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Ring-Opening and Ring-Forming Polymerization of 1,2:5,6:9,10-Triepoxydecane Leading to a Highly Regioselective Polymer Consisting of Octahydrobifuranyl Unit

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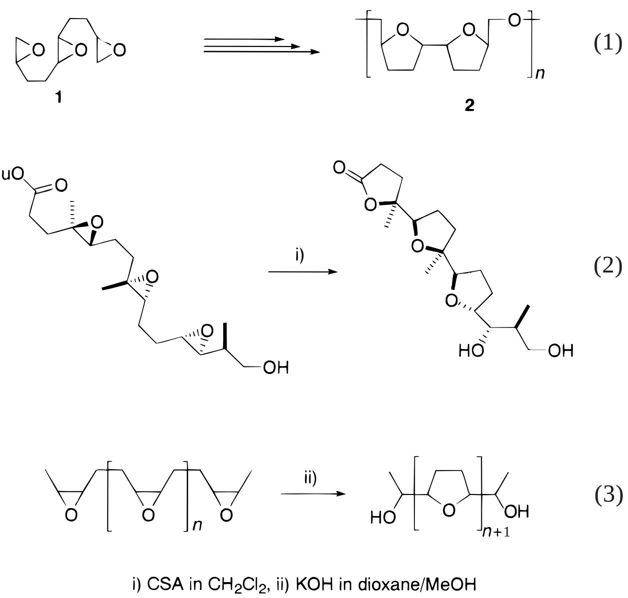
Di-, tri-, and oligoepoxy compounds are of importance from the viewpoint of the industrial production of cross-linked materials, such as coatings and adhesives. On the other hand, the diepoxide is a versatile monomer for cyclopolymerization leading to a gel-free polymer, in which 1,5- and 1,6-diepoxides are generally used as the monomer.[1] For example, we reported that 1,2:4,5-dianhydropentitol and 1,2:5,6-dianhydrohexitol were regio- and stereoselectively cyclopolymerized to yield novel carbohydrate polymers of (1→5)-2,4-anhydropentitol and (1→6)-2,5-anhydrohexitol, respectively.[2,3] In addition, the cyclopolymerization of suitably molecular-designed α,ω-diepoxides except for the 1,5- and 1,6-ones was the facile synthetic method for poly(crown ether)s such as poly(dibenzo-19-crown-6).[4] In the present study, we attempted to develop the cyclopolymerization of diepoxides into the ring-opening and ring-forming polymerization of the triepoxide as shown in eq 1 in Scheme 1, based on the analogy of the tandem technology for the construction of tetrahydrofurans using oligo- and polyepoxide openings, e.g., the formation of the characteristic cyclic ether skeleton from the designed oligoepoxide (eq 2)[5] and the synthesis of 2,5-poly(tetrahydrofuran)diyl from poly(butadiene epoxide) (eq 3).[6] Here we report the polymerization of 1,2:5,6:9,10-triepoxydecane (**1**) using $BF_3{\cdot}OEt_2$ and *t*-BuOK. The structures of the repeating units in the resulting polymers are confirmed by comparing their ^{13}C NMR spectra with that of 5,5′-bis(methoxymethyl)octahydro-2,2′-bifuran (**4**) which is obtained by the hydrolysis of **1**.

1,5,9-Decatriene was oxidized using *m*-CPBA to yield 1,2:5,6:9,10-triepoxydecane (**1**) as a colorless liquid.[7] Table 1 lists the results of the polymerization of **1** using *t*-BuOK and $BF_3{\cdot}OEt_2$ as the initiators. When the polymerization was carried out using $BF_3{\cdot}OEt_2$, the polymerization system was immediately heterogeneous. A part of the resultant polymer was insoluble in the usual organic solvents, such as $CHCl_3$ and THF. The number-average molecular weights (M_n) of the organic solvent-soluble polymers were 800−1850. Although the monomer concentration ([**1**]) for the polymerization using *t*-BuOK was higher than that using $BF_3{\cdot}OEt_2$, the anionic polymerization homogeneously proceeded to give organic solvent-soluble polymers in high yields. The polymerization solvent slightly affected the polymer yields and the M_ns of obtained polymers, and the M_n increased on the order of DMF > DMSO. For the polymerization in DMSO, the M_n values increased from 1560 to 4170 by increasing the molar ratio of **1** and *t*-BuOK ([**1**]/[cat.]).

