Chemistry Letters Vol.37, No.4 (2008)

A Novel Synthetic Route to Poly(crown ether) through Rotaxanation–Protection Protocol

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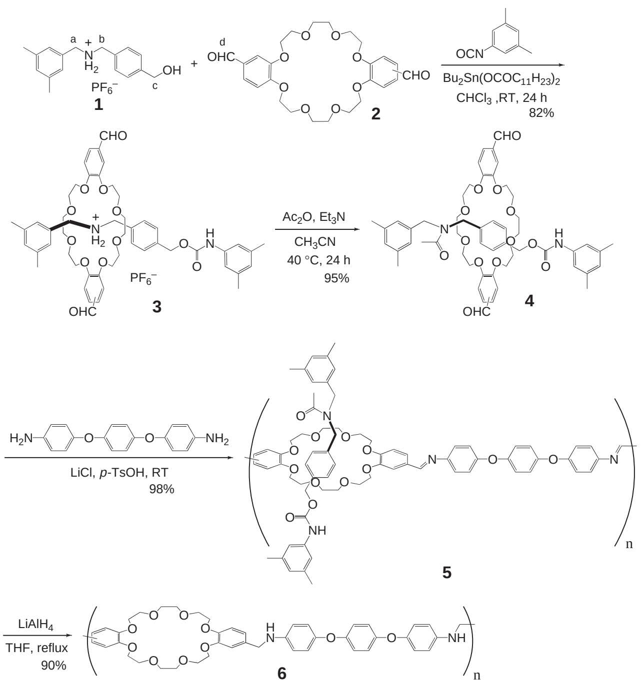
(Received January 28, 2008; CL-080094; E-mail: ttakata@polymer.titech.ac.jp)

Poly(crown ether) containing dibenzo-24-crown-8-ether moieties in the main chain was prepared by exploiting a rotaxanation–protection protocol, i.e., stepwise elaboration via the polymerization of cavity-filled [2]rotaxane and subsequent removal of the axle moiety.

Poly(crown ether)s,[1] a class of polymers possessing crown ether moieties in the main or side chains, have generated particular interest as a variety of polymer materials such as membranes for cation transport,[2] electrode,[3] backbone of polyrotaxane,[4] and polyrotaxane network.[5] Although a few synthetic methods of poly(crown ether)s have been developed so far,[6] they are limited to polymers containing small ring-size crown ethers. Synthesis of polymer bearing large ring-size crown ether moieties (e.g. more than 24 members) has long been suffered from the occurrence of the gelation during the synthetic process through polymerization, because the propagation end accidentally penetrates into the crown ether cavity of the polymer formed, leading to the crosslinking (Figure 1, route B).[7] Therefore, it is generally difficult to obtain soluble poly(crown ether) or that with narrow molecular weight distribution even by the carefully controlled polymerization. As a potential solution to this issue, we planned a novel synthetic route where ditopic [2]rotaxane serves as a crucial monomer giving poly(crown ether) with narrow molecular weight distribution. Namely, the [2]rotaxane as a cavity-filled crown ether successfully prevents the undesirable threading of the propagation end during the polymerization to yield poly[2]rotaxane without any gelation. The subsequent elimination of the axle components from poly[2]rotaxane results in the production of poly(crown ether) (Figure 1, route A).

Herein, we wish to describe a novel synthetic method for a poly(crown ether), according to the rotaxanation–protection protocol.

Scheme 1 features the synthesis of poly[2]rotaxane and its conversion to the corresponding poly(crown ether). Treatment of bis(formyl) crown ether **2** with *sec*-ammonium salt **1** gave [2]rotaxane **3** via the urethane end-capping[8] in 82% yield, while the ester end-capping with a bulky acid anhydride catalyzed by tributylphosphane[9] resulted in a low yield ($\approx$20%), due most likely to the decomposition of pseudo-rotaxane by the carboxylic acid generated in situ. Subsequent N-acylation with acetic anhydride afforded neutral [2]rotaxane **4** in 95% yield. The structures of **3** and **4** were determined by ^{1}H NMR, IR, and MALDI-TOF MS spectra (Figure 2, iii, iv). To obtain poly([2]-rotaxane) **5** from **4** and 1,4-bis(4-aminophenoxy)benzene as a typical diamine monomer, several classical imination protocols were examined but only gave a mixture of low molecular weight polymers. After many experimental works, this goal was achieved by the polycondensation catalyzed by *p*-TsOH (monohydrate, 5 mol %) in the presence of LiCl as the dehydrating agent.[10]



Scheme 1. Synthesis of poly(crown ether).

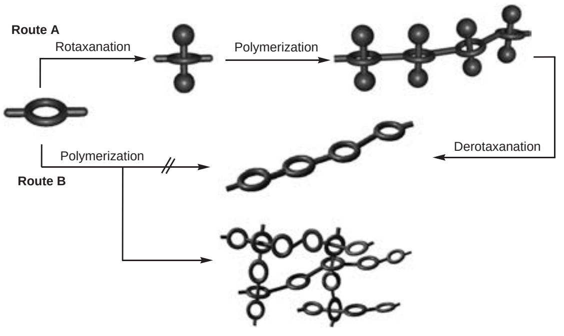


Figure 1. Synthetic routes to poly(crown ether).

