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Synthesis of poly(dibenzo-19-crown-6) via cyclopolymerization of diepoxide

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Summary

Synthesis and cyclopolymerization of 5,6;14,15-dibenzo- 1, 2; 18, 19-diepoxy- 4, 7, 10, 13, 16-pentaoxanonadeca- 5,14-diene(**3**) was carried out. The polymerization of **3** with tin tetrachloride and boron trifluoride etherate gave the polymers with lower molecular weight. Alternatively, triethylaluminium-water-acetylacetone (Vandenberg catalyst) was effective in preparing polymers of high molecular weight which were soluble in *p*-cresol and *p*-chlorophenol. The polymers were essentially composed of cyclic constitutional units corresponding to dibenzo-19-crown-6. The cation-binding ability of the polymer showed the highest selectivity for K^+.

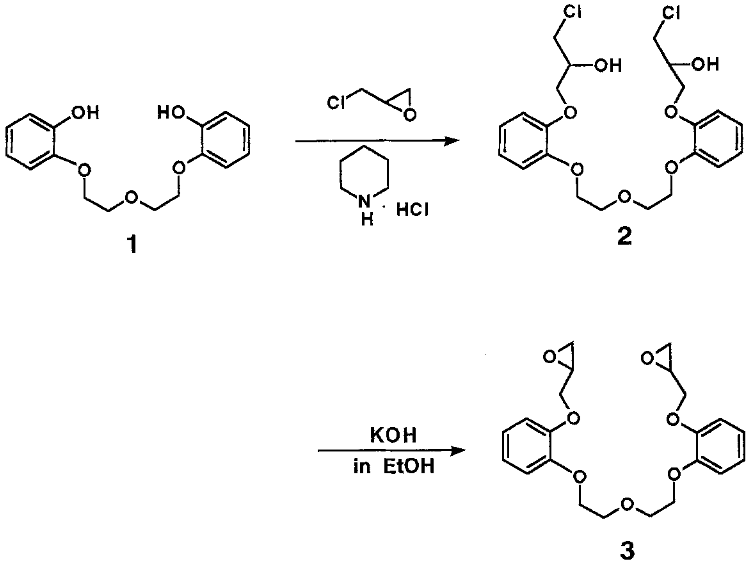
Introduction

Although various methods are used to prepare poly(crown ether)s, the authors have shown that cyclopolymerization is a facile method for preparing polymers with crown-like units, such as crown ethers*(1,2)*, thiacrown ethers*(3)*, crown lactones*(4)*, cryptands*(5)*, and especially chiral crown ethers*(6-11)*. Diepoxides, in addition to divinyl ether, are useful monomers for this purpose.

The diepoxides of suitable structure undergo cyclopolymerization to give linear polymers containing cyclic structural units. The monomers previously studied are 1,2;4,5-diepoxypentane*(12)*, 1,2;5,6-diepoxy-hexane*(12, 13)*, *N,N*-diglycidylaniline*(13)*, and *o*-di(epoxy ethyl)benzene *(14,15)*. Moreover, the cyclopolymerization of 1,2-bis[2-(2,3-epoxypropoxy)ethoxy]benzene was reported to give a polymer containing benzo-16-crown-5 units*(2)*. Recently, poly(benzo-9-crown-3) was synthesized from 1,2-bis(2,3-epoxypropoxy)benzene as well*(16)*. The facile synthesis of poly(crown ether)s from the epoxides gives additional interest to the formation of dibenzo-crown units. In this report, our study has been extended to the cyclopolymerization of 5,6;14,15-dibenzo-1,2;18,19-diepoxy-4,7,10,13,16-pentaoxanonadeca-5,14-diene(**3**).

Results and Discussion

The condensation of 1,2;10,11-dibenzo-1,11-dihydroxy-3,6,9-trioxaundeca-1,10-diene(**1**)(*17*) with 1-chloro-2,3-epoxypropane in the presence of piperidine hydrochloride was carried out at 60°C, and then the resulting chlorohydrin(**2**) was treated with alcoholic potassium hydroxide at -10°C to obtain 5,6;14,15-dibenzo-1,2;18,19-diepoxy-4,7,10,13,16-pentaoxanonadeca-5,14-diene(**3**).



