Taking advantage of this fact, we[10] and others[11,12] have successfully synthesized various mechanically interlocked molecules, including rotaxanes and (pseudo)polyrotaxanes. However, no side-chain (pseudo)polyrotaxane containing CB[6] as a molecular bead has been reported yet. Here we report novel side-chain pseudopolyrotaxanes in which CB[6] beads are threaded on (protonated) diaminobutane pendants attached to a main polymer chain (Scheme 1). A unique feature of the pseudopolyrotaxanes is that threading and dethreading of the CB[6] beads can be reversibly controlled by the pH of the solution.

Results and Discussion

Scheme 1. Side-Chain Pseudopolyrotaxane Incorporating CB[6]



Monomers **2** and **4** are prepared according to Scheme 2. Reaction of protected spermidine **1**[13] with acryloyl chloride in CH_2Cl_2 produces **2** in a decent yield. Reductive amination of 3-vinylbenzylaldehyde (**3**) with *N*-benzyloxycarbonyl (Cbz)−1,4-diaminobutane[14] followed by protection of the resulting secondary amine group with di-*tert*-butyl dicarbonate (Boc_2O) gives **4**. These monomers were characterized by ^1H and ^{13}C NMR spectroscopies as well as mass spectrometry. Polymerization of monomer **2** and **4** using 2,2′-azobis(isobutyronitrile) (AIBN) initiator produces polymers bearing protected diaminobutane pendants, **5** and **8**, respectively (Scheme 3). Polymers **5** and **8** are soluble in most organic solvents, including methanol, acetone, benzene, toluene, chloroform, DMSO, DMF, and THF, but are insoluble in water and hexane. No peaks corresponding to $-CH{=}CH_2$ are observed in the ^1H NMR spectra of these polymers. The average molecular weights of the polymers were estimated by GPC analysis. While **5** has M_n of 7.4×10^3 ($M_w/M_n = 1.2$), which corresponds to $P_n = \sim 17$, **8** has a slightly higher molecular weight: $M_n = 9.8 \times 10^3$, $M_w/M_n = 1.4$, $P_n = \sim 22$. Deprotection of **5** and **8** using 30% HBr in acetic acid gives water-soluble polymers **6** and **9**, respectively (Scheme 3). The complete removal of the Boc and Cbz protecting groups is confirmed by ^1H NMR spectroscopy (Figure 1a). Synthesis of side-chain pseudopolyrotaxanes **7** and **10** is easily achieved by mixing **6** and **9**, respectively, and a slight excess of CB[6] in water and stirring the mixture at room temperature for 10 h (Scheme 3). Although CB[6] itself is sparingly soluble in water, it slowly dissolves into the solution as the threading proceeds.

Formation of pseudopolyrotaxanes **7** and **10** was confirmed by ^1H NMR spectroscopy. Figure 1 compares the ^1H NMR spectra of **9** and **10**. Upon formation of pseudopolyrotaxane **10**, new broad signals appear at 4.4 and 5.7 ppm, which correspond to threaded CB[6]. At the same time, the methylene proton signals (● and ■) of the pendant diaminobutane unit of the polymer are shifted upfield due to the shielding effect of CB[6], while the signal (▲) for the benzylic protons, which are now located just outside of the CB[6] bead, is shifted downfield. Similar changes in the ^1H NMR spectra are observed upon formation of pseudopolyrotaxane **7**.

The amount of CB[6] threaded onto the side chains of the polymers can be estimated by comparing the intensities of the CB[6] and polymer side-chain peaks in the ^1H NMR spectra. Within experimental error, a CB[6] bead is threaded on every side chain containing a diaminobutane unit in **7** and **10**. This 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.[9]

As seen in Figure 1, the ^1H NMR signals of **10** are broader than those of **9**, which is attributable to the diminished molecular motion of the polymer upon threading CB[6]. The increased conformational rigidity of the polymer side chain upon threading of the molecular beads has been confirmed by measurement of the spin−lattice relaxation time (T_1) at variable temperatures (Table 1). The T_1 value of the side chain in **9**

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† Permanent address: Department of Chemistry, Shandong University, Jinan 250100, P.R. China.

