Polyslipping: A New Approach to Polyrotaxane-like Assemblies

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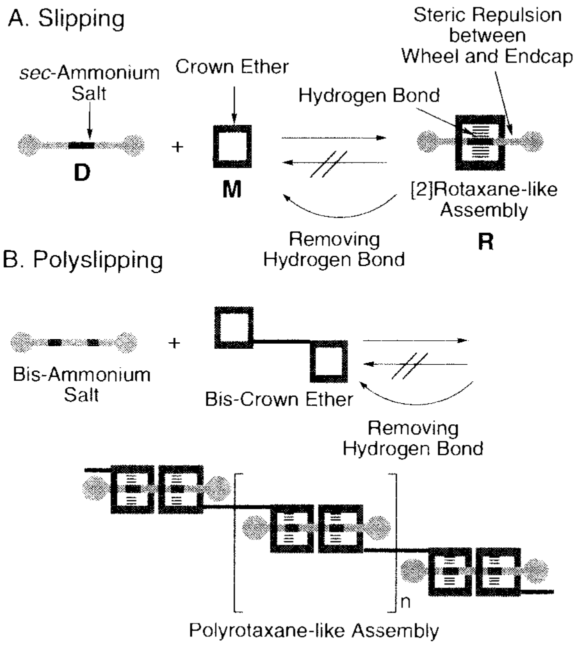
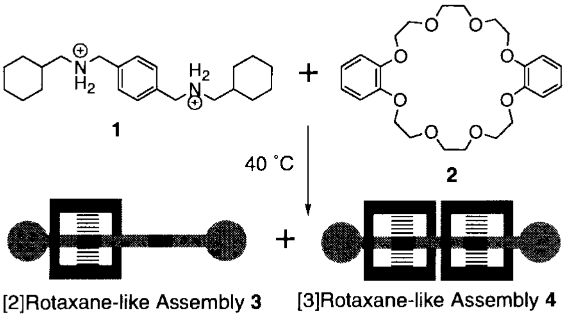
"Polyslipping", that is, multiple slipping of dumbbell components into macrocyclic ones having the appropriate size complementarity, of bis-ammonium salt **1** and bis-crown ether **5** in acetone or acetonitrile afforded polyrotaxane-like assembly **6**, which quantitatively reverted to the monomers **1** and **5** by dissolving in DMSO.

Rotaxanes are compounds comprised of macrocyclic and dumbbell components.[1] A slipping method is a way to prepare rotaxanes under thermodynamic conditions, which relies on the size complementarity between the endcaps and macrocycles (Scheme 1).[2] Heating a solution of a macrocycle **M** and a dumbbell **D** to an elevated temperature where the energy barriers of slipping-on and slipping-off processes are overcome, an equilibrium between the newly formed rotaxane-like assembly **R** and the free components **M** and **D** is achieved. On cooling the solution down, the energy required for both the slipping-on and slipping-off processes cannot be overcome, thereby making **R** kinetically stable.[3] We propose herein "polyslipping", a new protocol that is an extension of the slipping method to the synthesis of polyrotaxane-like assemblies. In this paper, we report the synthesis of polyrotaxane-like assemblies taking advantage of the size complementarity between 24-crown-8 ether and cyclohexyl group.[2a,4]



Scheme 1. Schematic illustration of the slipping and polyslipping approach.

Prior to polyslipping, double slipping was examined as a model reaction. A mixture of bis-secondary ammonium salt **1**[5] (6 μmol) and dibenzo-24-crown-8 **2** (12 μmol) in acetone-d_6 (0.6 mL) was heated at 40 °C in an NMR tube, and the reaction was monitored by ^{1}H NMR. Two new sets of signals appeared in the ^{1}H NMR spectrum, which were assigned to those of [2]rotaxane-like assembly **3** and [3]rotaxane-like assembly **4**. The system reached equilibrium after 70 days, where the yields of **3** and **4** were calculated to be 45% and 30%, respectively, from the ^{1}H NMR spectrum. The assemblies **3** and **4** were isolated with preparative GPC from the mixture in 41% and 32% yields, respectively, as white solids.[6] Use of acetonitrile-d_3 as a solvent resulted in a decrease in reaction rate. However, the equilibrium yields, after 100 days, were higher than those obtained in acetone-d_6, i.e., 43%, and 40% for **3** and **4**, respectively. The isolated **4** was stable in $CDCl_3$ without deslipping over 6 months, while it reverted to **1** and **2** within a day by dissolving in DMSO-d_6.

