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Synthesis of polymers with benzo-13-crown-4 and benzo-9-crown-3 units via cyclopolymerization

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SUMMARY

Polymers containing crown ether units were synthesized by cyclopolymerization of divinyl and diepoxide monomers. These are 1,2-bis-(2-ethenyloxyethoxy)-benzene **(1)** and 1,2-bis-(2,3-epoxypropyl)-benzene **(3)** producing polymers with 13 and 9-membered rings **4** and **5**, respectively. Both the monomers and polymers were characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy. Finally, the polymers were contacted with an aqueous solution of lithium chloride.

INTRODUCTION

Crown ether units have been introduced into the polymer chain by various methods. Cyclopolymerization, which does not need a derivative of a crown ether as monomer is a direct and facile method where the rings and polymer chains are formed at the same time. Some reports have been published on the cyclopolymerization of diepoxy and divinyl compounds (1-5).

Several types of polymers with crown ether and cryptand units have also been synthesized by step-growth polymerization (6,7), by chain-growth polymerization (8,9), and by polymer analogous reactions (10). Until recently, however, very little has been published on the synthesis via cyclopolymerization. This paper reports on the cyclopolymerization of 1,2-bis-(2-ethenyloxyethoxy)-benzene **(1)** and 1,2-bis-(2,3-epoxypropyl)-benzene **(3)** and on the cation-binding characteristics of the resulting poly(crown ether)s.

EXPERIMENTAL PART

Synthesis of 1,2-bis-(2-ethenyloxyethoxy)-benzene (1).

To a solution of 5.5 g (0.05 mol) of catechol and 4.0 g (0.10 mol) of sodium hydroxide in 20 ml of dimethyl sulfoxide was added dropwise 12 g (0.112 mol) of 2-chloroethylvinyl ether with stirring at 70°C. Heating was continued for 20 h, after an excess of water was added. A dark brown solid product was obtained. The pure product was obtained by crystallization from light-petroleum (b.p. 50-70°C). Yield 64%; m.p. 45°C.

Synthesis of 1,2-bis-(3-chloro-2-hydroxipropyl)-benzene (**2**).

Method 1: A solution of 55 g (0.5 mol) of catechol in 185 g (2 mol) of epichlorohydrin containing piperidine hydrochloride (0.5 g), was heated on the steam-bath for 20 h. After removal of excess epichlorohydrin at reduced pressure, distillation of the residue in vacuo yielded 12 g (8%) of **2** as an oil, b.p. 194°C/0.5 mmHg. The oil solidified gradually and then crystallized from a mixture of benzene-light petroleum (b.p. 40-60°C) as white needles, m.p. 62-65°C.

Method 2: The mixture used in the preceding method was left at room temperature for 40 days and the product distilled in vacuo, **2** was obtained in 90% yield, b.p. 160°C/0.001 mmHg.

Synthesis of 1,2-bis-(2,3-epoxypropyl)-benzene (**3**).

When **2** was stirred vigorously for 1 h with a slight excess of ethanolic potassium hydroxide, it was converted into diepoxy (**3**) in 99% yield; white needles from light-petroleum (b.p. 40-60°C) m.p. 50-55°C.

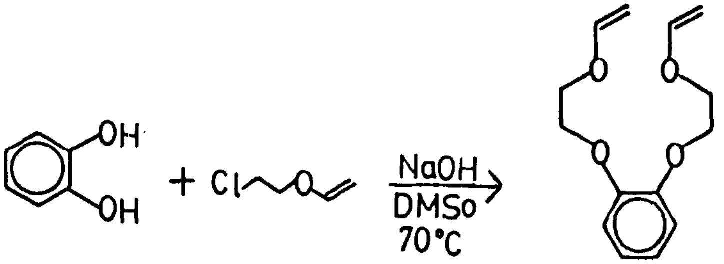
Polymerization of 1 and 3: The cationic polymerizations were initiated with boron trifluoride etherate. The conditions and results are given in Table 1.

Cation binding ability: The extraction of lithium was carried out in a solid-liquid system. The polymers were contacted for 8 h with a solution of lithium chloride.

Measurements: The IR spectra were recorded on a Perkin Elmer 577 spectrophotometer. The ^1H NMR and ^{13}C NMR spectra were recorded in a 60 MHz Varian T-60 A, and 20 MHz Varian CFT spectrometer, respectively. Lithium was analyzed on a Perkin Elmer 306 Atomic Absorption Spectrometer.

RESULTS AND DISCUSSION

The monomers were synthesized from catechol, 2-chloro-ethylvinyl ether and epichlorohydrin. The synthesis of 1,2-bis-(2-ethenyloxyethoxy)- benzene (**1**) is dependent of solvent polarity. In THF reaction was not observed, however, in DMSO **1** was obtained in 64%.