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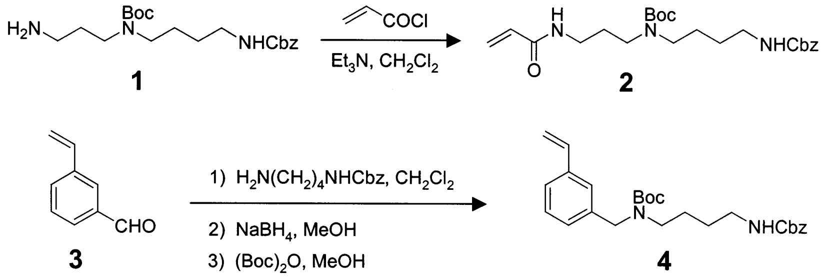
Scheme 2. Synthesis of Monomers 2 and 4



Scheme 3. Synthesis of Polymers 5, 6, 8, and 9, and Pseudopolyrotaxanes 7 and 10

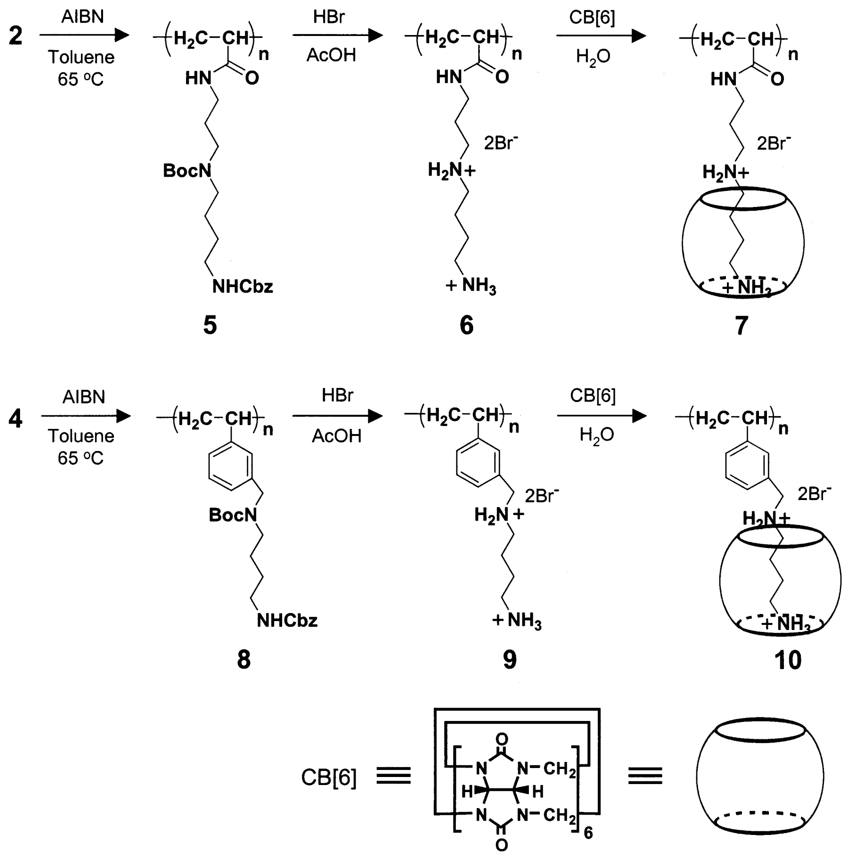


Table 1. ^{1}H T_1 Values of the Diaminobutane Units of Side-Chain Polymer 9 and Pseudopolyrotaxane 10 at Different Temperatures

	polymer **9**		pseudopolyrotaxane **10**	
	proton ■	proton ●	proton ■	proton ●
25 °C	0.84 s	0.95 s	1.71 s	1.78 s
40 °C	1.04 s	1.21 s	1.52 s	1.67 s

increases with increasing temperature: for example, T_1 values of the middle methylene protons (■, 1.6 ppm) of the diaminobutane unit are 0.84 at 25 °C and 1.03 at 40 °C. This result indicates that the correlation times (τ) are in a liquidlike region of the $T_1-\tau$ curve.[15] On the contrary, pseudopolyrotaxane **10** exhibits an opposite behavior. For example, T_1 values for the corresponding protons in **10** are 1.71 at 25 °C and 1.52 at 40 °C. Such a decrease in T_1 value with increasing temperature indicates that the molecular motion of the side chain in **10** resembles that in a solid phase.[16] Taken together, these results demonstrate that the side chains of the polymer become more rigid upon threading of CB[6]. Similar behavior has been observed in pseudorotaxane-terminated dendrimers.[17]

