Cyclopolymerization of (2*S*,3*S*,4*S*,5*S*)-1,2:5,6-Diepithio-3,4-dimethoxyhexane Leading to a Novel Polymer with a Cyclic Sulfide Unit Possessing High Ag^+- and Cu^{2+}-Binding Characteristics

Toshifumi Satoh, Daisuke Kitazawa, Hisaho Hashimoto,[†] and Kazuaki Yokota*

Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060, Japan

Toyoji Kakuchi*

Division of Bioscience, Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060, Japan

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In host−guest chemistry, various types of host molecules have been studied. Our ongoing interest is the macromolecular design and synthesis of host polymers having molecular discrimination properties using the cyclopolymerization method.[1−6] Diepoxide is one of the monomers, as are divinyl ethers, which can be used for the cyclopolymerization to form poly(crown ether)s.[2] Diepisulfide is easily derived from diepoxide and polymerized to produce poly(thia crown ether). There was a distinct different in the cation-binding property between poly(crown ether) and poly(thia crown ether) acting as hard and soft bases, respectively.[3] Recently, we reported that (1→6)-2,5-anhydrohexitol was synthesized by the highly regio- and stereoselective cyclopolymerization of 1,2:5,6-dianhydrohexitol and showed molecular recognition properties toward appropriate cationic guests.[7−14] Therefore, of great interest is the cyclopolymerization tendency of optically active 1,2:5,6-diepithiohexane derived from 1,2:5,6-dianhydrohexitol along with the molecular recognition properties of the resulting polymer. Here we report the cationic and anionic cyclopolymerizations of (2*S*,3*S*,4*S*,5*S*)-1,2:5,6-diepithio-3,4-dimethoxyhexane (**1**) leading to polymers with (2*R*,3*S*,4*S*,5*S*)-1-thiacyclopentane units, exhibiting high Ag^+- and Cu^{2+}-binding abilities.

Monomer **1** is obtained from the reaction of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-L-iditol (**3**) with potassium thiocyanate.[3,15,16] In the reaction, the inversion of configurations at the C-2- and C-5-epoxy carbons of **3** occurs. Thus monomer **1** has the C_2 symmetric character as well as the starting diepoxide **3**. Monomer **1** is a white solid with the specific rotation ($[\alpha]^{22}_{546}$) of −37.9° (*c* 0.88 in $CHCl_3$).

Scheme 1

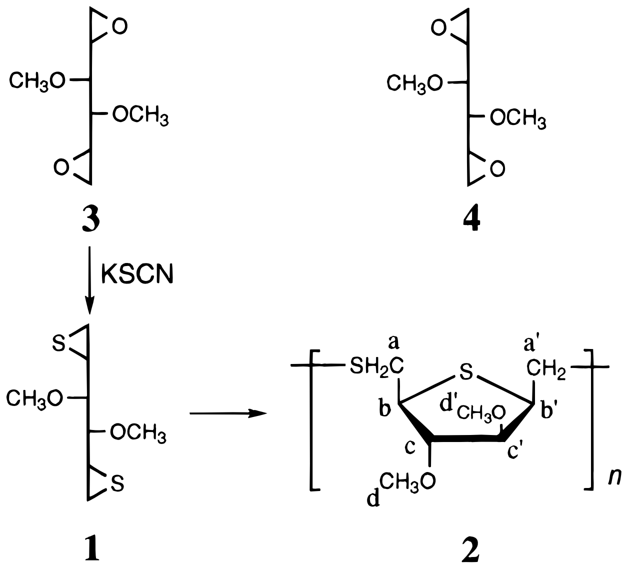

Table 1. Cationic and Anionic Polymerizations of (2*S*,3*S*,4*S*,5*S*)-1,2:5,6-Diepithio-3,4-dimethoxyhexane (1)

catalyst	[**1**]/[cat.]	time, h	yield, %	10^3M_n[a]	M_w/M_n[a]	DP	$[\alpha]^{22}_{546}$[b]
$BF_3{\cdot}OEt_2$[c]	10	48	27.2	3.3	2.2	16	+10.8
	20	48	24.5	3.5	2.1	17	+11.7
	40	48	17.2	3.9	1.7	19	+10.1
t-BuOK[d]	10	0.5	91.1	11.8	1.8	57	+24.9
	20	0.5	86.2	20.9	1.9	101	+23.4
	40	5	86.6	47.7	2.2	231	+22.9

[a] Measured in $CHCl_3$ by GPC using PSt as a standard. [b] *c* 1.0 chloroform. [c] $BF_3{\cdot}OEt_2$ catalyst system: [M] = 0.5 mol·L^{-1}, temperature 0 °C, solvent CH_2Cl_2. [d] *t*-BuOK catalyst system: [M] = 0.2 mol·L^{-1}, temperature 60 °C, solvent THF.

