Main Chain-type Polyrotaxane with Controlled Ratio of Rotaxanated Units

Toshikazu Takata,* Yasuhiro Kohsaka, and Gen-ichi Konishi
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552

(Received November 21, 2006; CL-061380; E-mail: takata.t.ab@m.titech.ac.jp)

A novel main-chain type polyrotaxane having a rotaxanated crown ether backbone was synthesized by the rotaxanation of poly(crown ether). The rotaxanated ratio of the main chain increased up to ca. 100% with increase of amount of *sec*-ammonium axle used.

Polyrotaxane,[1] a novel class of polymer containing mechanical linkage consisting of wheel and axle components, is expected to display unique properties such as mechanical and rheological ones. A variety of main-chain type polyrotaxanes with the polymer axles as the main chains have been reported so far.[2] Characteristic property has been actually found with cyclodextrin-based polyrotaxane networks by Ito et al.[3] Meanwhile, little is known about polyrotaxanes having their wheels in the main chains. Gibson et al. prepared this type of pseudopolyrotaxane and polyrotaxane network,[4] whereas we reported novel type of polyrotaxane and polyrotaxane network and its recyclability.[5] There are two ways of synthesizing this kind of main chain-type polyrotaxane: one goes through initial rotaxanation followed by its polymerization (route A) and the other undergoes initial polymerization of wheel followed by rotaxanation of the resulting polymer (route B), as shown in Figure 1. The authors have studied the synthesis of novel polyrotaxane with its wheels in the main chain along the polymerization–rotaxanation protocol. This paper describes the synthesis via route B and characterization of a main chain-type polyrotaxane with controlled rotaxanation ratio.

Poly(crown ether) (**1**) (M_w 4000, M_n 2400, and M_w/M_n 1.67, by GPC) was prepared by the polycondensation of bis(hydroxymethyl) derivative of dibenzo-24-crown-8-ether (DB24C8) with adipoyl chloride.[6] **1** was well soluble in organic solvents such as chloroform and THF, but insoluble in methanol, acetonitrile, and water. The axle **2**, an ammonium salt having hydroxy group and bulky stopper in its both termini, was synthesized according to our previous report.[7]

The pseudorotaxanation behavior of **1** (Scheme 1) with **2** was evaluated by the ^{1}H NMR spectra. [2]Rotaxane (**4**) having DB24C8 and an axle derived from **2** was synthesized as a model compound. The ^{1}H NMR spectra of **1**, **2**, and **4** are shown in

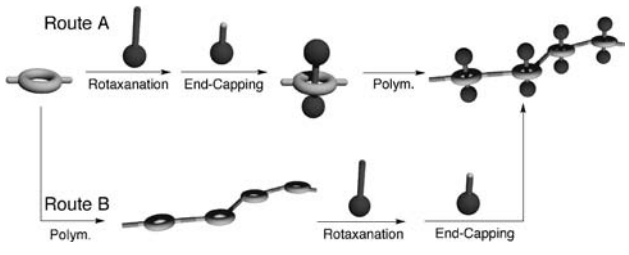
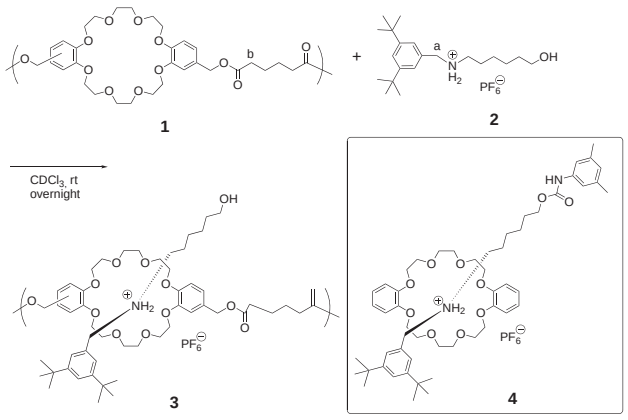


Figure 1. Synthetic strategy of polyrotaxane.



Scheme 1.

Figure 2. Clear downfield shift of the benzyl proton signal **a** of the axle **2** from 4.18 to 4.60 ppm was observed in the spectrum of **4**. This signal shift is known as the definite evidence for the pseudorotaxane or rotaxane formation.[8] Thus, the above NMR results suggest that the in situ observation of the formation of pseudopolyrotaxane between **1** and **2** can be monitored by ^{1}H NMR.

