Pseudopolyrotaxanes Made to Order: Cucurbituril Threaded on Polyviologen

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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ABSTRACT: Pseudopolyrotaxane **2** is synthesized from polyviologen (**1**) and cucurbituril (CB[6]) in water by simple stirring at room temperature. The degree of threading (number of CB[6] beads per repeat unit) can be precisely controlled from 0.1 to 1.0 by controlling the amount of CB[6] added. In **2**, CB[6] beads are localized at the middle of the decamethylene units of the polymer through *hydrophobic and charge−dipole interactions,* to afford a well-defined microstructure in aqueous medium as found by NMR studies. The pseudopolyrotaxane has higher intrinsic viscosity, but a lower shape-dependent Huggins constant, than the parent polymer. This is attributed to a larger hydrodynamic radius and more expanded chain conformation of the pseudopolyrotaxane compared to those of the parent polymer. The decomposition temperature of **2** increases with increasing amount of CB[6] threaded on the polymer.

Introduction

Supramolecular chemistry[1] has ushered polymer chemistry into a new era. Polymers in which their components are linked through noncovalent bonds have received much attention in recent years not only because of their interesting structures but also because of their unusual properties different from those of conventional covalent polymers.[2] Such mechanically linked polymers include (pseudo)polyrotaxanes in which a number of cyclic units are thread onto a polymer main chain or side chains.[1−9]

Most (pseudo)polyrotaxanes synthesized so far contain cyclodextrins (CDs)[3,4] or crown ethers[5,6a−h] threaded on organic polymers. For example, Harada[3] and Wenz[4] reported main-chain (pseudo)polyrotaxnes containing CDs as cyclic units (or molecular "beads"). On the other hand, Gibson utilized crown ether-type macrocycles as cyclic units to synthesize main-chain (pseudo)polyrotaxnes.[5] Side-chain polyrotaxanes containing rotaxane units on polymer side chains have also been synthesized by Ritter[6f−h] and others[6b,d] using CDs or crown ether-type macrocycles as cyclic units.

However, these systems in general lack structural regularity as the molecular "bead" 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 ether-type macrocycles) toward the recognition sites in the polymers is not high enough to ensure complete threading. Furthermore, the bucket-shaped CDs generate many possible orientational isomers of the resulting polyrotaxanes. These results suggest that a molecular "bead" should have a symmetrical structure and high affinity toward the recognition sites to produce polyrotaxanes with highly ordered structures. These requirements for a molecular "bead" seem to be met with cucurbituril.

Cucurbituril (CB[6]) is a macrocycle comprising six glycoluril units with a cavity that is accessible through two identical carbonyl-fringed portals.[10] Besides the rigid and highly symmetric structure, CB[6] has high chemical and thermal stability. Moreover, the polar carbonyl groups at the portals and a 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 with protonated diaminobutane, diaminopentane, or diaminohexane with a formation constant greater than 10^5. It also forms stable complexes with alkanes having two bipyridinium terminals ($K = 10^2 − 10^4$).[11] The easy synthesis, highly symmetric structure, and ability to form very stable inclusion complexes with amines and others make CB[6] attractive as a building block (as a cyclic unit or a molecular "bead") for the construction of interlocked molecules, in particular rotaxanes and polyrotaxanes.

Recently we developed a novel approach to polyrotaxanes, which involves threading a CB[6] "bead" with a short "string" to form a stable pseudorotaxane,[7] followed by linking the pseudorotaxane with transition-metal ion as a "linker" to organize into a polyrotaxane. The metal-ion-directed self-assembly produces polyrotaxanes with high structural regularity in the solid state.[7b−e] However, attempts to study solution properties of the polyrotaxanes have been hampered by their extremely poor solubility in any solvents.