Side-chain pseudopolyrotaxanes **7** and **10** are more thermally stable than their parent polymers. The TGA analysis shows that the decomposition of parent polymer **5**, **6**, **8**, and **9** occurs in several steps starting as early as ~150 °C (Figure 2a,b). However, pseudopolyrotaxanes **7** and **10** are stable up to ~330 °C after a small weight loss before 100 °C, which is attributed to dehydration. The higher thermal stability of these polyrotaxanes is due to threading of CB[6] beads on the side chains. A similar increase in thermal stability was observed in main-chain pseudopolyrotaxanes incorporating CB[6].[18]

A preliminary experiment shows that dethreading and rethreading of the CB[6] beads in these polymers can be reversibly controlled by the pH of the solution. Upon treatment with a base (NaOD), the CB[6] molecular beads of **10** start dethreading from pH ~8 as judged by ^{1}H NMR spectroscopy (Figure 3): a new set of sharp signals corresponding to free CB[6] appears. With increasing pH, the intensity of the signals for free CB[6] increases and that for the middle methylene protons (■, 0.6 ppm) of the diaminobutane unit in **10** decreases. At the same time, the other methylene signals (●) of

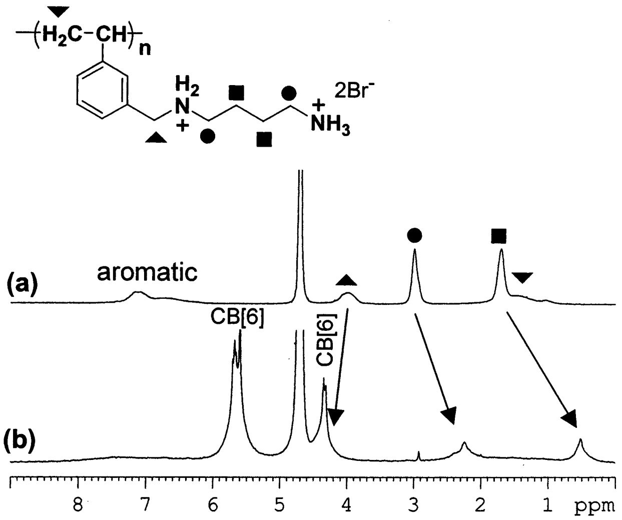


Figure 1. ^{1}H NMR spectra of (a) polymer **9** and (b) pseudopolyrotaxane **10** in D_2O at room temperature.