The monomer used is a mixture of three optical isomers which are difficult to separate.

Cationic polymerization of **3** was carried out with $SnCl_4$, $BF_3 \cdot OEt_2$, and triethylalumium-water-acetylacetone(a Vandenberg catalyst)(*18*). Some results of polymerization are listed in Table 1. All the polymerizations proceeded homogeneously. $SnCl_4$, which is an effective initiator, causes an increase in the polymerization rate with increasing polarity of the medium, especially in nitroethane, but $BF_3 \cdot OEt_2$ is obscure in the polarity effect. The products obtained with $SnCl_4$ or $BF_3 \cdot OEt_2$ are sticky semi-solids with lower molecular weight in the range from 1300 to 2100 and with specific viscosity of $\eta_{sp}/c = 0.07 dl \cdot g^{-1}$,

Table 1. **Cyclopolymerization of 5,6;14,15-Dibenzo-1,2;18,19-diepoxy-4,7,10,13,16-pentaoxanonadeca-5,14-diene(3)**

*Catalyst*a)	*Solvent*	*[M]* mol•l^{-1}	*Temp.* °C	*Time* h	*Yield* %	*fc*b) %	$\overline{Mn}$c)	η_{sp}/c $dl{\bullet}g^{-1}$
$SnCl_4$	$C_2H_5NO_2$	0.5	-30	48	73.5	95	2100	-
		0.4			72.6	93	2020	0.07d)
		0.3			56.6	90	1950	-
		0.2			40.4	92	1950	-
	CH_2ClCH_2Cl	0.5			52.1	94	2040	-
	CH_2Cl_2				38.6	87	1730	-
$BF_3{\bullet}OEt_2$	$C_2H_5NO_2$				41.5	82	1300	-
	CH_2ClCH_2Cl				60.7	92	1440	-
	CH_2Cl_2				61.4	86	1320	-
Vandenberge)	$C_6H_5CH_3$	0.5	80	1	24.9	-	-	-
				2	36.6	-	-	-
			50	5	15.3	-	-	1.11f)

a) Molar ratio, **3**/Catalyst=10/1.

b) Extent of cyclization determined by ^{1}H-NMR spectra.

c) Estimated by GPC using poly(styrene) as standard.

d) c=0.26$g{\bullet}dl^{-1}$ in *p*-chlorophenol at 50°C.

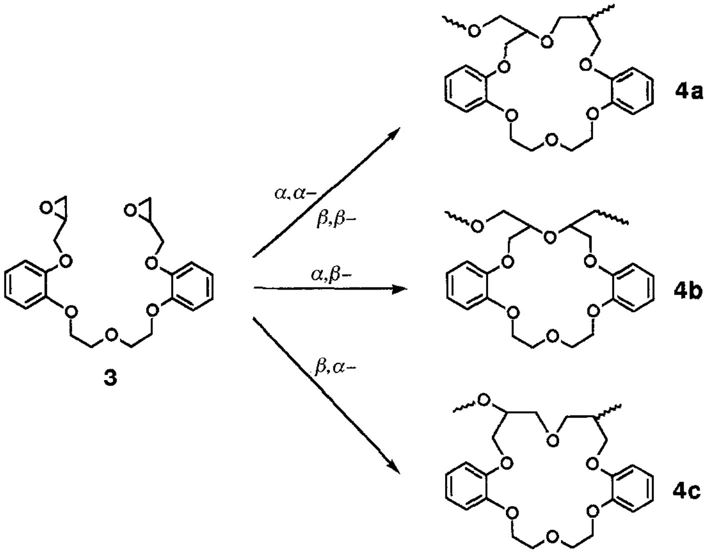
e) Molar ratio, Et_3Al/H_2O/acetylacetone=2/1/1.

f) c=0.27$g{\bullet}dl^{-1}$ in *p*-chlorophenol at 50°C.

and are soluble in methylene chloride, chloroform, and tetrahydrofurane. In the presence of the Vandenberg catalyst, polymerization was occurred in toluene only at higher temperature. The polymer obtained is a white solid, insoluble in methylene chloride, chloroform, and DMSO, and soluble in *p*-cresol and *p*-chlorophenol. This catalyst is effective in preparing polymers of high molecular weight as seen in specific viscosity of $\eta_{sp}/c=1.11 dl{\bullet}g^{-1}$.