We also synthesized (pseudo)polyrotaxanes containing CB[6] threaded on organic polymers by interfacial polymerization of CB[6]/spermine pseudorotaxane with diacid chlorides such as terephthaloyl chloride. The IR, DSC, and TGA data supported the formation of (pseudo)-polyrotaxanes, but their poor solubility in common solvents hampered further characterization of the novel polymers.[12] Buschmann and co-workers also reported similar (pseudo)polyrotaxanes of polyamides and CB[6] using interfacial polymerization of adipoyl chloride and the complexes of CB[6]/1,6-diaminohexane (protonated).[13] Although the thermal behavior of the pseudopolyrotaxanes was studied, here again further characterization was hampered by their poor solubility.

Steinke[14a] reported a novel way to produce polyrotaxanes containing CB[6] utilizing 1,3-dipolar cycloaddition between azide and alkyne inside the cavity of CB[6]. Very recently, he also reported new main-chain pseudopolyrotaxanes by threading CB[6] onto poly-

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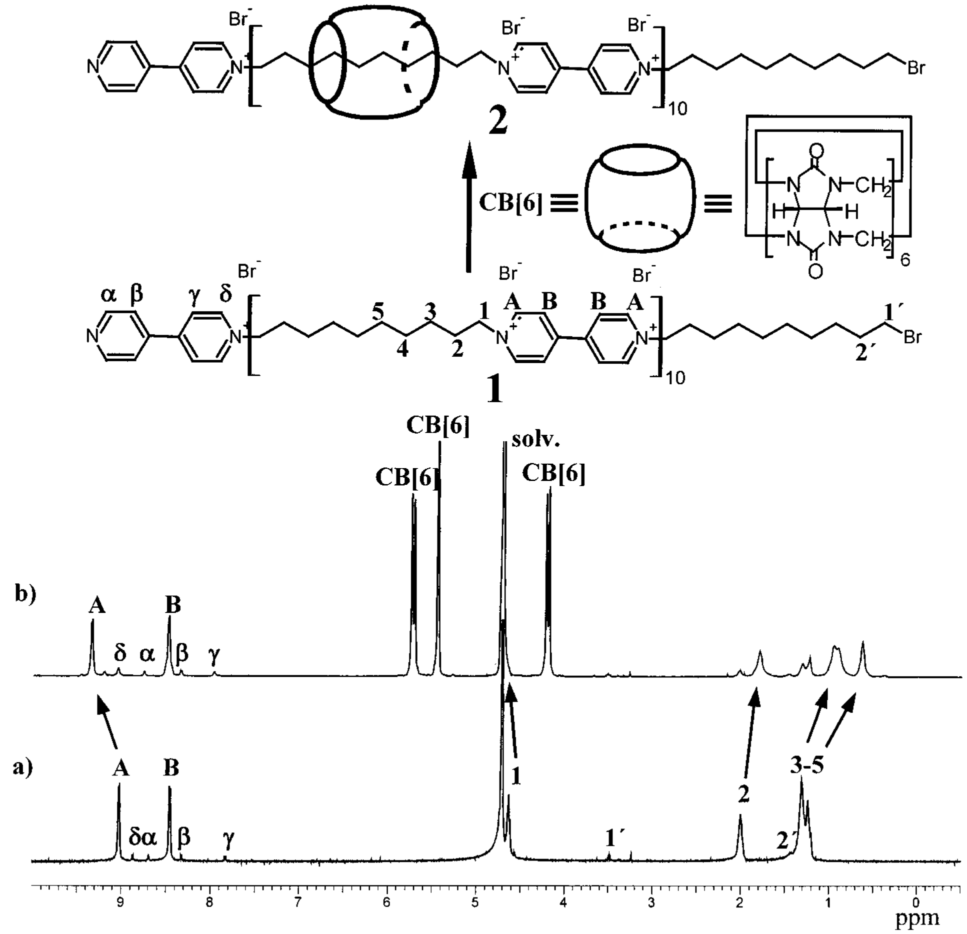


Figure 1. 500 MHz proton NMR spectra of (a) polymer (viologen) **1** and (b) polypseudorotaxane **2** in D_2O at room temperature.

