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# A Novel Ladder Polymer. Two-Step Polymerization of Oxetanyl Oxirane Leading to a “Fused 15-Crown-4 Polymer” Having a High $Li^+$−Binding Ability

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ABSTRACT: A novel ladder polymer, i.e., a “fused 15-crown-4 polymer”, has been synthesized by a two-step polymerization of 3-ethyl-3-oxiranylmethoxymethyloxetane (**1**). The anionic polymerization of **1** produced the polyoxirane (**2**) with multiple pendant oxetanyl groups. The second cationic cyclopolymerization of **2** homogeneously proceeded to form gel-free polymers (**3**), i.e., “fused 15-crown-4 polymers”, having $M_n$s of ca. 13 000 in 60−90% yield. The cation-binding ability of **3** has also been evaluated by a liquid−liquid extraction method using picrates of alkali, alkaline-earth, and transition metals. The metal cation-binding property of **3** strongly depended on the metal cation radius. For **3** having an $M_n$ of 13 200 and $M_w/M_n$ of 2.42, the extraction yields of $Li^+$, $Co^{2+}$, $Ni^{2+}$, and $Cu^{2+}$ (with radii of 0.68−0.72 Å) were relatively high. Ion selectivity values were similar to those of 14-crown-4.

## Introduction

The synthesis of ladder polymers has been extensively studied using the two-step polymerization of a specifically designed difunctional monomer using suitable polymerization conditions; in particular, the process of forming ladder segments depends on the nature of the zipping-up or multistage cyclization reactions of multiple functional groups as side chains of the precursor polymers. According to the method using a difunctional monomer, ladder polymers were prepared from the second-stage cyclopolymerization of the conventionally preformed 3,4-polyisoprene and 1,2-polybutadiene.[1−3] Other monomers such as acrolein, vinyl isocyanate, vinyl acetylene, and cyanoacetylene also lead to ladder polymers by using the appropriate polymerization initiators.[2−13]

Since the resulting ladder polymers have unique structures with fused cyclic segments in the polymer main chain, it is of interest to design and synthesize novel ladder polymers with intelligent cyclic structures. For example, the second cyclopolymerization of cyclic ethers in a preformed polyether should lead to a novel type of ladder polymer having crown ether units, i.e., a “fused crown polymer”. Thus, the difunctional monomer possessing oxetanyl and oxiranyl groups should be suitable for synthesizing the fused crown polymer, because the oxetanyl and oxiranyl groups are expected to undergo polymerization under different initiation conditions. In this paper, we report the synthesis of a ladder polymer, a “fused 15-crown-4 polymer”, through the initial ring-opening polymerization of oxiranyl groups in 3-ethyl-3-oxyranylmethoxymethyloxetane (**1**) using an anionic initiator and the second stage cyclopolymerization of residual multiple oxetanyl groups using a cationic initiator. In addition, the metal cation-binding ability of the “fused 15-crown-4 polymer” is discussed along with a comparison to those of the unsubstitued 12- to 16-crown-4.

## Experimental Section

**Materials.** Dry tetrahydrofuran and dry toluene were purchased from the Kanto Chemical Co. and used without further purification. Potassium *tert*-butoxode (*t*-BuOK) was purified by sublimation under vacuum before use. All other starting materials and solvents were of reagent quality and were used as received. 3-Ethyl-3-hydroxymethyloxetane was synthesized according to the method of Pattison.[14]

**Measurements.** The $^1H$ (400 MHz) and $^{13}C$ NMR (100 MHz) spectra were recorded using a JEOL JNM-A400 II spectrometer using chloroform-*d* ($CDCl_3$) with tetramethylsilane as an internal standard. The molecular weights of the polymer samples were measured by size exclusion chromatography (SEC) in tetrahydrofuran on a Jasco GPC-900 system equipped with three polystyrene gel columns (Shodex KF-804L). The number-average molecular weight ($M_n$) and the molecular weight distribution ($M_w/M_n$) were calculated on the basis of a polystyrene calibration. The UV spectra were measured using a Jasco V-550 UV/vis spectrophotometer for the liquid−liquid extraction experiments.

