Polymer Bulletin 27, 599–605 (1992)

Polymer Bulletin

# Synthesis of poly(hemispherand) via cyclopolymerization of diepoxide

**Toyoji Kakuchi[1],*, Osamu Haba[1], Yasuhiro Harada[1], Hisaho Hashimoto[2], and Kazuaki Yokota[1]**

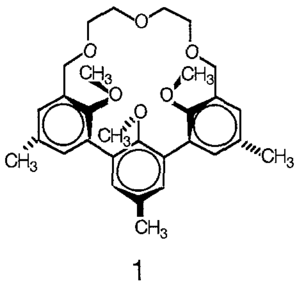
[1]Department of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan
[2]Department of Industrial Chemistry, Tomakomai National College of Technology, Nishikioka 443, Tomakomai 059-12, Japan

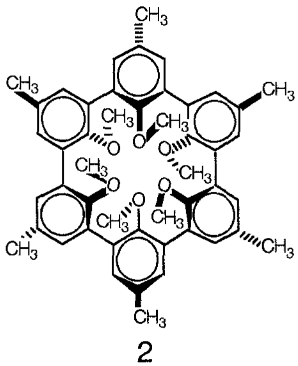
## Summary

Cyclopolymerization of 2,6-bis[3-(4,5-epoxy-2-oxapentyl)-2-methoxy-5-methylphenyl]-4-methylanisole was carried out with cationic, anionic, and coordination catalysts. The polymers obtained with $BF_3$•$OEt_2$ or $SnCl_4$ in dichloromethane and with *t*-BuOK in DMSO were soluble in benzene, chloroform, and THF. The mole fractions of the cyclic units in these polymers were from 0.65 to 0.75. The resulting poly(hemispherand) bound alkali metal cations and the selectivity was in the order of $Rb^+ > K^+ > Cs^+ > Na^+ > Li^+$.

## Introduction

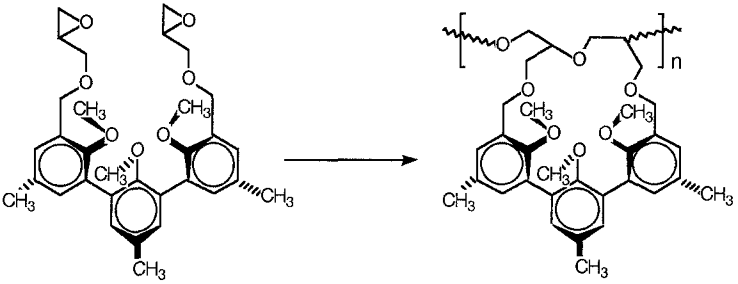
Since the discovery of dibenzo-18-crown-6 [1], many kinds of macrocyclic systems have been designed and synthesized as hosts in host-guest chemistry [2]. Hemispherand (**1**) and spherand (**2**), which are based on 2,6-disubstituted 4-methyl anisole units, are classified as a group of host compounds. They are organized prior to complexation and form a capsular complex with a cationic guest [3]. In polymer chemistry, various polymers with crown ether or other macrocyclic units are synthesized and their host abilities are examined in the appropriate host-guest systems [4]. However, there has been no attempt to prepare polymers with **1** or **2** unit. In this paper, we report the synthesis and the


1


2

---

*To whom offprint requests should be sent cyclopolymerization of diepoxide, 2,6-bis[3-(4,5-epoxy-2-oxapentyl)-2-methoxy-5-methylphenyl]-4-methylanisole (**3**), and the cation binding property of the resulting poly(hemispherand) (**4**).