(iminohexamethylene). Their good solubility in water allows better characterization of the novel (pseudo)-polyrotaxanes. In the latter, the degree of threading can vary from 0.1 to 0.5 where a CB[6] bead appears to be threaded on every other hexane-1,6-diamine repeating unit. However, the threading process is slow, requiring high temperatures and long reaction times (~400 h at 90 °C), which has been attributed mainly to slow "hopping" of the bead along the polymer chain due to the high binding affinity between the diaminohexane motif and CB[6].[14b]

We now synthesized a novel water-soluble main-chain pseudopolyrotaxane containing CB[6] threaded onto a polyviologen polymer where approximately 10 bipyridinium units are linked by decamethylene units in between. One of the interesting properties of the pseudopolyrotaxane is that the degree of threading (the number of CB[6] beads per repeat unit) can be precisely controlled between 0.1 and 1.0. Furthermore, the threading is completed within 10 min at room temperature, and the resulting pseudopolyrotaxane is stable so that no appreciable dethreading is observed. Here we report the synthesis, characterization, and properties of the novel pseudopolyrotaxane.

Results and Discussion

Synthesis and Characterization of Polyviologen (1) and Pseudopolyrotaxane (2). The polyviologen **1** was synthesized by the reaction of 4,4′-bipyridine and dibromodecane in methanol/*N*-methylformamide and purified by dialysis in water.[15] The polymer has been characterized by ^1H NMR spectroscopy (Figure 1a) and elemental analysis. The internal 4,4′-bipyridine units of **1** show two doublet signals at 8.46 (A) and 9.02 (B) ppm, whereas the terminal 4,4′-bipyridine unit displays four different signals ($\alpha-\delta$) between 7.7 and 8.9 ppm. Likewise, the terminal decamethylene protons (particularly, the ones at the end such as 1′ and 2′) exhibit chemical shifts markedly different from those for the internal decamethylene protons (1−5) as shown in Figure 1. Based on the integral ratio of the terminal bipyridyl and internal bipyridyl signals, the average degree of polymerization of **1** is estimated to be ~10, which corresponds to an average molecular weight of ~5000.

The synthesis of pseudopolyrotaxane **2** is achieved simply by mixing **1** and slightly excess CB[6] (~1.1 equiv per repeating unit of **1**) in water and stirring the mixture at room temperature. Although CB[6] itself is sparingly soluble in water, it slowly dissolves into the solution as the threading proceeds. The threading is essentially completed within 10 min at room temperature. It is in sharp contrast to the pseudopolyrotaxanes containing CB[6] threaded on poly(iminohexamethylene) which require elevated temperatures and much longer reaction time (~400 h at 90 °C) for complete threading. ^1H NMR spectroscopy (1D and 2D COSY and NOESY) provides direct evidence for the formation of pseudopolyrotaxane **2**. Besides the appearance of new CB[6] signals, significant changes in chemical shift for the polymer **1** are observed in the ^1H NMR spectrum of **2** (Figure 1). For example, the signal for internal bipyridyl proton A is significantly shifted downfield whereas that for internal bipyridyl proton B remains