The pseudorotaxanation between **1** and **2** was studied under several conditions.[9] A similar downfield shift was observed in any case when the complexation proceeded (Figure 2). Therefore, the rotaxanation ratio of polypseudorotaxane **3** was deter-

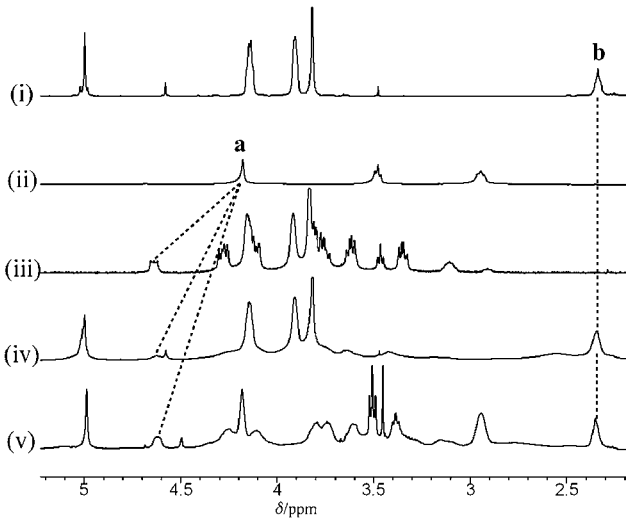
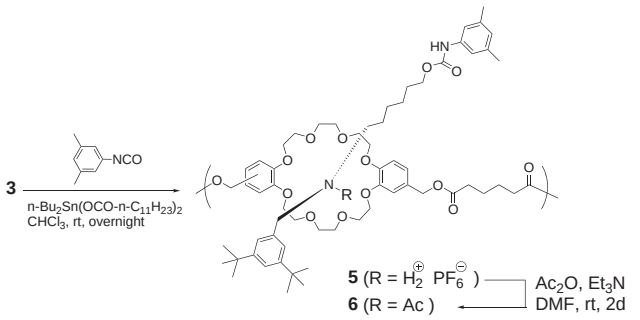


Figure 2. Partial ^{1}H NMR spectra of (i) wheel **1**, (ii) axle **2**, (iii) model [2]rotaxane **4**, (iv) polypseudorotaxane **3** with 20% rotaxanation ratio, and (v) polypseudorotaxane **3** with complete rotaxanation ratio (400 MHz, $CDCl_3$, 25 °C). For signals **a** and **b**, see Scheme 1.

Copyright © 2007 The Chemical Society of Japan



Scheme 2.

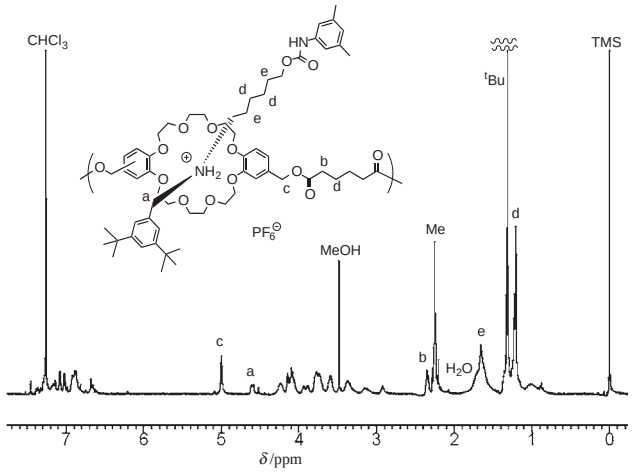


Figure 3. ^{1}H NMR spectrum of polyrotaxane **5** (400 MHz, $CDCl_3$, 298 K).

mined from the integral ratio of signals **b** and **a**. When 0.2 equiv. of **2** to **1** was added, the rotaxanation ratio reached about 20% (Figure 2 (iv)). Meanwhile, the complete rotaxanation was achieved when 2.0 equiv. of **2** to **1** was used (Figure 2 (v)). Thus, the rotaxanation ratio can be controlled with the amount of **2** used.

The conversion of **3** to polyrotaxane **5** was carried out according to the urethane end-capping protocol.[10] Polypseudorotaxane **3** with complete pseudorotaxanation reacted with 3,5-dimethylphenyl isocyanate in the presence of a Lewis acid to give **5** in 84% isolated yield (Scheme 2).[11] By the ^{1}H NMR analysis of **5** (Figure 3), it was found that the end-capping reaction completely occurred, and there was no signal for free crown ether unit. In addition, **5** was *N*-acetylated with acetic anhydride in the presence of triethylamine in order to evaluate the molecular weight of **5** (Scheme 2).[12] *N*-Acetylated polyrotaxane **6** was characterized by ^{1}H NMR, IR, and MS spectra which were well consistent with the rotaxanated structure of **6**. For example, both disappearance of PF_6 anion and appearance of amide group in the IR spectrum were observed. Molecular weight of **6** was determined by GPC as M_w 6100 and M_n 4400 (M_w/M_n 1.40). Thus, the results obtained here support not only the complete rotaxanation of **1** but also the complete end-capping of **3**.

In summary, polypseudrotaxane **3** with controlled rotaxanation ratio was obtained and the urethane end-capping of **3** quantitatively proceeded to afford the corresponding polyrotaxane **5** with complete rotaxanation ratio. *N*-Acylation of **5** yielded the corresponding neutral polyrotaxane **6** that made possible the molecular weight measurement by GPC.