3 4

## Results and Discussion

Table 1 gives some results of the polymerization of diepoxide **3** with cationic, anionic and coordinate catalysts. The polymerizations with $BF_3{\bullet}OEt_2$ or $SnCl_4$ in dichloromethane and with *t*-BuOK in DMSO proceed homogeneously. The resulting polymers are white powders and are soluble in chloroform, benzene, and THF. The number average molecular weights ($\overline{Mn}$) are from 8,300 to 12,500 which correspond to the polymerization degree from 15.5 to 23.4. In nitroethane, however, monomer **3** tends to form a gel during the polymerizations with $BF_3{\bullet}OEt_2$ or $SnCl_4$. Potassium hydroxide, which was the effective initiator for the

**Table 1.** Cyclopolymerization of 2,6-bis[3-(4,5-epoxy-2-oxapentyl)-2-methoxy-5-methylphenyl]-4-methylanisole (**3**) [a]

| Catalyst (C) | Solvent | [M] $mol{\bullet}l^{-1}$ | Temp. °C | Time h | Yield % | fc[b] | $\overline{Mn}$[c] $x10^{-3}$ |
|---|---|---|---|---|---|---|---|
| $BF_3{\bullet}OEt_2$ | $CH_2Cl_2$ | 0.5 | -30 | 24 | 17.8 | 0.65 | 8.3 |
| | | 0.2 | | 11day | 14.6 | 0.75 | 11.3 |
| | $C_2H_5NO_2$ | 0.5 | | 24 | gelation | | |
| $SnCl_4$ | $CH_2Cl_2$ | 0.5 | | 24 | 7.6 | 0.67 | 9.7 |
| | $C_2H_5NO_2$ | 0.5 | | 24 | gelation | | |
| *t*-BuOK | DMSO | 0.5 | r.t. | 7 | 7.8 | 0.65 | 12.5 |
| KOH | DMSO | 0.5 | r.t. | 7day | 0 | - | - |
| Vandenberg[d] | $C_6H_5CH_3$ | 0.5 | 80 | 2 | 5.3 | - | - |

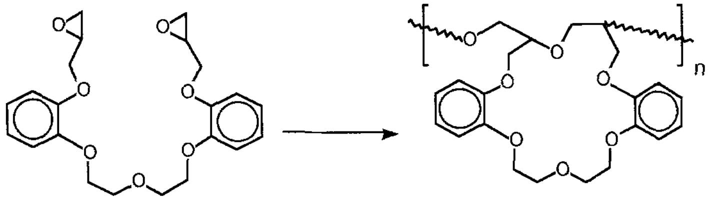
a) [M] / [C] = 10 / 1.

b) Mole fraction of cyclic structural units in the polymers were determined by $^1$H-NMR analysis.

c) Determined by GPC.

d) $2AlEt_3 / H_2O / CH_3COCH_2COCH_3$

polymerization of diepoxide **5** [5], does not perform the initiation of **3**. In the presence of the Vandenberg catalyst ($2AlEt_3$ / $H_2O$ / $CH_3COCH_2COCH_3$), the polymerization system is homogeneous but the polymer obtained is insoluble in chloroform, THF, *p*-chlorophenol, and other common organic solvents. The polymer from **5** with this catalyst had a significantly higher viscosity than that with cationic ones [5]. With regard to **3**, the insolubility is accordingly caused not by the presence of a three-dimensional network structure in the polymer but by its higher molecular weight.



5

6

Figure 1 shows the $^1$H-NMR spectra of monomer **3** and its polymer obtained with *t*-BuOK. In the spectrum of the polymer, the characteristic resonance due to the methylene protons of the epoxy groups at 2.6 and 2.8 ppm diminished after polymerization. On the other hand, a broad absorption appeared at 3.3-3.9 ppm due to the polymer main chain was apparently observed. Because the epoxy groups significantly participated during the polymerization giving gel-free, soluble polymers, they should contain cyclic constitutional units formed through a cyclopolymerization mechanism.

The residual epoxy groups were observed, and hence the resulting

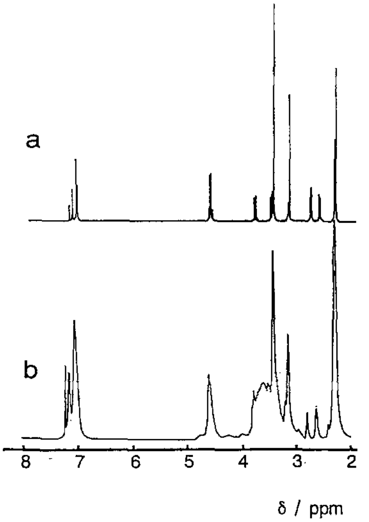
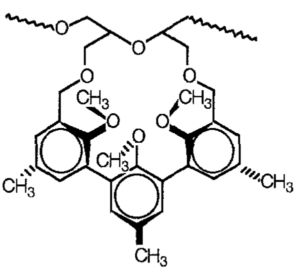