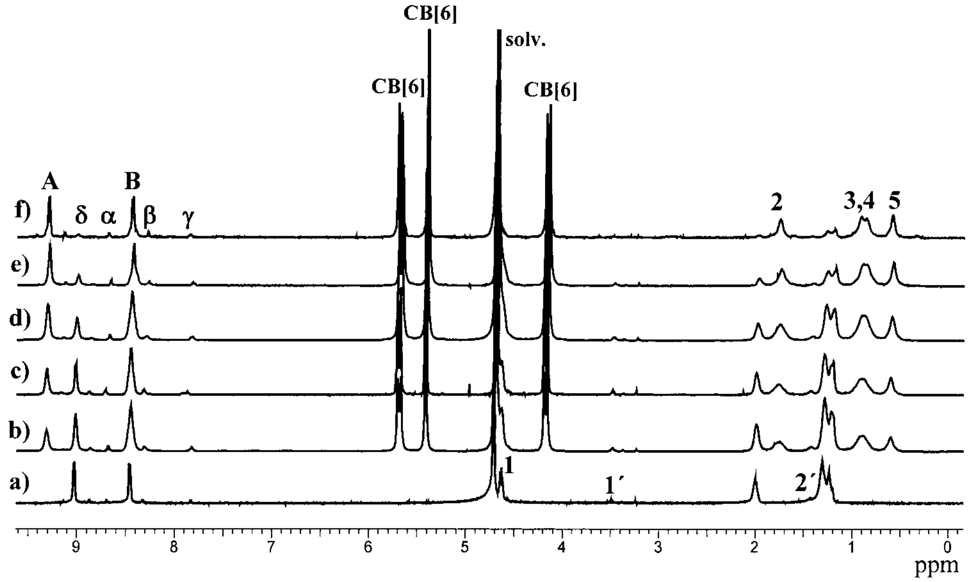


Figure 2. 500 MHz proton NMR spectra of solutions containing different equivalents of CB[6] to polymer **1**: (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, and (f) 1.0 equiv at room temperature.

unchanged. At the same time, relatively large upfield shifts of the signals for internal methylene protons 2–5 are also observed. On the other hand, the signal for proton 1 is slightly shifted downfield to overlap with that of the solvent. The NMR data support that the CB[6] beads threaded in **2** are localized on the internal *decamethylene* units, not on the internal *bipyridyl* units as illustrated in Figure 1. A similar observation has been reported for the pseudorotaxanes formed between CB[6] and 4,4′-bipyridine derivatives in which two 4,4′-bipyridine units are connected by five, six, and seven methylene units.[11] The driving force for the threading appears to be the hydrophobic interaction between decamethylene unit and the interior of CB[6] cavity and the charge–dipole interaction[11] between bipyridinium unit and the CB[6] portal oxygen atoms. The downfield shifted signals for protons 1 and A (see Figure 1) upon threading suggest that the positively charged nitrogen atom of the bipyridinium unit lies just outside the CB[6] portal, which allows it to interact with the carbonyl groups through charge–dipole interaction. Because of the multiple noncovalent interactions, the resulting pseudopolyrotaxane **2** is quite stable in solution and solid state; no appreciable dethreading is observed after long standing in solution.

Control of the Degree of Threading. The degree of threading (the number of CB[6] threaded per repeating unit of polymer backbone) of pseudopolyrotaxane **2** can be precisely controlled. Figure 2 shows a series of ^{1}H NMR spectra of the pseudopolyrotaxane taken with different molar ratios of **1** to CB[6]. As the amount of CB[6] added increases from 0.2 equiv (b) to 1.0 equiv (f), the intensity of the signals for CB[6] threaded increases, and at the same time, a new set of signals for the polymer backbone appear with growing intensities. Although the time required for complete threading increases in general with increasing amount of CB[6] to be threaded, the threading is completed essentially within 10 min in all cases. However, the inhomogeneous nature of the initial mixtures due to poor solubility of CB[6] discouraged us from studying kinetics of the threading process. Once again, these NMR data are consistent with the fact that the CB[6] beads threaded are localized on the decamethylene units of the polymer backbone in all cases. Since two sets of signals for the decamethylene units are observed when less than 1.0 equiv of CB[6] is added, the "hopping" of CB[6] from one decamethylene site to the neighboring site is slow on NMR time scale. Within a decamthylene unit, however, the CB[6] bead shuttles back and forth rapidly on the NMR time scale so that the chemical shifts of the methylene protons appear as a time-average value.