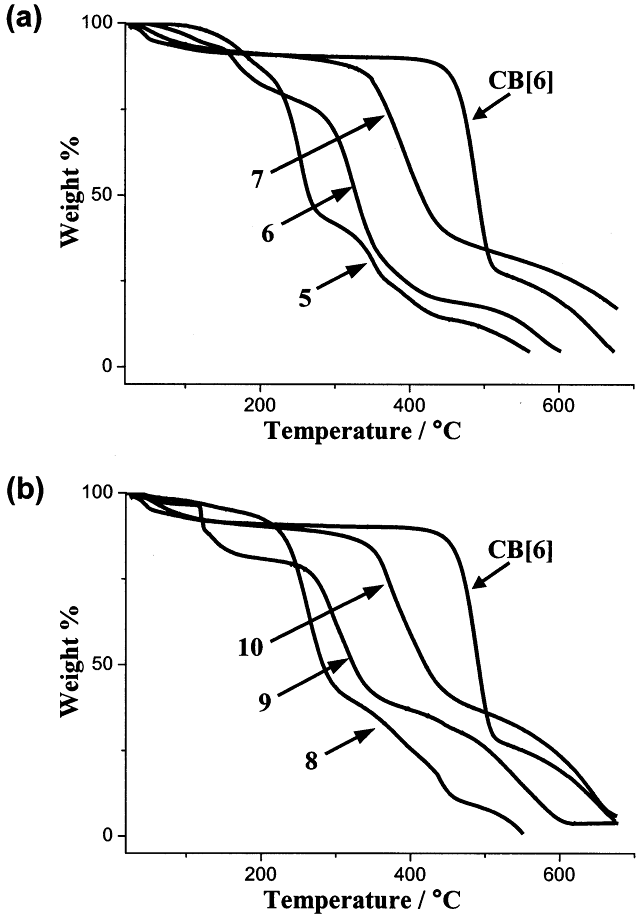


Figure 2. TGA curves of (a) side-chain polymers **5** and **6** and pseudopolyrotaxane **7** and (b) side-chain polymers **8** and **9** and pseudopolyrotaxane **10** in comparison with CB[6].

the diaminobutane unit become broad and complex, which may be attributed to deprotonation of the (protonated) amine units and partial dethreading of CB[6] from the side chain. The degree of dethreading steadily increases and finally reaches up to ~70% at pH ~12. Upon lowering the pH of the solution back to ~5 by adding an acid (DCl), however, most of the side chains are rethreaded with CB[6].

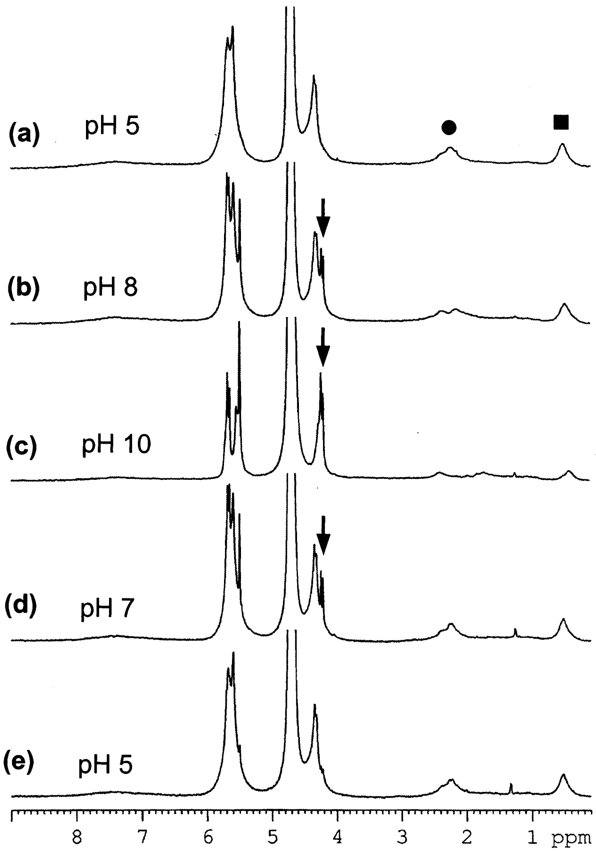


Figure 3. A series of ^{1}H NMR spectra of pseudopolyrotaxane **10** showing dethreading and rethreading of the CB[6] beads upon pH change of the solution. The CB[6] beads are dethreaded from pseudopolyrotaxane **10** as the pH increases ((b) pH = 8 and (c) pH = 10). The CB[6] beads are rethreaded onto the side chains as the pH decreases ((d) pH = 7 and (e) pH = 5). The CH signal for free CB[6] is indicated by an arrow.

In summary, we have synthesized and characterized novel side-chain pseudopolyrotaxanes incorporating CB[6]. The side-chain pseudopolyrotaxanes exhibit higher conformational rigidity and thermal stability than their parent polymers. Most interestingly, threading and dethreading of the molecular beads in these polymers can be reversibly controlled by pH of the solution. We are currently investigating the threading/dethreading mechanisms as well as other properties of these novel polymers.

