Polymeric Chiral Crown Ethers. 8. Synthesis of Optically Active Poly(dibenzo-19-crown-6)s via Cyclopolymerization of Diepoxides[†]

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ABSTRACT: Chiral diepoxides, (2*R*,18*R*)-(−)- and (2*S*,18*S*)-(+)-5,6:14,15-dibenzo-1,2:18,19-diepoxy-4,7,10,13,16-pentaoxanonadeca-5,14-diene [(*R*,*R*)-(−)-1 and (*S*,*S*)-(+)-1], were synthesized enantiomerically and polymerized with a Lewis acid and KOH. All the polymers obtained were soluble in $CHCl_3$ and consisted essentially of cyclic repeating units. The CD spectra of polymers from (*R*,*R*)-(−)-1 showed a positive Cotton effect, while the polymers from (*S*,*S*)-(+)-1 presented a mirror image CD curve with a negative Cotton effect. The polymers obtained with KOH possessed higher stereoregularity than those with a Lewis acid. The stereochemistries of polymers from (*R*,*R*)-(−)- and (*S*,*S*)-(+)-1 with KOH were poly[(*R*,*R*)-dibenzo-19-crown-6] and poly[(*S*,*S*)-dibenzo-19-crown-6], respectively. Polymers 2 and 8 obtained from (*S*,*S*)-(+)-1 with $SnCl_4$ and KOH, respectively, formed the host–guest complex dominantly with the D-isomers of phenylglycine, phenylalanine, and methionine methyl esters. The optical purities of guests extracted by the both polymers were as low as values ranging from 0.5 to 5.4%. For every host–guest system, the chiral recognition property of polymer 8 was higher than that of polymer 2.

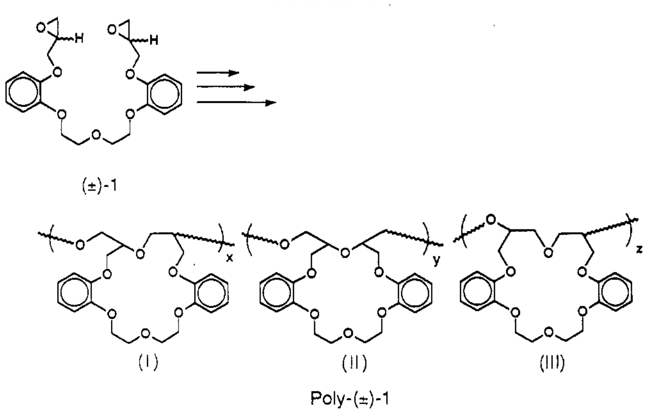
Introduction

Although chiral crown ethers are important hosts in host–guest chemistry, limited works have reported polymers with chiral crown ether units.[1] We have established that optically active poly(crown ether)s are easily synthesized through the cyclopolymerization of divinyl ethers incorporating (*R*)- and (*S*)-1,1′-bi-2-naphthol,[2] D-mannitol,[3] L-threitol,[4] and altro-, galacto-, gluco-, and mannopyranoside[5] residues, in which the crown ethers exhibit a chiral recognition ability toward the α-amino acid.

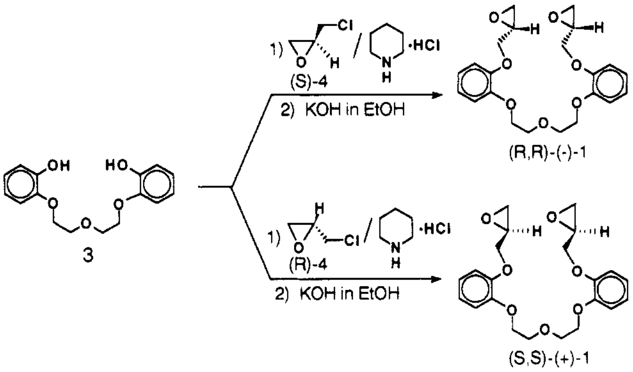
Optically active macromolecules have been reported to be synthesized by many methods.[6] For the cyclopolymerization system, therefore, a suitable design and the controlled polymerizations of bifunctional monomers may produce chiral polymeric crown ethers. Diepoxide is one of the monomers, as in the case of chiral divinyl ethers, that can be used for the cyclopolymerization forming polymers with crown ether units.[7,8] For example, optically inactive 5,6:14,15-dibenzo-1,2:18,19-diepoxy-4,7,10,13,16-pentaoxanonadeca-5,14-diene [(±)-1] was polymerized with anionic, cationic, and Vandenberg catalysts to yield polymers with dibenzo-19-crown-6 (I) as the main unit and dibenzo-18-crown-6 (II) and dibenzo-20-crown-6 (III) as the minor ones, as shown in Scheme I.[9] The present study then aims at the preparation of polymeric chiral crown ethers through regio- and stereospecific cyclopolymerization of the enantiomerically pure diepoxides.