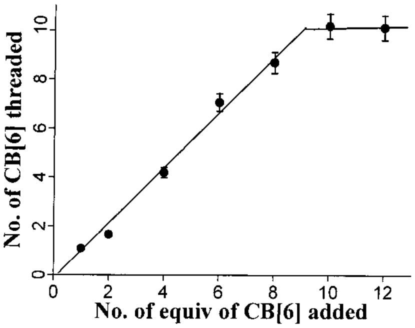


Figure 3. Relationship of the number of CB[6] threaded vs the degree of threading (molar ratios of polymer **1** to CB[6] = 1:0, 1:1, 1:2, 1:4, 1:6, 1:8, 1:10, and 1:12).

The number of CB[6] beads threaded in **2** is determined by comparing the intensity of the CB[6] methylene signal (5.76 ppm) and that of the terminal methylene signal of the polymer (1′; 3.47 ppm in Figures 1 and 2). Figure 3 shows that the number of CB[6] beads threaded in **2** linearly increases with the increasing amount of CB[6] added and levels off at 10 where all the internal decamethylene units are fully occupied by CB[6]. The linear relationship indicates that the CB[6] beads are tightly bound to **1**, which is consistent with the fact that no appreciable dethreading is observed on long standing in solution as described above. The degree of threading of pseudopolyrotaxane **2** can thus be precisely controlled between 0.1 and 1.0 simply by adding a desired amount of CB[6] into the solution of **1**.

Spin–Lattice Relaxation Time and Hydrodynamic Radius Measurements. The formation of pseudopolyrotaxane **2** is also manifested in changes in spin–lattice relaxation time (T_1). T_1 values of the polymer backbone decrease upon threading of CB[6]. For

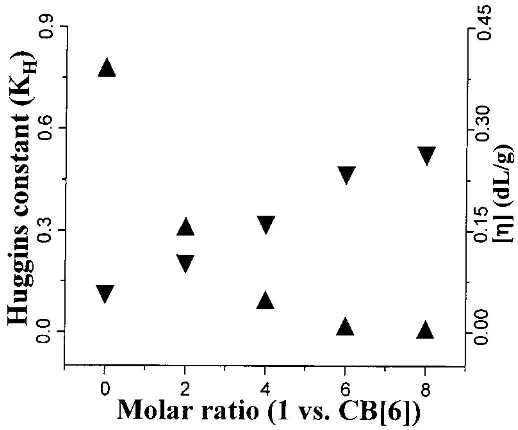


Figure 4. Relationship of the Huggins constant (K_H, ▲) and intrinsic viscosities ([η], ▼) vs the molar ratio for polymer 1 and CB[6]: 1:0, 1:2, 1:4, 1:6, and 1:8.

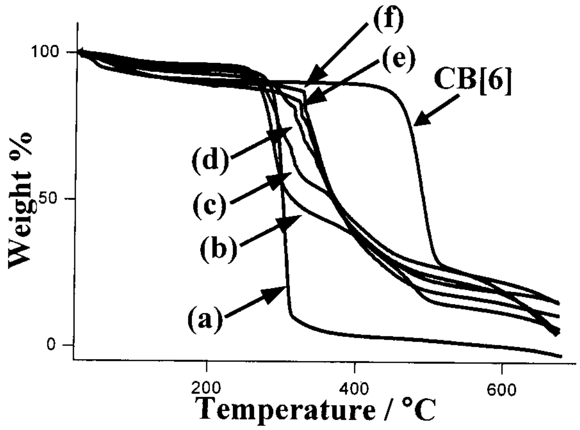


Figure 5. TGA curves of polymer **1** (a) and pseudorotaxane **2** with different degree of threading: (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, and (f) 1.0.