The polymerization of **1** was done using $BF_3{\cdot}OEt_2$ as the cationic catalyst.[17] Table 1 lists the results of the polymerization. The cationic polymerization in CH_2Cl_2 proceeded homogeneously without gelation. The obtained polymers **2** were white powders and soluble in chloroform, sparingly soluble in tetrahydrofuran, and insoluble in methanol. The number-average molecular weights (M_n's) ranged from 3300 to 3900, corresponding to the degree of polymerization (DP) of 16−19. An anionic catalyst, *t*-BuOK, was also effective,[18] and the obtained polymers were similar in character to those produced by the cationic one. The anionic polymerization in tetrahydrofuran was gradually converted to a heterogeneous system as the reaction progressed, and the polymer was obtained in about 90% yield. The M_n's of polymers **2** proportionally increased with the [monomer]/[catalyst] molar ratio. The yields, M_n's, and specific rotations of polymers **2** were higher for the polymerization with *t*-BuOK than for that with $BF_3{\cdot}OEt_2$.

In all polymers, the epithio group was not detected in the ^1H and ^{13}C NMR measurements. This indicates both the cationic and anionic polymerizations of **1** proceeded according to a cyclopolymerization mechanism, thus leading to the polymers with cyclic constitutional repeating units. Figure 1 shows the ^{13}C NMR spectra of polymers **2** obtained using $BF_3{\cdot}OEt_2$ and *t*-BuOK. Eight main peaks were found in Figure 1A, in which four signals at 86.51, 86.13, 50.74, and 50.39 ppm were assigned to the methine carbons, two signals at 37.60 and 31.97 ppm to the methylene ones, and two signals at 57.94 and 57.40 ppm to the methoxy ones. For polymers **2** obtained using $BF_3{\cdot}OEt_2$, the proportion of the main constituent was about 80%, which is estimated by ^{13}C NMR using the inverse gated spin decoupling technique. The signals due to the main constituent were also found in polymers **2** obtained with *t*-BuOK, and the proportion was about 60% (Figure 1B). The ^{13}C NMR measurements showed that the cationic cyclopolymerizations with $BF_3{\cdot}OEt_2$ are more stereospecific than the anionic one with *t*-BuOK.

In analogy with the cyclopolymerization of the diepoxide, 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-mannitol (**4**),[8,9] the cationic and anionic cyclopolymerizations of

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* To whom correspondence should be addressed. Tel: +81-11-706-6605. Fax: +81-11-706-6602. E-mail: satoh@cfa.hokudai.ac.jp.

[†] Department of Science and Engineering of Materials, Tomakomai National College of Technology, Nishikioka 443, Tomakomai 059-12, Japan.

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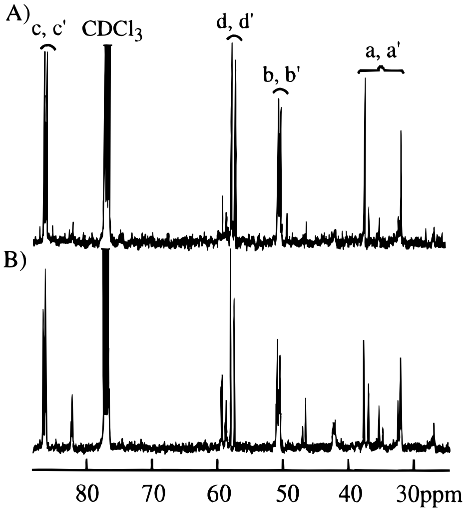
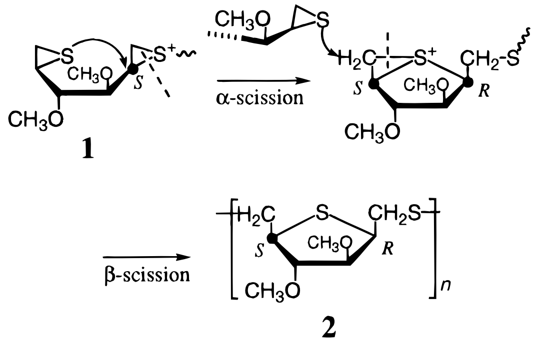


Figure 1. ^{13}C NMR spectra of polymers prepared from (2*S*,3*S*,4*S*,5*S*)-1,2:5,6-diepithio-3,4-dimethoxyhexane using (A) $BF_3{\cdot}OEt_2$ and (B) *t*-BuOK.

Scheme 2



monomer **1** hold the possibility for forming four kinds of recurring units, that is, a five-, two six-, and a seven-membered ring, by the ring-opening modes of two episulfides in a monomer. The cyclopolymerization of monomer **4** being a parent monomer of **1** produced the polymer consisting of a five-membered ring unit. The ^{13}C NMR spectrum of polymer **2** (Figure 1) shows each of the three pairs of carbons (b and b′ c and c′, and d and d′) situate in similar surroundings and two methylene carbons (a and a′) in different surroundings. Therefore, the structure consisting of a five-membered cyclic sulfide, i.e., (2*R*,3*S*,4*S*,5*S*)-3,4-dimethoxy-1-thiacyclopentane, is most suitable for the observation. This is also confirmed on the basis of the comparison between the ^{13}C NMR spectra in Figure 1 and that of the *O*-analog.[9] The chemical shifts for C-3, C-4, and the OCH_3 groups, respectively, are about the same for both polymers, whereas the carbon atoms (C-1, -6, -2, -5) bearing sulfur atoms resonate at about 30−37 ppm upfield, as expected for the assignments proposed. The several weak peaks shown in Figure 1A,B should be attributed to other structures, such as six- or seven-membered ring units. The detailed analysis for the polymer structure is now being investigated, and more details will be published in the near future.