The ^{1}H-NMR spectra of the polymers obtained with Lewis acid catalysts showed that the characteristic resonance at δ=2.7 and 3.3 ppm, due to the methylene and the methine protons of the epoxide, can be slightly detected. Since most of the epoxy groups participated in the polymerization forming soluble and gel-free polymers, the polymers should contain cyclic constitutional units formed through a cyclopolymerization mechanism. For the polymerization with $SnCl_4$ and $BF_3{\bullet}OEt_2$, the extent of cyclization changed from 82 to 95% according to the polymerization conditions. In the CP/MAS-NMR spectrum of the polymer obtained with the Vandenberg catalyst, only a trace of the characteristic resonance at 44.7ppm, due to the methylene carbon of the epoxide, appeared. Therefore, the polymer also possesses cyclic constitutional units.

Ring-opening of mono-substituted epoxides occurs in two ways, i.e. by α- or β- scissions*(19)*. In the polymerization of **3** the intramolecular cyclization with α,α- or β,β-scissions of two epoxides forms 19-membered rings(**4a**), whereas α,β- and β,α-scissions leads to the formation of 18- and 20-membered rings(**4b** and **4c**), respectively.



Because many epoxides have shown to subject to both α- and β-scissions under acidic conditions, the polymer **4** obtained with ordinary acid catalyst may represent a mixture of three possible cyclic units. The random orientation of ring opening, however, gives 50% of dibenzo-19-crown units, **4a**, as main constitutional units. In the polymerization of propylene oxide with the coordinating catalyst, ring opening of epoxide has been found to be occurred predominantly in β-position*(18,20)*, suggesting, therefore, the polymer prepared with the Vandenberg catalyst contains essentially dibenzo-19-crown-6 units. It appears well established that the polymerization of **3** gives the cyclic polymer mainly consisting of dibenzo-19-crown-6 units, namely poly(dibenzo-19-crown-6).

The CH_2Cl_2-soluble polymer prepared with $SnCl_4$ in nitroethane was used for extraction of alkali metal picrates. The cation-binding ability of polymer **4** compares with those of a monomeric crown ether, dibenzo-18-crown-6, in Table 2. The former is slightly less

Table 2. Extraction of alkali picrates by using polymer 4[a)]

Complexing agent	% *Picrate extracted*				
	Li^+	Na^+	K^+	Rb^+	Cs^+
Polymer **4**	6.3	31.4	82.2	77.4	67.5
Dibenzo-18-crown-6	3.7	18.3	93.5	84.9	81.6

[a)] Extractability(Ex %) of the picrates from aqueous solution into methylene chloride. The aqueous solution contained 0.1M metal hydroxide and $7x10^{-5}M$ picric acid. The methylene chloride was of equal volume and was $3.5x10^{-3}M$ in complexing agent.

effective and selective in binding for cation than the latter. The cation-binding ability of polymer **4** compares with those of poly(benzo-16-crown-5) and poly(benzo-19-crown-6) prepared by the cyclopolymerization of diepoxide(*2*) and divinyl ether(*1*), respectively. The highest selectivity for K^+ is the same with polymer **4** as with dibenzo-18-crown-6. Poly(benzo-16-crown-5) also showed the highest selectivity for K^+, but poly(benzo-19-crown-6) for Rb^+.

Epoxide have a chiral center. Further studies in order to synthesis a chiral crown polymer *via* cyclopolymerization of chiral diepoxy monomer are presently in progress.