This paper reports the preparation of (*R*,*R*)-(−)- and (*S*,*S*)-(+)-1 using chiral epichlorohydrin, as shown in Scheme II, the cyclopolymerization of them with cationic and anionic initiators, the stereoregularity and the chiroptical property of the resulting polymers, and their chiral recognition property toward methyl esters of α-amino acid.

Scheme I



Scheme II



Experimental Section

Materials. (*R*)-(−)- and (*S*)-(+)-epichlorohydrin [(*R*)- and (*S*)-4] were obtained from Daiso Co., Ltd., and their optical purities are more than 98% ee. Boron trifluoride etherate ($BF_3{\cdot}OEt_2$) and tin(IV) chloride ($SnCl_4$) were purified by distillation of commercial products under reduced pressure. Potassium hydroxide (KOH) was obtained from Kanto Chemical Co., Inc., and used without further purification. Nitroethane and dimethyl sulfoxide were purified by the usual methods and distilled over calcium hydride.

Measurements. ^1H and ^{13}C NMR spectra were recorded with a Bruker MSL 400 instrument. UV spectra were recorded on a Jasco 660 UV/vis spectrophotometer. Optical rotations were made with a Jasco DIP-140 digital polarimeter. CD spectral measurements were carried out at 25 °C in hexafluoroisopropyl alcohol (HFIP) with a sample of 0.5 mg/1 mL using a Jasco J-720 spectropolarimeter. The path length of the cell was 0.1 cm.

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Table I
Cyclopolymerization of (2*R*,18*R*)-(−)-, (2*S*,18*S*)-(+)-, and (±)-5,6:14,15-Dibenzo-1,2:18,19-diepoxy-4,7,10,13,16-pentaoxanonadeca-5,14-diene ((*R*,*R*)-(−)-1, (*S*,*S*)-(+)-1, and (±)-1)[a]

monomer	initiator (I)	[1]/[I]	solvent	temp, °C	time, day	polymer	yield, %	f_c,[b] %	$\bar{M}_n$[c]	$[\alpha]^{25}_{435}$[d]
(*R*,*R*)-(−)-1	$SnCl_4$	10	$C_2H_5NO_2$	−30	2	1	>99.9	100	1400	−4.4
(*S*,*S*)-(+)-1						2	85.5	100	3900	+4.3
(±)-1						3	73.5	95	2100	
(*R*,*R*)-(−)-1	$BF_3{\cdot}OEt_2$	10	$C_2H_5NO_2$	−30	2	4	77.5	100	2500	−4.7
(*S*,*S*)-(+)-1						5	50.8	100	2500	+4.0
(±)-1						6	41.5	82	1300	
(*R*,*R*)-(−)-1	KOH	5	$(CH_3)_2SO$	rt	7	7	96.5	100	3200	+5.0
(*S*,*S*)-(+)-1						8	78.7	100	2500	−6.0
(±)-1						9	79.3	100	2400	

[a] [1] = 0.5 mol·L^{-1}. [b] Mole fraction of cyclized units in the polymer. [c] Measured in THF for polymers 1–6 and in chloroform for polymers 7–9. [d] c = 1.0 g·dL^{-1}, $CHCl_3$.