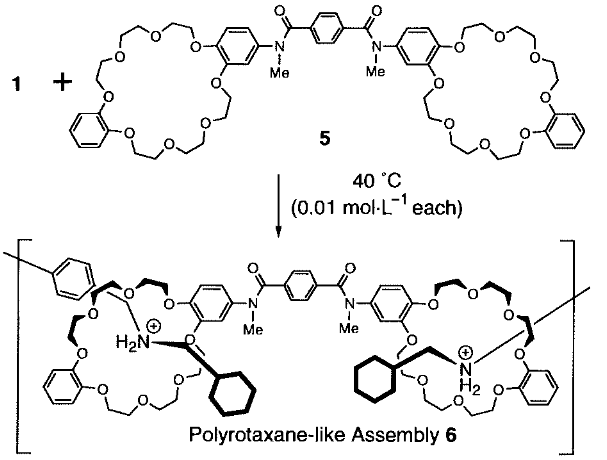


		NMR Yield / %^{a}	
Solvent	Time / day^b	3	4
CD_3COCD_3	127 (70)	45 (41)	30 (32)
CD_3CN	113 (100)	40 (43)	38 (40)

^{a}Isolated yields are given in parenthesis. ^{b}Periods required to reach equilibrium are given in parenthesis.

Scheme 2. Synthesis of [2]- and [3]rotaxane-like assemblies using the slipping approach.

Polyslipping was achieved by heating a mixture of **1** and bis-crown ether **5**[7] in acetone-d_6 at 40 °C. The reaction progress was monitored by ^{1}H NMR. The reaction system reached equilibrium after 70 days. The degree of polymerization of the resulting polyrotaxane-like assembly **6** was estimated to be 6.2 from the ^{1}H NMR spectrum.[8] The GPC ($CHCl_3$) profile of **6** has a bimodal feature as shown in Figure 1. The M_n of the higher molecular weight part was estimated to be 3300, while that of the lower molecular weight part was 1200, as estimated on the basis of polystyrene standards. The overall M_n was calculated at 1500, which was much smaller than the expected value, ca. 5100, based on the ^{1}H NMR spectra. Moreover, the M_n of [3]rotaxane **4** was underestimated to be 1100 (fw 1517), which is much smaller that that of bis-crown ether **5** (M_n 1300, fw 1085). Thus, the GPC analysis should considerably underestimate the molecular weight of **6** because of the ammonium salt moieties and the interlocked structure. The lower molecular weight part might comprise cyclic oligomers, as often observed for this kind of polyrotaxanes.[9] Polyslipping in acetonitrile-d_3 afforded **6** with a bimodal GPC profile, similarly to the case of acetone-d_6. The M_n of **6** obtained in acetonitrile-d_3 increased, as expected from the results of the double slipping. The deslipping of **6** completed in a day by dissolving in DMSO-d_6 to yield the monomers **1** and **5**, quantitatively.



			Higher	Lower
Solvent	Time / d	M_n (M_w/M_n)	M_n (M_w/M_n)	M_n (M_w/M_n)
CD_3COCD_3	113	1500 (1.4)	3300 (1.2)	1200 (1.1)
CD_3CN	107	1700 (1.5)	3800 (1.2)	1200 (1.1)

Scheme 3. Synthesis of polyrotaxane-like assembly **6**.

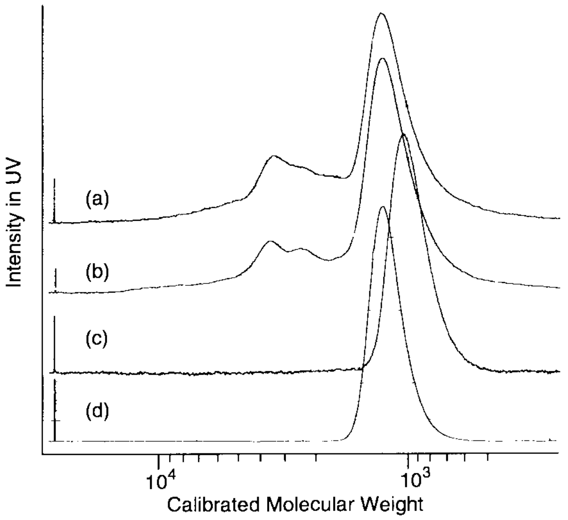


Figure 1. GPC ($CHCl_3$) profiles of (a) **6** obtained in acetone-d_6, (b) **6** obtained in CD_3CN, (c) [3]rotaxane **4**, and (d) bis-crown ether **5**.

In conclusion, we have demonstrated that polyslipping of bis-ammonium salt **1** and bis-crown ether **5** yielded polyrotaxane-like assembly **6**. Use of a polar solvent such as DMSO easily converted **6** to the monomers **1** and **5**. Because of the facile operation for the assembly and disassembly, together with the interlocked structures of the polyrotaxane-like assemblies, polyslipping can be a new protocol to create novel polymer materials, such as recycling polymers.

We thank the financial support by Showa Shell Sekiyu Environmental Research Foundation.