References and Notes

1 a) G. Wenz, B. Han, A. Müller, *Chem. Rev.* **2006**, *106*, 782. b) T. Takata, *Polym. J.* **2006**, *38*, 1. c) F. Huang, H. W. Gibson, *Prog. Polym. Sci.* **2005**, *30*, 982. d) *Molecular Catenanes, Rotaxanes and Knots*, ed. by J. P. Sauvage, C. Dietrich-Buchecker, Willy-VCH, Weinheim, **1999**, p. 277. e) F. M. Raymo, J. F. Stoddart, *Supramolecular Polymers*, ed. by A. Cifferi, Marcel Dekker, **2000**, p. 323. f) F. Huang, H. W. Gibson, *Prog. Polym. Sci.* **2005**, *30*, 982. g) T. Takata, N. Kihara, Y. Furusho, *Adv. Polym. Sci.* **2004**, *171*, 1.

2 a) A. Harada, J. Li, M. Kamachi, *J. Am. Chem. Soc.* **1994**, *116*, 3192. b) K. Nagapudi, J. Hunt, C. Shepherd, J. Baker, H. W. Beckham, *Macromol. Chem. Phys.* **1999**, *200*, 2541. c) C. Gong, Q. Ji, C. Subramanimam, H. W. Gibson, *Macromolecules* **1998**, *31*, 1814. d) H. W. Gibson, P. T. Engen, S. Lee, *Polymer* **1999**, *40*, 1823. e) N. Kihara, K. Hinoue, T. Takata, *Macromolecules* **2005**, *38*, 223.

3 a) Y. Okumura, K. Ito, *Adv. Mater.* **2001**, *13*, 485. b) C. Zhao, Y. Domon, Y. Okumura, S. Okabe, M. Shibayama, K. Ito, *J. Phys.: Condens. Matter* **2005**, *17*, S2841.

4 a) C. Gong, H. W. Gibson, *Macromol. Chem. Phys.* **1998**, *199*, 1801. b) C. Gong, H. W. Gibson, *J. Am. Chem. Soc.* **1997**, *119*, 8585.

5 a) T. Oku, Y. Furusho, T. Takata, *J. Polym. Sci., Polym. Chem.* **2003**, *41*, 119. b) T. Oku, Y. Furusho, T. Takata, *Angew. Chem., Int. Ed.* **2004**, *43*, 966.

6 To a solution of bis(hydroxymethyl) derivative of dibenzo-24-crown-8-ether (508 mg, 1.00 mmol) dissolved in dry THF (1.0 mL) were added pyridine (178 μL, 2.20 mmol) and adipoyl chloride (183 mg, 1.00 mmol) in dry THF (1.0 mL). The mixture was heated at 40 °C for 3 h. The resulting mixture was reprecipitated into diethyl ether. The precipitates collected were dried in vacuo to give poly(crown ether) **1** (379 mg, 61%) was obtained. IR: 1730 (C=O) cm^{-1}. T_g and T_{d10} were 11.3 and 339 °C, respectively.

7 Y. Tachibana, N. Kihara, T. Takata, *J. Am. Chem. Soc.* **2004**, *126*, 3438.

8 a) H. Kawasaki, N. Kihara, T. Takata, *Chem. Lett.* **1999**, 1015. b) Y. Furusho, T. Oku, T. Hasegawa, A. Tsuboi, N. Kihara, T. Takata, *Chem.—Eur. J.* **2003**, *9*, 2895. c) Y. Tachibana, H. Kawasaki, N. Kihara, T. Takata, *J. Org. Chem.* **2006**, *71*, 5093.

9 A typical procedure. A $CDCl_3$ solution of an equimolar (60.5 mM) mixture of the wheel **1** and the axle **2** was allowed to stand for 3 d at 25 °C to afford polypseudorotaxane **4**.

10 Y. Furusho, H. Sasabe, D. Natsui, K. Murakawa, T. Takata, T. Harada, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 179.

11 A solution of a mixture of **1** (100 mg, 162 μmol) and **2** (152 mg, 323 μmol) in $CDCl_3$ (2 mL) was stirred overnight at room temperature. To the solution were added 3,5-dimethylphenyl isocyanate (28.5 mg, 194 μmol) and di *n*-butyltin dilaurate (12.3 μL, 19.4 μmol). After the mixture was stirred at room temperature overnight, 10 mL of methanol was added to precipitate polyrotaxane **5**. The precipitates were collected by filtration and dried in vacuo to give **5** (102 mg, 84%). IR: 3396 (N–H), 1730 (C=O), 844 (PF_6), 558 (PF_6) cm^{-1}.

12 To a solution of **5** (124 mg, 0.100 mmol) dissolved in DMF (1.5 mL) were added triethylamine (69.5 μL, 0.500 mmol) and acetic anhydride (33.0 μL, 0.300 mmol). The mixture was stirred for 2 d at room temperature. After addition of 3 M HCl, the resulting mixture was extracted with chloroform three times. The collected extract was dried over anhydrous $MgSO_4$, filtered. The concentrated filtrate was purified to yield **6** (53.3 mg, 55%). IR: 1635 (C=O amide), 844 (PF_6), 558 (PF_6) cm^{-1}.

Published on the web (Advance View) January 18, 2007; doi:10.1246/cl.2007.292