**Synthesis of 3-Ethyl-3-oxyranylmethoxymethyloxetane (1).** Compound **1** was synthesized by a phase transfer reaction according to the method of Mouzin et al.[15] A mixture of 50% w/w aqueous sodium hydroxide (400 mL), epichlorohydrin (250 mL), and tetra-*n*-butylammonium hydrogen sulfate (8.4 g) was vigorously stirred at room temperature. 3-Ethyl-3-hydroxymethyloxetane (69.6 g, 0.6 mol) was gradually added over 30 min with cooling below 25 °C. The progress of the reaction was monitored by gas chromatography. After 5 h, the reaction mixture was poured into ice/water (2 L), and the aqueous phase was extracted three times with diethyl ether (200 mL). The combined organic phase was washed with brine until neutral and dried with anhydrous sodium sulfate. After the solvent was evaporated off, the residue was distilled using calcium hydride under vacuum: yield, 84.4 g (82%); bp,

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82−84 °C (0.6 mmHg). $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 4.47 (dd, $J_{gem} = 5.9$ Hz, $J = 2.9$ Hz, 2H, oxetanyl group $CH_2$), 4.38 (d, $J_{gem} = 5.9$ Hz, 2H, oxetanyl group $CH_2$), 3.82 (dd, $J = 11.8$ Hz, $J = 2.8$ Hz, 1H), 3.67 (d, $J = 9.3$ Hz, 1H), 3.60 (d, $J = 9.3$ Hz, 1H), 3.41 (dd, $J = 11.7$ Hz, $J = 6.1$ Hz, 1H), 3.17−3.15 (m, 1H, oxiranyl group CH), 2.80 (dd, $J_{gem} = 5.1$ Hz, $J_{cis} = 4.6$ Hz, 1H, oxiranyl group *cis*-$CH_2$), 2.61 (dd, $J_{gem} = 5.1$ Hz, $J_{trans} = 2.7$ Hz, 1H, oxiranyl group *trans*-$CH_2$), 1.76 (q, $J = 7.6$ Hz, 2H, ethyl $CH_2$) and 0.90 ppm (t, $J = 7.6$ Hz, 3H, ethyl $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$): 77.8 (oxetanyl group O−$CH_2$), 73.6 (O-$C$H$_2$−C), 71.7 (O-$C$H$_2$−CH), 50.4 (oxiranyl group CH), 43.5 (oxiranyl group $CH_2$), 43.0 (oxetanyl group C), 26.3 (ethyl $CH_2$) and 7.8 ppm (ethyl $CH_3$). IR (film): 1250 (oxiranyl group $CH_2$−O−$CH_2$) and 980 cm$^{-1}$ (oxetanyl group $CH_2$−O−$CH_2$). Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36, Found C, 62.53; H, 9.42.

**Anionic Polymerization of 1.** A typical polymerization procedure is as follows: The polymerization was carried out in an H-shaped glass ampule (diameter, 16 mm; height, 100 mm). *t*-BuOK (23 mg, 0.205 mmol) and dry tetrahydrofuran (1.4 mL) were placed in the one side of the ampule, and **1** (721 mg, 4.19 mmol) was placed in the other side of the ampule under a nitrogen atmosphere. After sealing, the monomer and the catalyst solution were mixed at 60 °C. After 48 h, the reaction mixture was poured into a large amount of methanol and the entire solution was evaporated under reduced pressure. The residue was twice reprecipitated with chloroform/*n*-hexane. The *n*-hexane-insoluble part was dissolved in chloroform and washed with water. After evaporation of the chloroform, the remaining water was removed by azeotropic evaporation with benzene. The obtained polymer was a yellowish viscous semisolid. Yield: 687 mg (95.3%). $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 4.80−4.40 (m, 2H, oxetanyl group $CH_2$), 4.40−4.12 (m, 2H, oxetanyl group $CH_2$), 3.80−3.35 (m, 7H), 1.72 (q, $J = 7.3$ Hz, 2H, ethyl $CH_2$) and 0.88 ppm (t, $J = 7.3$ Hz, 3H, ethyl $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$): 78.8 (CH), 78.7 (oxetanyl group O−$CH_2$), 74.1 (O−$C$H$_2$−C), 71.7 (O−$C$H$_2$−CH), 69.8 ($CH_2$), 43.4 (oxetanyl group C), 26.8 (ethyl $CH_2$) and 8.2 ppm (ethyl $CH_3$).