References and Notes

1 a) G. Schill, "Catenanes, Rotaxanes, and Knots," Academic Press, New York (1971). b) J.-C. Chambron and J.-P. Sauvage, *Top. Curr. Chem.*, **165**, 131 (1993). c) D. B. Amabilino and J. F. Stoddart, *Chem. Rev.*, **95**, 2725 (1995). d) E. G. Gillard, F. M. Raymo, and J. F. Stoddart, *Chem. Eur. J.*, **3**, 1933 (1997). e) R. Jäger and F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, **36**, 930 (1997). f) "Molecular Catenanes, Rotaxanes and Knots," ed. by J.-P. Sauvage and C. O. Dietrich-Buchecker, John Wiley & Sons, New York (1999).

2 P. R. Ashton, I. Baxter, M. C. T. Fyfe, F. M. Raymo, N. Spencer, J. F. Stoddart, A. J. P. White, and D. J. Williams, *J. Am. Chem. Soc.*, **120**, 2297 (1998) and references cited therein.

3 The distinction between rotaxanes and pseudorotaxanes is subtle. In this case, **R** is a rotaxane at lower temperatures and a pseudorotaxane at elevated temperatures. By definition, **R** is not a rotaxane but a pseudorotaxane, since the endcaps are not bulky enough to prevent deslipping under all circumstances.[2a] In this context, we use the term "rotaxane-like assembly" for rotaxane at lower temperatures.

4 Gibson et al. have recently reported the formation of supramolecular polymers from homoditopic crown ethers and secondary ammonium salts. These assemblies are trivial pseudopolyrotaxanes, since they do not have any endcaps. N. Yamaguchi and H. W. Gibson, *Angew. Chem. Int. Ed.*, **38**, 143 (1999).

5 **1** was synthesized by reductive amination of cyclohexanecarbaldehyde with *p*-xylylenediamine. Data for **1**: white crystals: mp 230 °C (decomp.); ^{1}H NMR (CD_3CN, 270 MHz, 295 K): δ 7.53 (s, 4H, ArH), 4.18 (s, 4H, $ArCH_2$), 2.89 (d, J = 5.8 Hz, 4H, NH_2CH_2), 1.74–1.62 (m, 12H, c-Hex-H), 1.33-0.92 (m, 10H, c-Hex-H).

6 Data for **3** and **4**: **3**: white solid: mp 88–90 °C; ^{1}H NMR (270 MHz, CD_3CN, 295 K) δ 7.55 (d, J = 8.3 Hz, 2H, ax-ArH), 7.33 (s, J = 8.3 Hz, 2H, ax-ArH), 7.09–6.82 (m, 12H, ce-ArH + ax-NH), 4.73–4.68 (m, 2H, ax-$ArCH_2$), 4.20–3.60 (m, 26H, ce-OCH_2 + ax-$ArCH_2$), 3.34 (m, 2H, ax-c-Hex-CH_2), 3.03 (m, 2H, ax-c-Hex-CH_2), 1.74–0.66 (m, 22H, ax-c-Hex-H). **4**: white solid: 217.5–219.0 °C (decomp.); ^{1}H NMR (270 MHz, CD_3CN, 295 K) δ 7.09 (s, 4H, ax-ArH), 6.92–6.82 (m, 20H, ce-ArH + ax-NH_2), 4.52–4.49 (m, 4H, ax-$ArCH_2$), 4.10–3.97 (m, 16H, ce-OCH_2), 3.82–3.41 (m, 32H, ce-OCH_2), 3.09–3.02 (m, 4H, ax-c-Hex-CH_2), 1.58–0.76 (m, 22H, ax-c-Hex).

7 **5** was synthesized from DB24C8 in 4 steps. Data for **5**: white solid: mp 160.5–161.0 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 295 K) δ 7.10 (4H, s, ArH), 6.88 (8H, s, ArH), 6.60–6.35 (6H, m, ArH), 4.16–3.68 (48H, m, CH_2), 3.38 (6H, s, N–CH_3); IR (KBr): 1630 ($\nu_{C=O}$).

8 The DP was calculated by comparing the signal area of the aromatic protons of the "uncomplexed" ammonium moiety of **1** with that of TMS as an internal standard. The DP was estimated to be larger than expected from the model experiment. This is due to the fact that **5** has an acylamino substituent on the DB24C8 moiety, which increases its complexation ability towards secondary ammonium salts; see, P. R. Ashton, M. C. T. Fyfe, S. K. Hickingbottom, J. F. Stoddart, A. J. P. White, and D. J. Williams, *J. Chem. Soc., Perkin 2*, **1998**, 2117.

9 For examples of cyclic oligorotaxanes, see, a) S. J. Rowan, S. J. Cantrill, J. F. Stoddart, A. J. P. White, and D. J. Williams, *Org. Lett.*, **2**, 759 (2000). b) T. Hoshino, M. Miyauchi, Y. Kawaguchi, H. Yamaguchi, and A. Harada, *J. Am. Chem. Soc.*, **122**, 9876 (2000).