example, at 25 °C, T_1 values of the protons 3, 4, and 5, which are located inside the cavity of CB[6] upon threading, are 0.56, 0.56, 0.59 s for **1** and 0.51, 0.51, 0.53 s for **2**, respectively. The T_1 values increase with increasing temperature: at 40 °C, for example, T_1 values of the protons 3, 4, and 5 are 0.72, 0.72, 0.77 s for **1** and 0.53, 0.55, 0.56 s for **2**, respectively. The increasing T_1 values with increasing temperature suggest that the correlation times (τ) are in a liquidlike region of the $T_1-\tau$ curve, where a shorter T_1 corresponds to higher rigidity.[16] Therefore, the shorter T_1 values for **2** compared with those of **1** indicate that the aliphatic chain of the polymer backbone becomes more rigid (or displays restricted motion) upon threading of CB[6].[17]

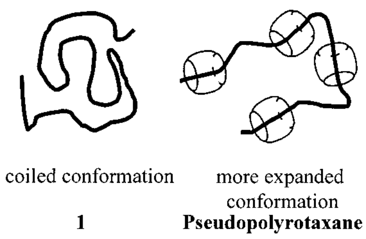
The hydrodynamic radii of **1** and pseudopolyrotaxane **2** were measured in a dilute solution (0.6 mM in D_2O) by diffusion NMR spectroscopy. The overall size of the polymer increases from 56 ± 1 to 62 ± 1 Å upon full threading of CB[6].

Viscosity. To understand the effects of threading on polymeric chain conformation, the intrinsic viscosities of **1** and pseudopolyrotaxane **2** with different degree of threading were measured (in H_2O, at 30 °C) (Figure 4). The intrinsic viscosities [η] and shape-dependent factors (Huggins constant K_H) can be obtained using Huggins plots according to the equation

$$\eta_{sp}/C = [\eta] + K_H[\eta]^2C$$

where η_{sp}/C is the reduced viscosity, K_H the Huggins constant, and C the polymer concentration. The Huggins constant is related to the molecular weight distribution or the branching of the macromolecule.[5−a,b,f,18] Interestingly, the Huggins constants for the pseudopolyrotaxanes are smaller than that of **1**, although intrinsic viscosities of the polypseudorotaxanes are higher (Figure 4). The unusual behavior appears to be caused by conformational changes of the polymer backbone upon threading, as illustrated in Scheme 1. Compared to the free polymer, the pseudopolyrotaxanes adopt a more expanded form because of the bulkiness of the threaded CB[6] beads, giving rise to a greater hydrodynamic volume and higher intrinsic viscosity.[19] The polymer **1** is a random coil that becomes more and more expanded upon dilution, resulting in a higher Huggins constant. However, the polymer backbone in **2** is already expanded even at higher concentration, and thus the dependence of chain conformation on concentration is less, resulting in a smaller Huggins constant. A similar behavior has been observed in other polyrotaxanes.[5i]

Scheme 1



Thermal Properties. Pseudopolyrotaxane **2** shows higher thermal stability than the parent polymer (Figure 5). The parent polymer **1** is a crystalline polymer which decomposes at 300 °C upon heating in DSC traces. TGA measurements show that **1** loses most of its weight (85%) at 305 °C. The polypseudorotaxanes **2** (in Figure 5b−f) exhibit small initial weight loss corresponding to hydration, followed by large weight loss corresponding to decomposition of the polymer and CB[6]. The decomposition temperature of the pseudopolyrotaxanes increases with increasing amount of CB[6] threaded and approaches that of pure CB[6]. This thermal behavior suggests that the threading of CB[6] increases the polymer stability at least in part by protecting the aliphatic chain with the rigid shell.

UV−vis Spectroscopy. Figure 6 shows UV−vis spectra (taken in water) of pseudopolyrotaxanes **2** with different degree of threading. The parent polymer **1** exhibits a weak absorption band centered around 262 nm, which is presumably attributed to the bipyridinium chromophore. Upon threading of CB[6], the intensity of the band increases with increasing amount of CB[6] threaded. The peak attains saturation when the threading is complete upon addition of 10 equiv of CB[6] to the polymer solution. Obviously, the bipyridinium chromophore is indirectly affected by the threading of CB[6] on the decamethylene units in the polymer, but the nature of the UV−vis spectral changes upon threading remains to be established.