Table 1 summarizes the effect of solvent on the polymerization. While the polycondensation reaction in DMAc, $CHCl_3$, THF, or *m*-cresol afforded the high viscosity suspension after 12 h, it turned out that *o*-chlorophenol was the most suitable solvent to afford the clear solution after 12 h probably owing to its good solubilizing power to polymer formed (Entry 5). Poly[2]rotaxane **5** with high molecular weight was obtained in 98% yield by a similar polymerization in *o*-chlorophenol for a prolonged reaction time (36 h, Entry 6, M_n 15900, M_w 64200, and M_w/M_n 4.04 by GPC).[11]

Table 1. Effect of solvent on the polycondensation[a]

Entry	Solvent	M_n[b]	M_w[b]	$M_\mathrm{w}/M_\mathrm{n}$[b]	Yield/%
1	DMAc	4500	9500	2.12	93
2	$CHCl_3$	5200	12300	2.35	91
3	THF	2800	6100	2.16	98
4	*m*-Cresol	5400	13000	2.42	93
5	*o*-Chlorophenol	6500	16200	2.49	98
6[c]	*o*-Chlorophenol	15900	64200	4.04	98

[a]Polymerization of [2]rotaxane **4** and 1,4-bis(4-aminophenoxy)-benzene was carried out in the presence of *p*-TsOH•H_2O (5 mol %) and LiCl at room temperature for 12 h. [b]Estimated by GPC based on polystyrene standards. [c]The polymerization was continued until the stirring was stopped due to the high viscosity (36 h).

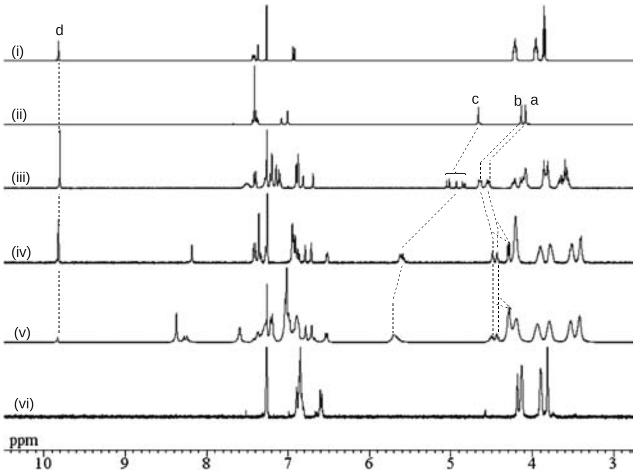


Figure 2. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (i) wheel **2**, (ii) axle **1**, (iii) [2]rotaxane **3**, (iv) *N*-acetyl[2]rotaxane **4**, (v) poly([2]rotaxane) **5**, (vi) poly(crown ether) **6**.

The remaining task was the removal of the axle moieties from **5** (M_n 15900, M_w 64200, and $M_\mathrm{w}/M_\mathrm{n}$ 4.04) to complete poly(crown ether) backbone. The removal of the axle component with $LiAlH_4$ proceeded smoothly to give poly(crown ether) **6** in 90% yield. By this treatment, the imine group was also reduced to amine group. The structure was determined by ^{1}H NMR, IR and MALDI-TOF MS spectra {Figure 2, (vi), *m*/*z* 6260–9485 (M^+) determined by MALDI-TOF MS spectrum}.[12] Solubility of **6** was very good: **6** was readily soluble in chloroform, THF, and methanol, while insoluble in hexane and ether.

Figure 2 shows the ^{1}H NMR spectra of polymers **5**, **6**, and related compounds **1**–**3**. The signals of the benzylic methylene protons **a** and **b** of **1** (ii) shifted downfield upon the complexation to **3** (iii); this is consistent with the existence of through-space interaction owing to hydrogen bonding between the two components, from 4.09 and 4.14 to 4.53 and 4.62 ppm, respectively. Meanwhile, the signals **a** and **b** shifted clearly upfield in **4** and **5**, suggesting that the wheel moved to the urethane moiety by the acylation. In the spectrum of **6**, disappearance of the signals of the axle afforded the direct evidence for the fact that the rotaxane structure was broken.

To confirm the usefulness of the present synthetic method of poly(crown ether), a mixture of bis(formyl) crown ether **2** and diamine was treated under a similar polymerization conditions, but only obtained a completely gelled polymer with little soluble material. Thus, the rotaxanation–protection protocol provides the significant entry to poly(crown ether) having large cavity crown ether moieties. Application to polyrotaxane network exploiting poly(crown ether) with high polymerization degree are currently in progress.

References and Notes

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11 To a solution of **4** (200 mg, 206 mmol), and 1,4-bis(4-aminophenoxy)benzene (60.2 mg, 206 mmol) in *o*-chlorophenol (480 mL) was added a catalytic amount of *p*-TsOH•H_2O (20 mg, 5 mol %) and LiCl (60 mg) under argon atmosphere. After stirring the mixture for 36 h at room temperature, the mixture was added to half-saturated aq. $NaHCO_3$ to precipitate yellow solids. The precipitates were collected by filtration and dried in vacuo to afford **5** (252 mg, 98%). For physical data, Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

12 To a suspension of $LiAlH_4$ (307 mg, 8.08 mmol) in THF (10 mL) was added a solution of **5** (100 mg, 80.8 mmol) in THF (20 mL) under an argon atmosphere. The mixture was refluxed for 24 h. After the reaction mixture was cooled to 0 °C, the mixture was poured into a saturated aq. Na_2SO_4. The resulting mixture was filtrated through Celite pad. The filtrate was evaporated to dryness. The residue was decanted by ether and hexane, and dried in vacuo to give **6** (58.1 mg, 90%). For physical data, see Supporting Information.