Experimental Section

Materials and Methods. CB[6] was prepared according to the literature.[19] Other chemicals were of reagent grade and used as received from Aldrich. Gel permeation chromatography (GPC) measurements were performed on a TSP (Thermo Separation Products) GPC system equipped with a solvent delivery system and RI/UV detectors. All measurements were made at 25 °C with a set of 100 and 500 Å PLgel 5 μm columns from Polymer Laboratories. THF was used as an eluent with a flow rate 0.7 mL/min. The molecular weights were computed using a calibration curve constructed by polystyrene standards with a narrow molecular weight distribution. TGA analysis was carried out using a Perkin-Elmer Pyris 1 TGA system from 25 to 700 °C with a heating rate of 20 °C/min under a nitrogen atmosphere. All NMR experiments were performed on either a Bruker DPX300 or DRX500 NMR spectrometer. D_2O 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 (sodium 3-(trimethylsilyl)propionic-*2,2,3,3*-d_4 acid salt (TSP, 0 ppm)). 2D NMR techniques such as COSY and NOESY were used to assign each peak in **9** and **10**. The spin–lattice relaxation times (T_1) were obtained using the standard inversion recovery pulse sequence (PD–180°–τ–90°–AC), and a delay of 10 T_1 between acquisitions was employed.

Monomer 2. Acryloyl chloride (0.20 g, 2.0 mmol) was added to a solution of **1** (0.40 g, 1.1 mmol) and Et_3N (0.23 g, 2.3 mmol) in CH_2Cl_2 (6 mL) in an ice–water bath, and the mixture was stirred for 1 h at the same temperature and 10 h at room temperature. The resulting solution was washed with brine. The organic phase was dried with sodium sulfate, concentrated, and purified by column chromatography using EtOAc/*n*-hexane (5:1) as an eluent to provide **2** (0.38 g, 82%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.46 (s, $(CH_3)_3C$, 9 H), 1.52 (m, $NCH_2CH_2CH_2CH_2N$, 4 H), 1.66 (q, J = 6.7 Hz, $NCH_2CH_2CH_2N$, 2 H), 3.21 (m, 4 CH_2N, 8 H), 4.98 (br, NHCbz, 1 H), 5.10 (s, OCH_2Ph, 2 H), 5.63 (d, J = 10.1 Hz, $CH{=}CH_2$, 1 H), 6.15 (d, J = 16.7 Hz, $CH{=}CH_2$, 1 H), 6.30 (dd, J = 10.1 Hz, 16.7 Hz, $CH = CH_2$, 1 H), 6.98 (br, NH, 1 H), 7.35 (m, 5 aromatic *H* of Cbz, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.0 (CH_2), 27.7 (CH_2), 27.9 (CH_2), 28.8 ($C(CH_3)_3$), 36.0 (CH_2), 41.0 (CH_2), 43.7 (CH_2), 46.9 (CH_2), 66.9 (OCH_2Ph), 80.2 ($OC(CH_3)_3$), 126.1 (CH), 128.4 (CH), 128.9 (CH), 131.8 (CH_2), 137.0 (CH), 156.9 (C = O), 166.0 (C=O). MS (EI): *m*/*z* 433 [M^+]. HRMS (EI) calcd for $C_{23}H_{35}N_3O_5$: 433.2577. Found: 433.2579. 16.7.