Experimental part

General: ^1H-NMR spectra were recorded with a Hitachi R90H FT-NMR spectrometer. CP/MAS-NMR spectrum was obtained on a Brucker MSL 400 instrument. Gel permeation chromatography(GPC) in tetrahydrofuran was performed on a WATERS M45 high performance liquid chromatograph equipped with three columns(Shodex KF-804F). UV spectra were recorded on a Shimazu UV-210 spectrometer.

Materials: Methylene chloride, 1,2-dichloroethane, and nitroethane were dried over CaH_2 and distilled before use for polymerization. Toluene was distilled from sodium-benzophenone. Dibenzo-18-crown-6 was prepared by the method of Pedersen(*21*).

5,6;14,15-dibenzo- 1,2;18,19-diepoxy-4,7,10,13,16- pentaoxanonadeca-5,14-diene(**3**): A mixture of 1,2;10,11-dibenzo-1,11-dihydroxy-3,6,9-trioxaundeca-1,10-diene hydrate(**1**)(*17*)(27.2g, 88.2mmol), 1-chloro-2,3-epoxypropane(65.3g, 706mmol), and piperidine hydrochloride (0.09g, 0.78mmol) was heated at 60°C for 38h. The removal of excess 1-chloro-2,3-epoxypropane give 5,6;14,15-dibenzo-

1,19-dichloro-2,18-dihydroxy-4,7,10,13,16-penta-oxanonadeca-5,14-diene (**2**) which was used without further purification.

To a stirred solution of absolute ethanol(110ml) containing KOH(11.9g, 211.7mmol) added a solution of **2** (88.2mmol) in absolute ethanol (110ml) for 1h at -10 °C. After this temperature being maintained for 1h, the precipitated sodium chloride was filtered off, the alcoholic solution was concentrated, and the residue was dissolved in water and extracted with dichloromethane. Recrystallization from methanol gave a product(5.0g, 32%) of m.p. 70.5-71.8 °C.

IR(KBr): 3050, 2990(ν, epoxy), 2920, 2875(ν, C-H), 1585, 1502, 1445(ν, C=C), 1253, 1219(ν_{as}, Ar-O-C), 1121(ν_{as}, C-O-C), 1020(ν_{s}, Ar-O-C), 908, 853(ν_{as}, epoxy), 739(δ, benzene ring C-H).

^{1}H-NMR($CDCl_3$): δ=2.71(d•d, 2H, epoxy methylene), 2.84(d•d, 2H, epoxy methylene), 3.33(m, 2H, epoxy methine), 3.90-4.32(m, 12H, oxy-methylene), 6.92(s, 8H, arm.).

^{13}C-NMR($CDCl_3$): δ=149.11, 148.72, 122.15, 121.62, 115.4, 114.86 (aromatic carbons), 70.40, 69.95, 68.95(oxymethylene carbons), 50.29 (methine carbon of epoxy group), 44.70(methylene carbon of epoxy group).

$C_{22}H_{26}O_7$ (402.43)	Calc.	C	65.66	H	6.51
	Found	C	65.42	H	6.61

Polymerization of 3 with $SnCl_4$ and BF_3•OEt_2: The solvent and **3** were weighed to a glass ampul. The catalyst solution was charged to the ampul at -30°C. After standing for 48h at this temperature, the polymer were worked up by precipitation in excess methanol and then dried in vacuum.

$(C_{22}H_{26}O_7)_n$ $(402.43)_n$	Calc.	C	65.66	H	6.51
	Found	C	63.35	H	6.42

Polymerization of 3 with the Vandenberg catalyst(18): A dried toluene and **3** were charged into an ampul. The ampul was then cooled in liquid nitrogen, evacuated, sealed, and then placed in a constant temperature bath. The polymers was obtained by precipitation in methanol and then dried in vacuum.

Cation-binding ability: The extraction of metal picrate was carried out using a similar procedure as the one developed by Pedersen*(22)*.

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