Conclusions

A novel water-soluble pseudopolyrotaxane containing CB[6] threaded on a polyviologen polymer in which approximately 10 bipyridinium units are linked by decamethylene units in between. The degree of threading can be precisely controlled between 0.1 and 1.0. In

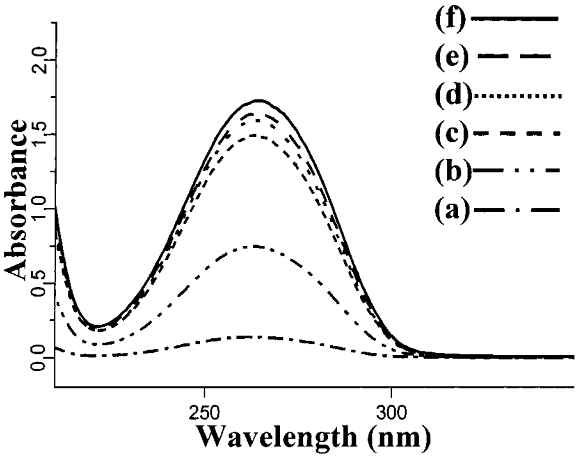


Figure 6. UV−vis spectra (taken in water at 25 °C) of polymer **1** (a) and pseudorotaxane **2** with different degree of threading: (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, and (f) 1.0.

the pseudopolyrotaxane, the CB[6] beads are localized at decamethylene sites. The polymer backbone of the pseudopolyrotaxane has much shorter T_1 than its free counterpart, indicating the restricted motion of the polymer backbone. The pseudopolyrotaxane has higher intrinsic viscosity but a smaller shape-dependent constant than the parent polymer, which is consistent with the expanded structure of the pseudopolyrotaxane. The decomposition temperature of the pseudopolyrotaxanes increases with the increasing amount of CB[6] threaded.

Experimental Section

Chemical Reagents and Measurements. All chemicals were of reagent grade and used as received from Aldrich unless otherwise specified. All NMR experiments have been performed on a Bruker DRX500 NMR spectrometer operating at the proton Larmor frequency of 500.23 MHz. D_2O was used for field-frequency lock, and the observed ^1H chemical shifts are reported in parts per million (ppm) relative to an internal standard (sodium 3-(tri-methylsilyl)propionic-*2,2,3,3-d*$_4$ acid salt (TSP, 0 ppm)).

$^1H-^1H$ correlation spectroscopy (COSY) and two-dimensional nuclear Overhauser effect spectroscopy (NOESY) were used to assign the proton resonances of polyviologen. COSY spectra were recorded using a recycle delay of 1.5 s at 295 K. NOESY experiments were performed using the time-proportional-phase-increment method with a mixing time of 0.3 s and a recycle delay of 2 s.

The spin−lattice relaxation times (T_1) were obtained using the standard inversion recovery pulse sequence, and a delay of $5T_1$ between acquisitions was employed.

The diffusion coefficient measurements were carried out using a 5 mm Bruker QNP probe with an actively shielded *z* gradient coil. Diffusion coefficients were extracted from a series of ^1H NMR spectra measured by the bipolar pulse longitudinal encode−decode (BPPLED) pulse sequence[20] as a function of gradient amplitude. In each experiment, the gradient duration time was 2.0 or 2.5 ms and the amplitudes of the gradient pulses ranged from 1 to 40 G/cm. The diffusion coefficients were calculated from the data using diffusion-ordered spectroscopy (DOSY) as described previously.[21]

UV spectra were recorded with a diode array spectrophotometer (model 5824, Hewlettt-Packard, Palo Alto, CA). The TGA were carried out using a Perkin-Elmer Pyris 1 TGA system at a rate of 20 °C/min for heating from 25 to 700 °C. The intrinsic viscosities were measured with an Ubbelohde viscometer (type 50103, capillary 0a, Schott, Mainz, Germany) in H_2O at 30 °C. On the basis of the measured intrinsic viscosity at different concentrations (3.3, 1.7, 1.1, and 0.8 mg/mL), the plot of η_{sp}/C vs C afforded the intrinsic viscosities and shape-dependent factors (Huggins constant) for the polymer **1** and pseudopolyrotaxane **2** via the Huggins equation.