X-ray diffraction profiles were obtained in a Rigaku–Denki Geigerflex D-3F apparatus with monochromatized Cu Kα radiation. Differential scanning calorimetry was performed with a Seiko SSC 5200 thermal analysis system. The molecular weights of the resulting polymers were measured by gel permeation chromatography (GPC) in tetrahydrofuran on a Waters M45 high-performance liquid chromatograph equipped with three polystyrene gel columns (Shodex KF-804) and in chloroform on a Shodex DS-4 with two columns of Shodex K-801 and K-802.5. The number-average molecular weight ($\bar{M}_n$) was calculated on the basis of a polystyrene calibration.

Monomer. The syntheses of chiral diepoxides [(*R*,*R*)-(−)- and (*S*,*S*)-(+)-1] followed the reported procedure for the enantiomeric and diastereomeric mixtures of 1 ((±)-1).[9]

(2*R*,18*R*)-(−)-5,6:14,15-Dibenzo-1,2:18,19-diepoxy-4,7,10,13,16-pentaoxanonadeca-5,14-diene [(*R*,*R*)-(−)-1]. A mixture of 8.3 g (28.6 mmol) of 1,2:10,11-dibenzo-1,11-dihydroxy-3,6,9-trioxaundeca-1,10-diene (**3**), 20 g (216 mmol) of (*S*)-(+)-epichlorohydrin [(*S*)-**4**], and 28.3 mg (0.24 mmol) of piperidine hydrochloride was heated at 60 °C for 40 h. The excess (*S*)-4 was removed under reduced pressure (recovered in 60%) to give bischlorohydrin as a syrup, which was used without further purification. $[\alpha]^{26}_D = +11.2°$ (c = 0.9, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 3.6–4.2 (m, 18 H, aliphatic), 6.91 (s, 8 H, aromatic).

To the bischlorohydrin in 36 mL of absolute ethanol was added a solution of 3.85 g (68.6 mmol) of KOH in 30 mL of absolute ethanol at −10 °C, and the mixture was stirred at this temperature. After 1 h, the reaction mixture was diluted with water and dichloromethane. The organic layer was separated, washed with water, dried with anhydrous Na_2SO_4, and evaporated in vacuum. The residue was purified by recrystallization from methanol to give 5.6 g of (*R*,*R*)-(−)-1 (yield 48%) as a white powder. Mp: 91.3–92.9 °C. $[\alpha]_D = -0.64°$, $[\alpha]_{435} = +1.22°$, $[\alpha]_{405} = +2.60°$. (c = 1.28 in $CHCl_3$, 24 °C). ^1H NMR ($CDCl_3$): δ 2.71 (dd, 2 H, epoxy $-CH_2-$), 2.84 (dd, 2 H, epoxy $-CH_2-$), 3.33 (m, 2 H, $-CH-$), 3.90–4.32 (m, 12 H, $-OCH_2-$), 6.92 (s, 8 H, aromatic). ^{13}C NMR ($CDCl_3$): δ 149.11, 148.72, 122.15, 121.62, 115.4, 114.86 (aromatic), 70.40, 69.95, 68.95 ($-OCH_2-$), 50.29 ($-CH-$), 44.70 (epoxy $-CH_2-$). IR (KBr): 3050, 2990 (ν, epoxy), 2920, 2875 (ν, CH), 1585, 1502, 1445 (ν, C=C), 1253, 1219 (ν_{as}, ArOC), 1121 (ν_{as}, COC), 1020 (ν_s, ArOC), 908, 853 (ν_{as}, epoxy), 739 (δ, benzene ring CH). Anal. Calcd for $C_{22}H_{26}O_7$: C, 65.66; H, 6.51. Found: C, 65.42; H, 6.54.