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The ^{1}H NMR spectrum of 1 (C_6D_6, room temperature, 60 MHz and TMS), shows a multiplet and a doublet between δ =3.87-4.27 ppm assigned to methylene and terminal vinylic protons, respectively (12H). The quartet at δ=6.23-6.63 ppm is attributed to other type of vinylic protons (2H, -CH=, Jcis=7 Hz and Jtrans=14 Hz) and the singlet at 6.73 ppm corresponds to the aromatic protons (4H).

The ^{13}C NMR spectrum (C_6D_6, room temperature, 20 MHz and TMS), shows 7 signals that corroborate the structure of 1 which has a plane and C_2 axis of symmetry. The signal at 152.12 ppm is assigned to the vinylic (-CH=) carbons. The three signals at 149.58, 122.14 and 115.79 ppm were assigned to the aromatic carbons. At 86.98 ppm appears a signal corresponding to terminal vinylic carbons (=CH_2) and at 68.23 and 66.96 ppm two signals assigned to the methylene carbons (see figure 1).

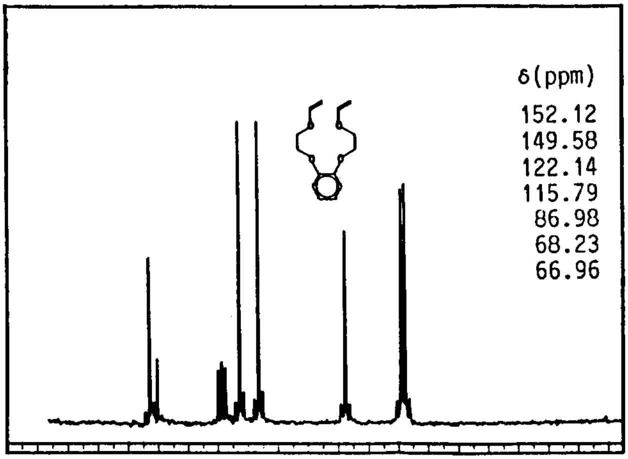
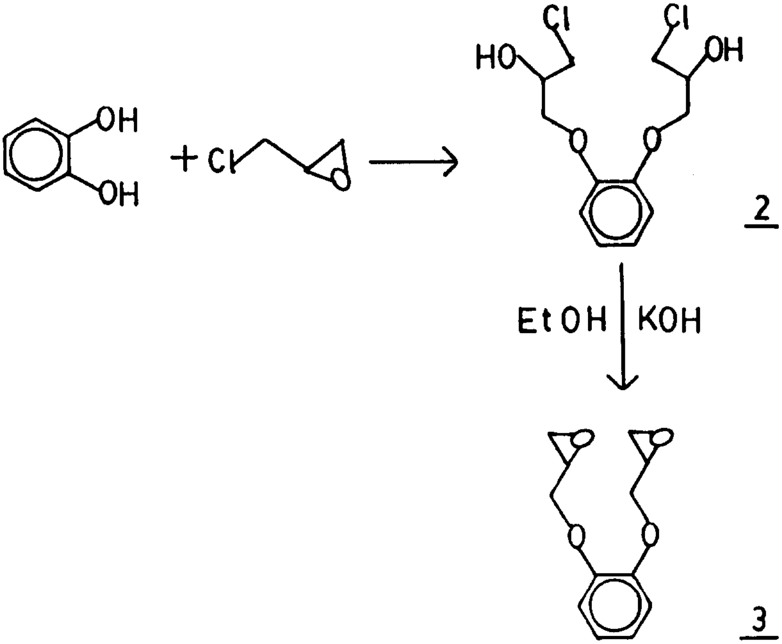


Figure 1: ^{13}C NMR of 1,2-bis-(2-ethenyloxyethoxy)-benzene (1).

With respect to 1,2-bis-(2,3-epoxypropyl)-benzene (3), two methods were attempted but in both cases we obtained the 1,2-bis-(3-chloro-2-hydroxipropyl)-benzene (2) intermediate. When 2 was treated with KOH in ethanol at room temperature 3 was formed in 99% yield.

The IR spectrum of 2 presents characteristic absorption bands correspoding to νOH at 3400 cm^{-1} and νC-Cl at 750 cm^{-1}. These bands are not present in the IR spectrum of 3.

The ^{1}H NMR spectrum of 3 shows a multiplet (4H) at 2.37 ppm assigned to the methylene protons of the epoxy ring. At 3.10 ppm there is other multiplet (2H) corresponding to the methyne protons of the epoxy function. In the region between 3.53-4.10 ppm a third multiplet is observed (4H) assigned to the methylene protons of the ether function, and at 6.90 ppm a singlet (4H) corresponding to the aromatic protons.



^{13}C NMR spectroscopy supports structure 3 showing 6 signals. The three signals at 149.49, 122.04 and 115.50 ppm were assigned to the carbons of the aromatic ring. The signal at 70.57 ppm was assigned to the methylene carbons of the ether function; the two signals at 49.98 and 43.92 ppm correspond to the methyne and methylene carbons, respectively, of the epoxy ring (see figure 2).