A comparison between parts A and B of Figure 1 indicates that the cationic cyclopolymerization was more regio- and stereospecific than the anionic one. The cationic mechanism is presented in Scheme 2. The intramolecular cyclization occurs via the ring opening of the first episulfide with inversion (*S* → *R*) of the configuration by an S_N2 attack of the second episulfide (α-scission). The ring opening of the second episulfide takes place at the β-carbon with retention (*S* → *S*) of the configuration on the asymmetric carbon atoms (β-scission). The attack at the β-carbon is sterically favored during the intermolecular propagation. The anionic polymerization also primarily proceeded through the α- and β-scissions of the intra- and intermolecular reactions, respectively, though it contained small proportions of the other cyclic units besides the five-membered cyclic sulfide unit.

Polymer **2** containing the ether and sulfide groups as hard and soft donors, respectively, is of high interest concerning cation-binding characteristics. The cation-binding property was evaluated by the solvent extraction method using CH_2Cl_2/H_2O systems.[19] The polymer with a M_n of 3500, prepared with $BF_3{\cdot}OEt_2$, showed extraction yields less than 10% for Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}, as well as for the alkali metal ions. However, the extraction yields for Ag^+ and Cu^{2+} were more than 99%. Polymer **2** was more effective in binding metal ions belonging to soft acids. The metal ions belonging to the borderline acids were unfavorable, but Cu^{2+} was favorable. The binding characteristics differed essentially from those of (1→6)-2,5-anhydro-3,4-di-*O*-methyl-D-glucitol synthesized by the cyclopolymerization of **4**.

In conclusion, a new sulfur-containing polymer was synthesized by the cationic and anionic cyclopolymerizations of the diepisulfide (2*S*,3*S*,4*S*,5*S*)-1,2:5,6-diepithio-3,4-dimethoxyhexane. Although the polymerizability of the monomer was higher for the polymerization with *t*-BuOK than for that with $BF_3{\cdot}OEt_2$, the stereoregularity of the polymer was higher in that with $BF_3{\cdot}OEt_2$ than in that with *t*-BuOK. The polymer is mainly composed of five-membered cyclic units, i.e., the (2*R*,3*S*,4*S*,5*S*)-3,4-dimethoxy-1-thiacyclopentane unit. The higher cation-binding ability for Ag^+ and Cu^{2+} was observed in the polymer. This indicates that the characteristics of the polymer with the sulfide group are like a soft base that has a high affinity for a soft acid. Further work concerning the molecular discrimination property is in progress.

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(16) Monomer **1** was prepared from **3** and KSCN by a previously reported procedure.[3,15] The obtained crude product was

purified by column chromatography on Florisil (100−200 mesh) with toluene (R_f 0.3). The product was distilled using a Kugelrohr apparatus before polymerization.

(17) Cationic polymerization procedure: Monomer **1** (0.41 g, 2.0 mmol) was dissolved in dry CH_2Cl_2 (4.0 mL), and $BF_3{\cdot}OEt_2$ in CH_2Cl_2 (130 μL in 0.77 mol·L^{-1}, 0.10 mmol) was added using a microsyringe at 0 °C. After 48 h, the reaction mixture was poured into a large amount of methanol containing a drop of aqueous ammonia, and the precipitated polymer was filtered off. The residue was washed with methanol several times and then dried under vacuum to give the polymer (101 mg, 24.5%).

(18) Anionic polymerization procedure: The polymerization was carried out in an H-shaped glass ampule. *t*-BuOK (21.7 mg, 0.19 mmol) and dry THF (2.0 mL) were added to one side of the ampule, and **1** (0.4 g, 1.94 mmol) was added to the other side under a nitrogen atmosphere. After sealing under a vacuum, the monomer and the catalyst solution were mixed at 60 °C. After 30 min, the reaction mixture was poured into a large amount of methanol, giving the polymer (364 mg, 91.1%).

(19) Metal extraction was carried out as follows: For Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and alkali ions, the aqueous phase contained 5 mL of 1.0×10^{-2} M metal chloride and 7.0×10^{-5} M picric acid in water and the organic phase contained 5 mL of methylene chloride with 5.75×10^{-3} M/repeating unit of the polymer. The procedure for Cd^{2+}, Ag^{+}, and Pb^{2+} used the metal nitrate instead of the metal chloride. Transported guest salts were followed by measuring the UV absorbance at 357 nm for the organic phase.

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