Monomer 4. A solution of *N*-benzyloxycarbonyl-1,4-diaminobutane·HCl (3.0 g, 11 mmol), 3-vinylbenzaldehyde (1.3 g, 10 mmol), and Et_3N (2.0 g, 20 mmol) in CH_2Cl_2 (50 mL) was stirred for 20 h at room temperature. The resulting solution was filtrated, and the filtrate was concentrated to give a Schiff base product. $NaBH_4$ (0.48 g, 12 mmol) was slowly added to a solution of the Schiff base in MeOH (30 mL) and stirred for 12 h at room temperature. After the reaction mixture was concentrated, aqueous $NaHCO_3$ (50 mL) and CH_2Cl_2 (100 mL) were added. The organic phase was separated and concentrated to give N^1-3-vinylbenzyl-N^2-benzyloxycarbonyl-1,4-diaminobutane. Boc_2O (3.0 g, 14 mmol) was carefully added to a solution of the crude product in MeOH (50 mL) and then stirred for 12 h at room temperature. The resulting solution was concentrated and purified by column chromatography using EtOAc/*n*-hexane (4:1) as an eluent to afford **4** (3.3 g, 79%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.42 (s, $(CH_3)_3C$, 9 H), 1.69 (m, $NCH_2CH_2CH_2CH_2N$, 4 H), 3.18 (m, $NCH_2CH_2CH_2CH_2N$, 4 H), 4.39 (s, $ArCH_2N$, 2 H), 4.98 (br, NHCbz, 1 H), 5.02 (s, OCH_2Ph, 2 H), 5.26 (d, J = 10.9 Hz, $CH{=}CH_2$, 1 H), 5.76 (d, J = 17.6 Hz, $CH{=}CH_2$, 1 H), 6.74 (dd, J = 10.9 Hz, 17.6 Hz, $CH{=}CH_2$, 1 H), 7.11 (m, 1 aromatic *H* of Ar, 1 H), 7.24–7.35 (m, 3 aromatic *H* of Ar and 5 aromatic *H* of Cbz, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.7 (CH_2), 27.6 (CH_2), 28.8 ($C(CH_3)_3$), 41.1 (CH_2), 46.5 (CH_2), 50.4 (CH_2Ph), 66.9 (OCH_2Ph), 80.2 ($OC(CH_3)_3$), 114.4 (CH_2), 125.4 (CH), 127.6 (CH), 128.5 (CH), 128.9 (CH), 129.1 (CH), 137.1 (CH), 138.2 (CH), 139.2 (CH), 156.0 (C=O), 156.8 (C=O). MS (EI): *m*/*z* 438 [M^+]. HRMS (EI) calcd for $C_{26}H_{34}N_2O_4$: 438.2519. Found: 438.2523.

Polymers 5 and 8. Under an N_2 atmosphere, a round-bottom flask (10 mL) was charged with toluene (5 mL) and a small magnetic stir bar. Monomer **2** (0.43 g, 1.0 mmol) was added to make a solution, and the flask was placed in an oil bath at 65 °C. After the solution was bubbled for 0.5 h, AIBN in toluene (0.5 mL) was added. After 24 h, the flask was cooled to room temperature. Addition of *n*-hexane produced a precipitate, which was collected, washed with benzene/hexane, and dried under reduced pressure to give polymer **5** (0.37 g, 86%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.39 (br, 9 $(CH_3)_3C$, 9 H), 1.50 (br, $NCH_2CH_2CH_2CH_2N$, 4 H), 1.68 (br, $NCH_2CH_2CH_2N$, 2 H), 1.77 (br, CH_2 of polymer backbone, 2 H), 3.14 (br, 4 CH_2N, 8 H), 4.98 (br, NHCbz, 1 H), 5.10 (br, OCH_2Ph, 2 H), 7.29 (br, 5 aromatic *H* of Cbz, 5 H). Polymer **8** was synthesized from **4** (0.44 g, 1.0 mmol) using the same procedure (0.36 g, 82%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.40 (br, $(CH_3)_3C$, 9 H), 1.52 (br, $NCH_2CH_2CH_2CH_2N$, 4 H), 1.59 (br, CH_2 of polymer backbone, 2 H), 3.10 (br, $NCH_2CH_2CH_2CH_2N$, 4 H), 4.14 (br, $ArCH_2N$, 2 H), 5.04 (br, OCH_2Ph, 2 H), 6.32 (br, 1 aromatic *H* of Ar, 1 H), 6.90 (br, 3 aromatic *H* of Ar, 3 H), 7.27 (br, 5 aromatic *H* of Cbz, 5 H). The molecular weights of the polymers were estimated by GPC analysis (polystyrene standard, THF): polymer **5**: $M_n = 7.4 \times 10^3$, $M_w = 8.7 \times 10^3$; polymer **8**: $M_n = 9.8 \times 10^3$, $M_w = 1.4 \times 10^4$.