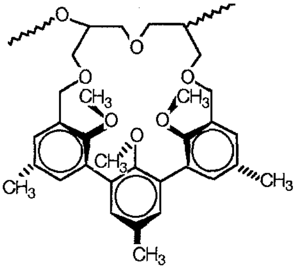
**Figure 1**. $^1$H-NMR spectra of monomer 3 (a) and its polymer obtained with *t*-BuOK in DMSO (b).

polymers consist of the cyclic and the pendant units. This was confirmed by the $^1$H-NMR resonance except for the epoxy groups. The two resonances of the inner methoxy protons at 3.15 and 3.20 ppm correspond to the cyclic and the pendent units, respectively. The dependence of the mole fraction of the cyclic structural units (*fc*) on the monomer concentration ([M]) is generally found in cyclopolymerization. In the case of **3**, *fc* increases from 0.65 and 0.67 for [M] of 0.5mol•l$^{-1}$ to 0.75 for 0.2mol•l$^{-1}$. On the other hand, the polymerization of **5** gave the polymer mainly consisting of dibenzo-19-crown-6 units, poly(dibenzo-19-crown-6) (**6**), whose *fc* was 1.0 even at a [M] of 0.5mol•l$^{-1}$. The lower cyclopolymerization tendency of **3** is caused by its sterically crowded structure being composed of three *p*-anisole units.

The polymerization of monosubstituted epoxides proceeds through ring-opening at the CH-O and/or the $CH_2$-O bonds ($\alpha$- and $\beta$-bonds). During the polymerization of **3** the intramolecular cyclization with $\alpha,\alpha$- or $\beta,\beta$-scissions of the two epoxides forms 19-membered rings (**4**), whereas $\alpha,\beta$- and $\beta,\alpha$-scissions leads to the formation of 18- and 20-membered rings (**7** and **8**), respectively. The cationic catalyst cleaves at both the $\alpha$ and $\beta$ positions to yield polymers having a mixture of three possible cyclic units, **4**, **7**, and **8**. The random orientation of ring-opening forms the main constitutional units with at least 50% of the 19-membered hemispherand, **4**, as the main cyclic units. On the other hand, an anionic catalyst cleaves the $\beta$ bond. The polymer prepared with *t*-BuOK therefore contains the 19-membered hemispherand (**4**) as the cyclic constitutional units.



7



8

The $CH_2Cl_2$-soluble polymer obtained with $BF_3$•$OEt_2$ in $CH_2Cl_2$ (*fc*=0.65) was used for the experiment of alkali metal picrates-extraction. The cation-binding property of polymer **4** compares with hemispherand **1** which corresponds closely to the cyclic units in **4**, and with those of poly(dibenzo-19-crown-6) (**6**) and dibenzo-18-crown-6 (**9**), in Figure 2. The selectivity which is estimated by the extraction equilibrium constant (Kex) [7] is in the order of $Rb^+ > K^+ > Cs^+ > Na^+ > Li^+$ for **4**, $Na^+ > K^+ > Rb^+ > Cs^+ > Li^+$ for **1**, and $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$ for **6** and **9**. Polymer **6** is slightly less selective and effective in binding for cation than **9**, whereas polymer **4** is noticeably less than **1**. These results indicate that the

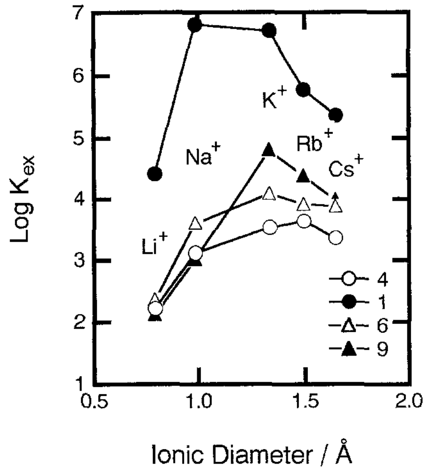


**Figure 2.** Logarithmic plots of extraction equilibrium constant ($K_{ex}$) of hemispherand (**1**), poly(hemispherand) (**4**), poly(dibenzo-19-crown-6) (**6**), and dibenzo-18-crown-6 (**9**) toward alkali metal cations. [picric acid] = $3.5\times10^{-5}$ M, [metal hydroxide] = 0.1 M, [**1**] = $3.5\times10^{-5}$ M, [**4**] = $7\times10^{-3}$ M, [**6**] = [**9**] = $3.5\times10^{-4}$ M.