**Cationic Polymerization of Polymer 2.** To a solution of polymer **2** (258 mg, 1.5 mmol of repeating units) in dry $CH_2Cl_2$ (1.5 mL) was added $BF_3{\cdot}OEt_2$ (107 $\mu$L of 1.40 mol·L$^{-1}$−$CH_2Cl_2$ solution, 0.15 mmol). After 100 h at 0 °C, the reaction solution was poured into a large amount of methanol containing a drop of aqueous ammonia, and the solvent was then evaporated off under reduced pressure. The residue was twice reprecipitated with chloroform/methanol. The obtained polymer was then dried under vacuum (154 mg, 59.8%). The $M_n$ and $M_w/M_n$ values were 13 200 and 2.42, respectively. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 4.52−2.51 (br), 1.80−1.10 (br, ethyl $CH_2$) and 1.00−0.60 ppm (br, ethyl $CH_3$).

**Extraction Experiment.** The extraction of the alkali-metal picrates was carried out using a procedure similar to that developed by Pedersen.[16] A solution of polymers, **2** and **3**, in $CH_2Cl_2$ (2.5 mL, [the repeating unit in polymer] = $5.75 \times 10^{-3}$ mol·L$^{-1}$) was vigorously shaken with an aqueous solution (2.5 mL) containing an alkali metal hydroxide and picric acid ([picric acid] = $7.0 \times 10^{-5}$ mol·L$^{-1}$ and [alkali-metal hydroxide] = 0.1 mol·L$^{-1}$). After the resulting two phases were separated, the alkali metal picrate extracted into the $CH_2Cl_2$ phase was indirectly determined by measuring the absorbance of the picrate in the aqueous phase at 357 nm using a UV-spectrometer. The extractions of the alkaline-earth-metal chloride and transition-metal chloride were carried out under similar conditions ([picric acid] = $7.0 \times 10^{-5}$ mol·L$^{-1}$ and [alkaline-earth-metal chloride or transition-metal chloride] = 0.01 mol·L$^{-1}$).

## Results and Discussion

**Anionic Polymerization of Monomer 1.** Table 1 lists the results of the anionic polymerization of 3-ethyl-3-oxiranylmethoxymethyloxetane (**1**) using *t*-BuOK at 60 °C. The polymerization systems were homogeneous and exhibited a color change from colorless to dark brown as the reaction progressed. In addition, the viscosity of the medium for the bulk polymerization gradually increased with time. No evidence of gelation was observed, indicating that the oxiranyl and oxetanyl groups of **1** were not polymerized by simultaneous ring opening. The resulting polymers (**2**) were yellowish-brown sticky semisolids and were completely soluble in chloroform, tetrahydrofuran, and methanol but insoluble in *n*-hexane.