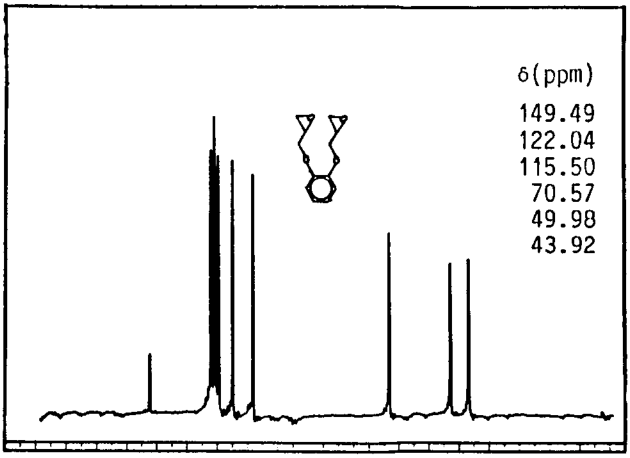
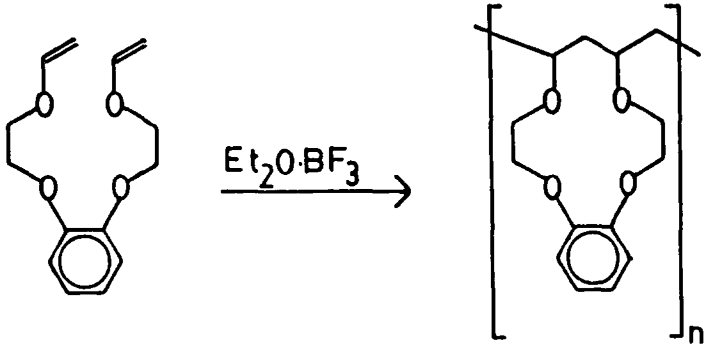


Fig. 2: ^{13}C NMR of 1,2-bis-(2,3-epoxypropyl)-benzene (3).

Synthesis of polymers.

The cationic polymerization, initiated with boron trifluoride etherate, of the monomers **1** and **3** produces polymers with benzo-13-crown-4 (4) and benzo-9-crown-3 (5) units, respectively.



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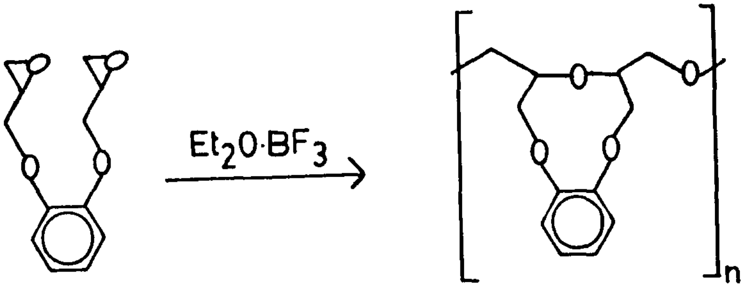

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Some typical results of cationic polymerization are given in Table 1.

Table 1. Polymerization of 1,2-bis-(2-ethenyloxyethoxy)-benzene (**1**) and 1,2-bis-(2,3-epoxypropyl)-benzene (**3**).

Monomers	Solvent	Temp. (°C)	Time (h)	Conv. (%)
1	$CH_3CH_2NO_2$	20	8	60.9
	$CH_3CH_2NO_2$	0	8	95.0
3	$CH_3CH_2NO_2$	-27	48	49.8
	$CH_3CH_2NO_2$	-10	48	20.0
	$CH_3CH_2NO_2$	0	48	-
	CH_2Cl_2	-27	48	74.0
	CH_2Cl_2	-10	48	35.0
	CH_2Cl_2	0	48	10.0

In all cases the reaction systems were homogeneous. With respect to monomer **1** an insoluble polymer was formed at 20°C. It is a yellow solid insoluble in water and common organic solvents. The polymer obtained at 0°C is a yellow powder, soluble in organic solvents.

Monomer **3** was polymerized in methylene chloride and nitroethane to give a white solid soluble in common organic solvents. The best yields were obtained in methylene chloride and at lower temperatures.

The IR spectra of polymers **4** and **5** indicate the absence of vinyl groups at 985 and 910 cm^{-1}, and the absence of epoxy groups at 912 and 860 cm^{-1}, respectively. Since vinyl and epoxy groups participate in the polymerization, the resulting products should contain cyclic units formed by cyclopolymerization.

The polymers were used for extraction of lithium chloride. Table 2 illustrates the cation-binding abilities of the polymers.

Table 2. Extraction of LiCl

Polymers	pH	Extraction (%)
4 (20°C)	7	5.5
4 (0°C)	7	3.6
5	7	1.6

The cation-binding ability of the insoluble polymer **4** obtained at 20°C, is higher than that of the soluble polymers. The ring size of the cyclic units in the polymer 5 is smaller than 4, therefore, its binding ability is small.

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