hemispherand units in **4** do not act as the preorganized spherical cavity like **1**. The chemical shifts of the outer methoxy protons for **1**, **3**, and **4** were almost same, showing in Table 2. On the other hand, the upfield shift of the inner from the outer methoxy protons for **1** is larger than those for **3** and **4**. The larger upfield shift for **1**, which is found in the other hemispherands, reflects that the three methoxy oxygens possess the down-up-down arrangement, which preorganizes the spherical cavity for **1** [8, 9]. On the other hand, the smaller upfield shift for the cyclic units in **4** as well as the acyclic compound, **3**, indicates that the arrangement of the three methoxy oxygens in the cyclic units for **4** is not suitable for the formation of the spherical cavity as in **1**.

These results suggest that the enforced structure of the cavity is different between poly(hemispherand) **4** prepared *via* the cyclopolymerization method and hemispherand **1**, and consequently, it has been necessary to design the monomer further.

**Table 2.** Chemical shifts of the inner and the outer methoxy protons for hemispherand **1**, monomer **3**, and poly(hemispherand) **4**

| | Chemical shift, δ in ppm | |
|---|---|---|
| | inner -$OCH_3$ | outer -$OCH_3$ |
| Hemispherand **1**$^{a)}$ | 2.56 | 3.39 |
| Monomer **3** | 3.20 | 3.49 |
| Poly(hemispherand) **4** | 3.15 (cyclic units)<br>3.20 (pendant units) | 3.42 |

a) ref. [7].

## *Experimental Section*

**Measurements.** $^1$H and $^{13}$C-NMR spectra were recorded with a Bruker MSL 400 instrument. UV spectra were recorded on a Jasco 660 UV/VIS spectrophotometer. The molecular weights of the resulting polymers were measured by gel permeation chromatography (GPC) in tetrahydrofuran on a WATERS M45 high-performance liquid chromatography equipped with three polystyrene gel columns (Shodex KF-804L).

**Materials.** $BF_3$•$OEt_2$ and $SnCl_4$ were purified by distillation of commercial products under reduced pressure. KOH and *t*-BuOK (1.0M solution in tetrahydrofuran) were purchased from Aldrich. Triethylaluminum ($AlEt_3$) was kindly supplied from Toyo Stauffer Chemical Co., Ltd. and used without further purification. Dichloromethane, nitroethane, and dimethylsulfoxide (DMSO) were purified by the usual methods and distilled over calcium hydride.

**2,3,4,5,6,7,8,9,10-Tris[1,3-(2-methoxy-5-methylbenzo)]-12,15,18-trioxa-cyclooctadeca-2,5,8-triene (1)** was prepared according to the method reported by Cram *et al.* [8].