**Table 1. Results of Anionic Polymerization of 3-Ethyl-3-oxiranylmethoxymethyloxetane (1) Using *t*-BuOK**[a]

| solvent | [**1**]/[*t*-BuOK] | time (h) | yield (%) | $M_n$[b] | $M_w/M_n$[b] | DP$_n$ |
|---|---|---|---|---|---|---|
| THF | 10 | 48 | 76.1[c] | 2100 | 1.15 | 12.2 |
| THF | 20 | 48 | 95.3 | 4100 | 1.28 | 23.8 |
| THF | 30 | 48 | 87.6 | 5600 | 1.44 | 32.6 |
| THF | 40 | 48 | 83.8 | 7600 | 1.57 | 44.2 |
| toluene | 30 | 48 | 72.2 | 5150 | 1.46 | 29.9 |
| none | 20 | 1.5 | 84.3 | 4600 | 1.39 | 26.7 |
| none | 20 | 3 | 98.4 | 6500 | 1.45 | 37.8 |

[a] Polymerization temperature: 60 °C. [**1**] = 3 mol/L. [b] Measured by SEC using THF as an eluent and estimated by polystyrene as a standard. [c] Perhaps some low molecular weight polymer was lost in the precipitation.

For the polymerization in THF, the $M_n$ of **2** varied with the molar ratio of monomer to initiator ([**1**]/[*t*-BuOK]), and a linear relationship between the $M_n$ and the [**1**]/[*t*-BuOK] molar ratio was found; i.e., the solution polymerization allowed the $M_n$ to approach the value estimated from the [**1**]/[*t*-BuOK] molar ratio. Toluene was also a good solvent for the polymerization and the $M_n$ of the resulting polymer was 5150, corresponding to a number-average degree of polymerization (DP$_n$) estimated from the [**1**]/[*t*-BuOK] molar ratio (30). The polydispersities ($M_w/M_n$) of **2** were relatively narrow with a value in the range 1.15−1.57. For the bulk polymerization, the conversion was ca. 100% for 3 h and the polymer with a $M_n$ of 6500 and a $M_w/M_n$ of 1.45 was obtained. These results indicated that the bulk polymerization was a more convenient way to produce **2** than that in solvent, though it was difficult to control the $M_n$.

Figure 1 shows the $^1$H NMR spectra of **1** and its anionic polymer **2**. For the spectrum of **2**, the characteristic absorption at 2.5−3.9 ppm due to the protons of the oxirane ring completely disappeared, while that at 4.3−4.5 ppm due to the protons of the oxetane ring was unchanged. This result means that no ring-opening reaction of the oxetane ring in **1** occurred during the anionic polymerization. Therefore, the resulting polymer was a polyoxirane with multiple pendant oxetanyl groups, as shown in Scheme 1.

**Cationic Polymerization of Precursor 2.** To prepare a ladder polymer consisting of crown ether moieties, the precursor **2** was polymerized using $BF_3{\cdot}OEt_2$ in dilute $CH_2Cl_2$ solution. If the second cyclopolymerization in a polymer chain take place among neighboring oxetanyl groups, the ladder polymer with 15-crown-4 repeating units might be expected. Table 2 lists the polymerization results. Precursor **2** with a $M_n$ of 5600 was used for the cationic polymerization. The polymerization with a molar concentration of the repeating units ([M]) of 0.1 proceeded homogeneously to afford gel-free polymers in 60−90% yields. The obtained products were white solids, which were soluble in chloroform and THF and insoluble in methanol. The $M_n$s were ca. 13 000, which were 2−3 times greater than that of **2**. This means that an unexpected intermolecular polymeriza-

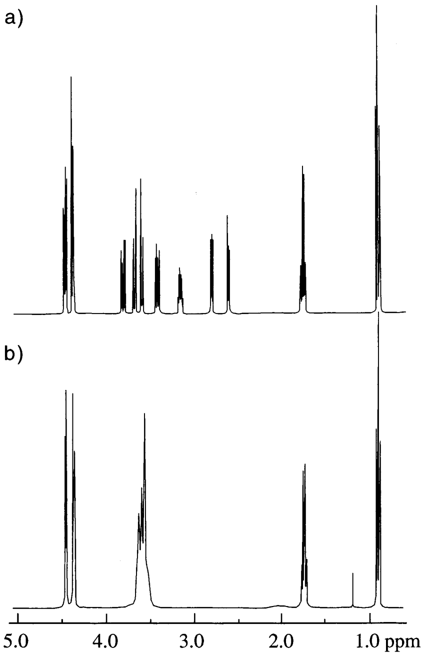

**Figure 1.** $^1$H NMR spectra of (a) 3-ethyl-3-oxyranylmethoxymethyloxetane (**1**) and (b) precursor **2** obtained from **1** using *t*-BuOK.