Preparation of Poly(*N*-4,4′-bipyridinium-*N*′-decamethylene dibromide) (1).[15] 4,4′-Bipyridine (20.00 g, 0.128 mol) and 1,10-dibromodecane (38.43 g, 0.128 mol) were dissolved 1:1 mixture of methanol/*N*-methylformamide (128 mL) and stirred for 10 days at 50 °C, until a green precipitate was obtained. The mixture became clear after adding a small amount of water. The polymer was precipitated by adding acetone (3 L), filtered, and washed with acetone. For the purification of the product, the product was dissolved in water and dialyzed (regenerated cellulose membrane, Spectra/Por MWCO 3500, Spectrum Laboratories Inc., The Netherlands) against water for 2 days. The retentate was evaporated, and the residue was dried in a vacuum. ^1H NMR (500 MHz, D_2O, δ): 1.25−1.32 (m, 132H), 1.44 (m, 2H), 2.00 (m, 42H), 3.47 (m, 2H), 4.61 (m, 2H), 4.64 (m, 40H), 7.84 (d, J = 5.6 Hz, 2H), 8.33 (d, J = 5.9 Hz, 2H), 8.46 (d, J = 6.1 Hz, 40H), 8.70 (d, J = 4.7 Hz, 2H), 8.89 (d, J = 6.3 Hz, 2H), 9.02 (d, J = 5.9 Hz, 40H). IR (KBr, cm^{-1}): 3033 (m), 2925 (s), 2853 (m), 1558 (m), 1507 (m), 1447 (m), 1352 (w), 1224 (w), 1175 (m), 836 (m), 719 (w). Anal. Calcd for $C_{220}H_{308}Br_{22}N_{22}O_{16}\cdot 16H_2O$: C, 49.79; H, 6.46; N, 5.81. Found: C, 49.57; H, 6.84; N, 5.84. The average degree of polymerization was estimated to be 10 by the end-group analysis using ^1H NMR spectroscopy.

Preparation of Pseudopolyrotaxane. Pseudopolyrotaxane **2** was prepared by stirring a mixture of **1** (50 mg, 0.01 mmol) and CB[6] (118 mg, 0.12 mmol) in water at room temperature. The excess CB[6] was removed by filtration, and the filtrate was evaporated to produce **2**. ^1H NMR (500 MHz, D_2O, δ): 0.63 (m, 40H), 0.91−0.96 (m, 80H), 1.23−1.31 (m, 12H), 1.44 (m, 2H), 1.81 (m, 40H), 2.03 (m, 2H), 3.47 (m, 2H), 4.23 (d, J = 15.4, 12H), 4.78 (m, 42H), 5.45 (s, 12H), 5.76 (d, J = 15.4, 12H), 7.97 (d, J = 4.3, 2H), 8.35 (d, J = 5.6, 2H), 8.49 (d, J = 5.1, 40H), 8.75 (d, J = 6.1, 2H), 9.04 (d, J = 4.2, 2H), 9.34 (d, J = 5.6, 40H). Anal. Calcd for $C_{580}H_{668}Br_{22}N_{262}O_{120}\cdot 90H_2O$: C, 42.40; H, 5.08; N, 22.34. Found: C, 41.37; H, 4.97 N, 22.41. Pseudopolyrotaxanes with different degree of threading (<1.0) were prepared by the same procedure as described above, except that proper amounts of CB[6] were added to the solution.

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