Scheme 1



i) CSA in CH_2Cl_2, ii) KOH in dioxane/MeOH

Table 1. Polymerization of 1,2:5,6:9,10-Triepoxydecane (1)

catalyst	solvent	[**1**]/ [cat.]	temp, °C	time, h	yield,[a] %	M_n (M_w/M_n)[b]
$BF_3{\cdot}OEt_2$[c]	CH_2Cl_2	10	0	0.25	72 (3)	1850 (4.7)
		10	0	15	87 (12)	1000 (1.8)
		50	−30	14	10 (7.1)	800 (2.4)
		100	−30	14	18 (7.9)	890 (1.9)
t-BuOK[d]	DMSO	5	60	2	90	1560 (1.7)
		10	60	3	97	3300 (2.0)
		20	60	4	98	4170 (2.4)
	DMF	5	60	2	92	1700 (1.5)
		10	60	3	99	2100 (1.7)

[a] Values in parentheses were yields of chloroform-insoluble polymers. [b] Determined by GPC in THF (polystyrene standard). [c] [**1**] = 0.5 mol·L^{-1}. [d] [**1**] = 1.0 mol·L^{-1}.

Figure 1 shows the ^{13}C NMR spectra of the polymers obtained using $BF_3{\cdot}OEt_2$ and *t*-BuOK. The signals at 51.52−52.35 and 46.94−47.12 ppm due to the CH and CH_2 of the epoxy groups, respectively, were observed for the polymer using $BF_3{\cdot}OEt_2$, while they completely disappeared for the polymer using *t*-BuOK. These results indicate that the anionic polymerization of **1** proceeded through ring-opening and ring-forming of three epoxy groups in a monomer to produce a polymer consisting of cyclic constitutional repeating units.

In previous studies, the cyclic compound, which was obtained from the hydrolysis of 1,2:5,6-dianhydrohexitol, was an important key for determining the polymer structure for the cyclopolymerization of 1,2:5,6-dianhydrohexitol.[3] Thus, **1** was reacted in aqueous KOH to yield 5,5′-bis(hydroxymethyl)octahydro-2,2′-bifuran (**3**) (Scheme 2).[8] Figure 1c shows the spectrum of its methylated product, 5,5′-bis(methoxymethyl)octahydro-2,2′-bifuran (**4**).[9] The ^{13}C NMR signals for the polymer using *t*-BuOK were very close to those **4**, indicating that the constitutional repeating structure in the polymer

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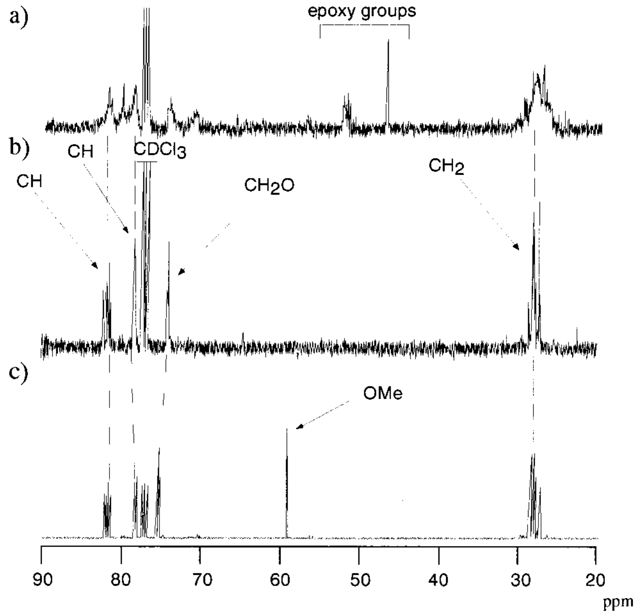
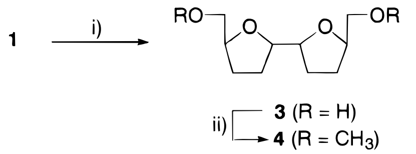


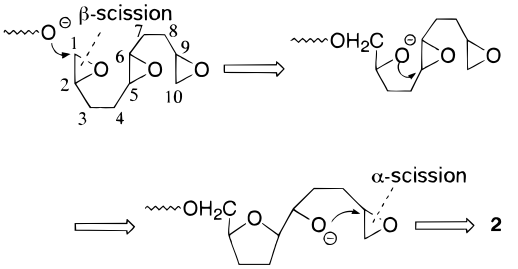
Figure 1. ^{13}C NMR spectra of the polymers obtained using $BF_3{\cdot}OEt_2$ (a) and *t*-BuOK (b) and 5,5′-bis(methoxymethyl)-octahydro-2,2′-bifuran (**4**) (c).