**Scheme 1**

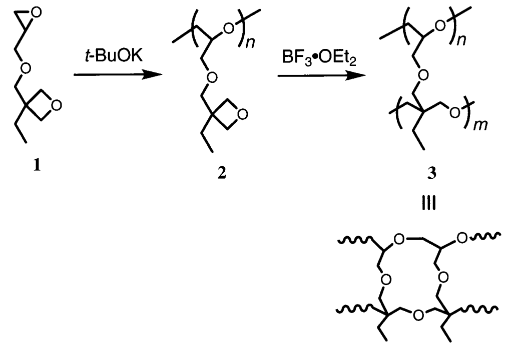

**Table 2. Results of Cationic Polymerization of Precursor 2**[a]

| [M][b] | [M]/[I] | time (h) | yield (%) | $M_n$[c] | $M_w/M_n$[c] |
|---|---|---|---|---|---|
| 0.1 | 10 | 100 | 59.8 | 13 200 | 2.42 |
| 0.1 | 20 | 160 | 90.3 | 13 200 | 2.57 |
| 0.2 | 20 | 15 | | gelation | |

[a] Polymerization condition: initiator, $BF_3$•$OEt_2$; solvent, $CH_2Cl_2$; temp., 0 °C. Polymer **2** with $M_n$ of 5600 was used. [b] Molar concentration of repeating unit in **2**. [c] Measured by SEC using THF as an eluent and estimated by polystyrene as a standard.

tion occurred to yield the dimer or trimer of **2**. On the other hand, the polymerization with [M] = 0.2 produced only gelled polymer even if the polymerization time was 15 h.

Figure 2 shows the $^1$H NMR spectrum of the resulting polymer. When compared with the spectrum of **2** in Figure 1b, the spectrum consisted of broad peaks. The characteristic resonance at 4.3−4.5 ppm due to the oxetanyl groups sufficiently decreased, indicating that most of the pendant oxetanyl groups were consumed. Because the products were soluble in common organic solvents, the polymerization should proceed according to a cyclopolymerization mechanism leading to a ladder polymer (**3**) consisting of 15-crown-4 repeating units, i.e., the “fused 15-crown-4 polymer”, as shown in Scheme 1.

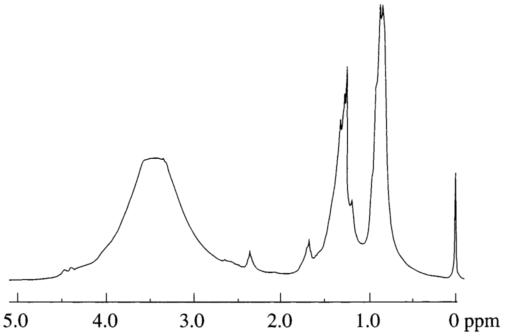

**Figure 2.** $^1$H NMR spectrum of ladder polymer (**3**) prepared from secondary cationic cyclopolymerization of precursor **2**.