Polymers 6 and 9. A solution of side-chain polymer **5** (0.22 g, 0.50 mmol) in 30% HBr–AcOH (5 mL) was stirred for 10 h at room temperature. Ether (50 mL) was added to produce a precipitate which was filtered, washed with ether, and dried to give polymer **6** (0.17 g, 92%). ^1H NMR (500 MHz, D_2O): δ 1.64 (br, CH_2 of polymer backbone, 2 H), 1.85 (br, $NCH_2CH_2CH_2CH_2N$, 4 H), 2.00 (br, $NCH_2CH_2CH_2N$, 2 H), 3.12 (br, CH_2N, 2 H), 3.20 (br, 2 CH_2N, 4 H), 3.31 (br, 2 CH_2N, 4 H). Polymer **9** was synthesized from **8** (0.22 g, 0.50 mmol) using the same procedure (0.17 g, 94%). ^1H NMR (500 MHz, D_2O): δ 1.54 (br,CH_2 of polymer backbone, 2 H), 1.79 (br, $NCH_2CH_2CH_2CH_2N$, 4 H), 3.08 (br, $NCH_2CH_2CH_2CH_2N$, 4 H), 4.09 (br, $ArCH_2N$, 2 H), 6.79 (br, 1 aromatic *H* of Ar, 1 H), 7.12 (br, 3 aromatic *H* of Ar, 3 H).

Side-Chain Pseudopolyrotaxanes 7 and 10. CB[6] (0.26 g, 0.26 mmol) was added in small portions to a solution of water-soluble polymer **6** (0.070 g, 0.20 mmol) in H_2O (50 mL) and stirred for 10 h at room temperature. 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 precipitate, which was filtered, washed with ethanol, and dried to produce pseudopolyrotaxane **7** (0.21 g, 75%). ^1H NMR (500 MHz, D_2O): δ 0.60 (br, $NCH_2CH_2CH_2CH_2N$, 4 H), 1.42 (br, CH_2 of polymer backbone, 2 H), 2.20 (br, $NCH_2CH_2CH_2N$, 2 H), 2.35 (br, $NCH_2CH_2CH_2CH_2N$, 4 H), 3.40 (br, CH_2N, 2 H), 3.44 (br, CH_2N, 2 H), 4.43 (br, 12 CH of CB-[6], 12 H), 5.69 (br s, 12 *H* from 12 NCH_2 of CB[6], 12 H), 5.77 (br, 12 *H* from 12 NCH_2 of CB[6], 12 H). Pseudorotaxane **10** was synthesized from **9** (0.073 g, 0.20 mmol) using the same procedure (0.19 g, 70%). ^1H NMR (500 MHz, D_2O): δ 0.61 (br, $NCH_2CH_2CH_2CH_2N$, 4 H), 1.56 (br, CH_2 of polymer backbone, 2 H), 2.33 (br, $NCH_2CH_2CH_2CH_2N$, 4 H), 4.42 (br, $ArCH_2N$ and 12 CH of CB[6], 14 H), 5.69 (br s, 12 *H* from 12 NCH_2 of CB[6], 12 H), 5.78 (br, 12 *H* from 12 NCH_2 of CB[6], 12 H), 7.40 (br, 4 aromatic *H* of Ar, 4 H).

Dethreading and Rethreading Experiments. Pseudopolyrotaxane **10** (12 mg) was dissolved in D_2O (2 mL), and 500 μL of the solution was transferred to an NMR tube. After 5 μL of 0.20 M NaOD was added to the sample, the ^1H NMR spectrum was recorded. This procedure was repeated until the pH of the solution reached ~12. For the rethreading experiment, 5 μL of 0.48 M DCl was added to the sample of pH 12, and the procedure was repeated until the pH returned to ~5. All the pH values of the sample were estimated by pH paper. The ^1H NMR spectra were recorded on a DRX500 NMR spectrometer by using the same NMR parameters (a 30° pulse, 5 s repetition time, a spectral width of 10 000 Hz, and 64 scans), and the spectra were processed with exponential multiplication using a line broadening factor of 3 Hz. Baseline correction was made before signal integration. The degree of dethreading was estimated by comparing the integral values of the signal for the middle methylene protons (■, 0.6 ppm) of the diaminobutane unit in **10** before and after adding the base.

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