Scheme 2



i) KOH in H_2O, ii) Me_2SO_4 / NaOH in DMSO / H_2O

Scheme 3



was the octahydro-2,2′-bifuran-5,5′-diylmethyleneoxymethylene unit. This means that the polymerization of **1** was highly regioselective, as shown in Scheme 3; i.e., the polymerization of **1** proceeded first through the *β*-scission of the 1,2-epoxy group during the intermolecular addition, and then the formed alkoxy anion reacted at the 5-position of the 5,6-epoxy group during the first intramolecular cyclization, and finally, the second intramolecular cyclization proceeded through the α-scission of the 9,10-epoxy group to give the octahydro-2,2′-bifuran-5,5′-diylmethyleneoxymethylene units.

In summary, we reported the ring-opening and ring-forming polymerization of a triepoxy monomer as a novel type of polymerization; i.e., the polymerization of 1,2:5,6:9,10-triepoxydecane using *t*-BuOK was highly regioselective to form the polymer consisting of octahydro-2,2′-bifuran-5,5′-diylmethyleneoxymethylene units. From the viewpoint of a macromolecular ionophore, the metal cation binding property of the obtained polymer is of interest in comparison with that of (1→6)-2,5-anhydrohexitol.[3a] Further work concerning the molecular discrimination property is now in progress.

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(7) Synthesis of 1,2:5,6:9,10-triepoxydecane (**1**): To a solution of *m*-CPBA (10.45 g, 60.6 mmol) in chloroform (120 mL) was added a solution of 1,5,9-decatriene (2.10 g, 15.4 mmol) in chloroform (40 mL) at 0 °C. The mixture was allowed to stand for 4 days at 0 °C. Excess peracid was quenched by the addition of a 10% aqueous solution of sodium sulfite until the peracid test paper was negative. The reaction mixture was extracted with chloroform, and the combined extracts were washed with 5% aqueous Na_2CO_3 and water, dried with anhydrous sodium sulfate, and evaporated under reduced pressure. The residual oil was distilled under vacuum to yield **1** (2.03 g) as a colorless liquid. Yield: 71.5%. Bp: 135−136 °C/1.0 mmHg. ^{1}H NMR ($CDCl_3$): δ 1.60−1.85 (m, CH_2, 8H), 2.49−2.53 (m, CH_2O, epoxy) 2.74−2.80, 2.98−3.00 (m, CH, epoxy). ^{13}C NMR ($CDCl_3$): δ 24.12−29.77 (CH_2), 47.00, 47.12 (CH_2, epoxy), 51.55, 51.83, 56.43−56.77, 57.96−58.32 (CH, epoxy). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.30; H, 8.83. Found: C, 65.19; H, 8.75.

(8) Cyclization of 1,2:5,6:9,10-triepoxydecane: To a solution of 1,2:5,6:9,10-triepoxydecane (0.5 g, 2.7 mmol) in water (100 mL) was added potassium hydroxide (0.76 g, 13.6 mmol) in water (10 mL) at 0 °C. After the mixture was stirred at 60 °C for 3 h, the solution was neutralized with 6 N HCl and then concentrated under reduced pressure. The residual oil was purified by column chromatography on SiO_2 using dichloromethane/methanol (9/1) to give 5,5′-bis(hydroxymethyl)octahydro-2,2′-bifuran (**3**) (0.35 g) as a colorless liquid. Yield: 64%. R_f: 0.44. ^{1}H NMR ($CDCl_3$): δ 1.70−2.04 (m, CH_2, 8H), 3.47−3.79 (m, CH_2OH, 8H), 3.79−4.16 (m, CH, 4H). ^{13}C NMR ($CDCl_3$): δ 26.58−29.04 (CH_2), 64.45−65.48 (CH_2OH), 79.91−81.33 (CH), 81.67−82.32 (CH). Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 57.23; H, 8.69.

(9) Methylation of **3**: To a solution of **3** (0.15 g, 0.99 mmol) in dimethyl sulfoxide (1.5 mL) was simultaneously added sodium hydroxide (0.15 g, 3.8 mmol) in water (0.15 mL) and dimethyl sulfate (0.24 g) as the temperature of the mixture did not exceed 60 °C. After for 30 min at 60 °C and then for 10 h at room temperature, the whole was poured into ice−water and extracted with chloroform. The combined extracts were washed with water, dried with anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was purified by flash column chromatography on SiO_2 using diethyl ether to give **4** (0.13 g) as a colorless liquid. Yield: 58%. ^{1}H NMR ($CDCl_3$): δ 1.63−2.06 (m, CH_2, 8H), 3.35−3.46 (m, CH_2O, OCH_3, 10H), 3.85−4.18 (m, CH, 4H). ^{13}C NMR ($CDCl_3$): δ 27.22−28.53 (CH_2), 59.11 (OCH_3), 75.22−75.57 (CH_2O), 78.05−78.26 (CH), 81.20−82.08 (CH). Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.81; H, 9.64.

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