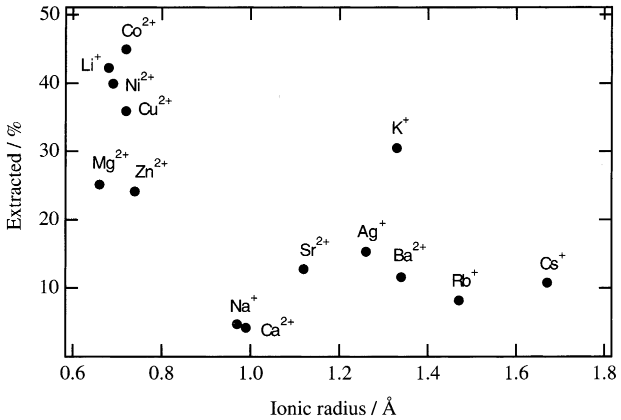

**Figure 3.** Plots of extraction yield vs metal cation radii. Temperature: 20 °C. [alkali-metal hydroxide] = 0.1 mol·L$^{-1}$ or [alkaline-earth-metal chloride or transition-metal chloride] = 0.01 mol·L$^{-1}$; [picric acid] = 7.0 × 10$^{-5}$ mol·L$^{-1}$; [repeating unit in polymer] = 5.75 × 10$^{-3}$ mol·L$^{-1}$. Solvent: $CH_2Cl_2$.

**Extraction Experiment of Metal Ions.** The metal-cation-binding ability of **3** was estimated by the liquid−liquid extraction method using the picrates of alkali, alkaline-earth, and transition metals. In Figure 3, the extraction yields were plotted vs the ionic radius. The metal cation-binding property of **3** strongly depends on the metal cation radius and the extraction yields of $Li^+$, $Mg^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Cu^{2+}$, and $Zn^{2+}$ (with radii of 0.66−0.74 Å) were relatively high. In particular, the extraction yields for $Li^+$, $Ni^{2+}$, $Co^{2+}$, and $Cu^{2+}$ were above 30%, meaning that the cavity size of 15-crown-4 repeating units in **3** had a radius of ca. 0.68−0.72 Å. In addition, **3** was considerably more efficient in binding $K^+$ which has a diameter of 1.33 Å larger than the crown cavity in **3**. This result can be explained by cooperative coordination effects, where neighboring crown ether rings combine with a single cation. Such a cation-binding property of **3** is similar to that of the usual polymeric crown ethers.[17−20]

Interestingly, **3** showed a higher selectivity for $Li^+$ over $Na^+$ as $Li^+/Na^+ = 16.6$, which was calculated from the distribution ratio of the metal ion between the organic and aqueous phases. Liu et al. reported the cation selectivities of unsubstituted 12- to 16-crown-4, e.g., the relative cation selectivity of $Li^+/Na^+$ was 0.16 for 12-crown-4, 0.20 for 13-crown-4, 16.3 for 14-crown-4, 1.38 for 15-crown-4, and 1.45 for 16-crown-4.[21] The characteristic of the 15-crown-4 cavities in **3** was quite similar to that of 14-crown-4, indicating that because the 15-crown-4 units were fused to each other in **3**, its cavity size should be slightly reduced when compared to that of 15-crown-4. Therefore, **3** exhibited a highly selective extraction for $Co^{2+}$, $Ni^{2+}$, and $Cu^{2+}$, which have similar radii to $Li^{+}$.

## Conclusions

A novel ladder polymer, i.e., a "fused 15-crown-4 polymer", was synthesized by the anionic ring-opening polymerization of 3-ethyl-3-oxiranylmethoxymethyloxetane followed by cationic cyclopolymerization. These processes homogeneously proceeded to afford a gel-free white polymer, which showed the metal-cation-binding property with strong dependence on the metal cation radius. The high extraction yields using the "fused 15-crown-4 polymer" were observed for $Li^{+}$, $Co^{2+}$, $Ni^{2+}$, and $Cu^{2+}$ with the radii of 0.68−0.72 Å, whose cation-binding selectivity was quite similar to that of the 14-crown-4. The ladder polymer may be useful as a fundamental material for a novel polymer electrolyte in a lithium polymer battery. We are currently studying the electric property of the polymer−metal-cation complexes.

**Supporting Information Available:** A table giving data for the solvent extraction of metal picrates by **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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