**2,6-Bis[3-(4,5-epoxy-2-oxapentyl)-2-methoxy-5-methylphenyl]-4-methylanisole (3).** A mixture of 40 mL of 50 % w/w aqueous sodium hydroxide, 40 mL of epichlorohydrin, and 1 g of tetrabutylammonium hydrogen sulfate was vigorously stirred at room temperature. To the mixture was added 6.9 g (16.4 mmol) of 2,6-bis(3-hydoxymethyl-2-methoxy-5-methylphenyl)-4-methylanisole [8] with cooling in ice so that the temperature did not exceed 25 °C. After 5 h, the reaction mixture was poured onto an ice/water. The aqueous phase was extracted with dichloromethane. The organic phase was washed with brine, dried with sodium sulfate, filtered, and evaporated under vacuum. The residue was purified by flash chromatography on silica gel (silica gel 60, 230-400 mesh, Merck) with ether/hexane (v/v, 7:3) to give 6.3 g (72 %) of **3** as a colorless oil. $^1$H-NMR(400MHz, $CDCl_3$); $\delta$=2.34 (s, outer $ArCH_3$, 6H), 2.36 (s, 3H, inner $ArCH_3$), 2.64 (d•d, $J_{gem}$=5.1Hz, $J_{trans}$=2.7Hz, 2H, epoxy $CH_2$), 2.81 (d•d, $J_{gem}$=4.9Hz, $J_{cis}$=4.3Hz, 2H, epoxy $CH_2$), 3.20 (s, 3H, inner $CH_3O$), 3.21-3.23 (m, 2H, epoxy CH), 3.49 (s, 6H, outer $CH_3O$), 3.53 (d•d, $J_{gem}$=11.4Hz, $J_{vic}$=5.9Hz, 2H, $ArCH_2OC\underline{H}_2$), 3.83 (d•d, $J_{gem}$=11.4Hz, $J_{vic}$ =3.1Hz, 2H, $ArCH_2OC\underline{H}_2$), 4.65 (AB, $J_{gem}$ =11.6Hz, 2H, $ArCH_2$), 4.69 (AB, $J_{gem}$ =11.6Hz, 2H, $ArCH_2$), 7.14 (d, $J$ =2.0Hz, 2H, ArH), 7.16 (s, 2H, ArH), 7.23 (d, $J$ =1.9Hz, 2H, ArH). $C_{32}H_{38}O_7$(534.65); Calcd: C, 71.89; H, 7.16, Found: C, 71.21; H, 7.20.

**Polymerizations.** The polymerizations with $BF_3$•$OEt_2$ and $SnCl_4$ were carried out in dichloromethane and nitroethane at -30 °C, and with KOH and *t*-BuOK in DMSO at room temperature. For the Vandenberg catalyst ($2AlEt_3$ / $H_2O$ / $CH_3COCH_2COCH_3$), toluene was used as solvent. The resulting polymers were purified by reprecipitation from chloroform-methanol.

**Mole fraction of cyclic structural units (*fc*).** The mole fraction of cyclic structural units in the polymers was determined from the relative areal ratio of the residual epoxy and the phenyl protons in the $^1$H-NMR spectra.

**Cation-binding property.** A solution of host compound in $CH_2Cl_2$ was vigorously shaken in a culture tube with a solution of alkali hydroxide and picric acid in water. After separating into two phases, the amount of alkali picrate extracted into dichloromethane was determined by measuring absorbance of picrate remaining aqueous phase at 357 nm on UV-spectrophotometer. Experimental conditions are presented in Figure 2. The extraction equilibrium constant ($K_{ex}$) was calculated according to the equation reported by Frensdorff [7].

## ***References***

1. C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 2495 (1962)
2. "*Host Guest Complex Chemistry / Macrocycles*", ed. by F. Vögtle, E. Waber, Springer-Verlag, Berlin 1985
3. J. A. Bryant, R. C. Helgeson, C. B. Knobler, M. P. deGrandpre, D. J. Cram, *J. Org. Chem.*, **55,** 4622 (1990)
4. a) J.Smid, *Ind. Eng. Chem. Prod. Res.Dev.*, **19**, 364 (1980)
   b) T.Kakuchi, O.Haba, K.Yokota, *Makromol. Chem.*, **192**, 1601 (1991) and references cited therein.
5. H. Hashimoto, T. Kakuchi, K. Yokota, *Polym. Bull.*, **25**, 153 (1991)
6. P.E.Parker, N.S.Isaacs, *Chem.Rev.*, **59**, 758 (1959)
7. H. K. Frensdorf, *J. Amer. Chem. Soc.*, **93**, 4684 (1971)
8. K. E. Koenig, G. M. Lein, P. Stuckler, T. Kaneda, D. J. Cram, *J. Amer. Chem. Soc.*, **101**, 3553 (1979)
9. G. M. Lein, D. J. Cram, *J. Amer. Chem. Soc.*, **107**, 448 (1985)

Accepted December 13, 1991 S