(2*S*,18*S*)-(+)-5,6:14,15-Dibenzo-1,2:18,19-diepoxy-4,7,10,13,16-pentaoxanonadeca-5,14-diene [(*S*,*S*)-(+)-1]. The procedure for (*R*,*R*)-(−)-1 was applied to 4.2 g (14.3 mmol) of 3 and 10 g (108 mmol) of (*R*)-(−)-4 to give 3.2 g (yield 56%) of (*S*,*S*)-(+)-1 as a white powder. Mp: 91.6–93.2 °C. $[\alpha]_D = +0.96°$, $[\alpha]_{435} = -1.07°$, $[\alpha]_{405} = -2.88°$ (c = 1.21 in $CHCl_3$, 28 °C). The ^1H and ^{13}C spectra of (*S*,*S*)-(+)-1 were identical with those of (*R*,*R*)-(−)-1. Anal. Calcd for $C_{22}H_{26}O_7$: C, 65.66; H, 6.51. Found: C, 65.36; H, 6.47.

Polymerizations. Cationic Polymerization. A solution of 0.8 g (2 mmol) of 1 in 4 mL of nitroethane was placed in the ampule with a septum-capped side arm and cooled to −30 °C. To the solution was added 24 μL (0.2 mmol) of $BF_3{\cdot}OEt_2$ through the side arm. After 2 days at −30 °C, the reaction mixture was poured into 200 mL of methanol containing a small amount of triethylamine. The methanol-insoluble polymers were purified by reprecipitation from chloroform–methanol and dried under vacuum for 48 h. For the polymerization with $SnCl_4$, it was used as solutions in dichloromethane or nitroethane (2.5 mol·L^{-1}).

Anionic Polymerization. To a slurry of 20 mg (0.4 mmol) of powdered KOH in 4 mL of dimethyl sulfoxide was added 0.8 g (2 mmol) of 1 at room temperature. After stirring for 7 days, the reaction mixture was poured into a large amount of methanol. The purification of the resulting polymers was carried out with the same procedure as used for the cationic ones.

Mole Fraction of the Cyclic Structural Units (f_c). The mole fraction of the cyclic structural units in the polymers was determined from the relative peak areas of the protons in the ^1H NMR spectra.

Chiral Recognition toward the Methyl Ester of α-Amino Acid. The procedure for the chiral recognition of chiral polymers was carried out as described in a previous paper.[5]

Results and Discussion

Synthesis of Chiral Poly(dibenzo-19-crown-6)s. Some results of the polymerizations of (*R*,*R*)-(−)- and (*S*,*S*)-(+)-1 and of the enantiomeric and diastereomeric mixtures of 1 ((±)-1) that were reported previously[9] are listed in Table I. The cationic polymerization of 1 with $BF_3{\cdot}OEt_2$ and $SnCl_4$ in nitroethane at −30 °C proceeded homogeneously up to high conversion. The resulting polymers were sticky, semisolid, and soluble in chloroform and tetrahydrofuran. The number-average molecular weights ($\bar{M}_n$) of the polymers varied in the range from 1300 to 3900 which corresponded to the polymerization degrees ($\bar{P}_n$) from 3 to 10.

The anionic polymerization was carried out with KOH in dimethyl sulfoxide (DMSO) at room temperature. The polymerization of chiral 1 was heterogeneous, while that of (±)-1 was homogeneous. The powdery polymers obtained were soluble in chloroform but only slightly soluble in tetrahydrofuran; this is different from the solubility of polymers obtained with cationic initiators. The $\bar{M}_n$s of polymers were from 2400 to 3200.

The lower $\bar{P}_n$s of the polymers obtained with cationic and anionic initiators (I) should be caused by the lower ratio of 1 and I such as [1]/[I] = 5 or 10. However, the polymer yields were extremely decreased with the increase of [1]/[I], and the unreacted monomers were recovered and the $\bar{P}_n$s of the polymers obtained were still low. The reactivity of these diepoxides should be effected by the five oxygens in the monomers, but this must be further investigated.

The ^1H NMR spectra of (*R*,*R*)-(−)-1, its polymer obtained with KOH (polymer 7), and the polymer of (±)-1 obtained with $SnCl_4$ (polymer 3) are shown in Figure 1. The characteristic absorption at 2.5–3.3 ppm due to the epoxy group disappeared in the ^1H NMR spectra of polymer 7 and other polymers. This result indicates that the polymers consist essentially of cyclic constitutional repeating units. On the other hand, the ^1H NMR spectra

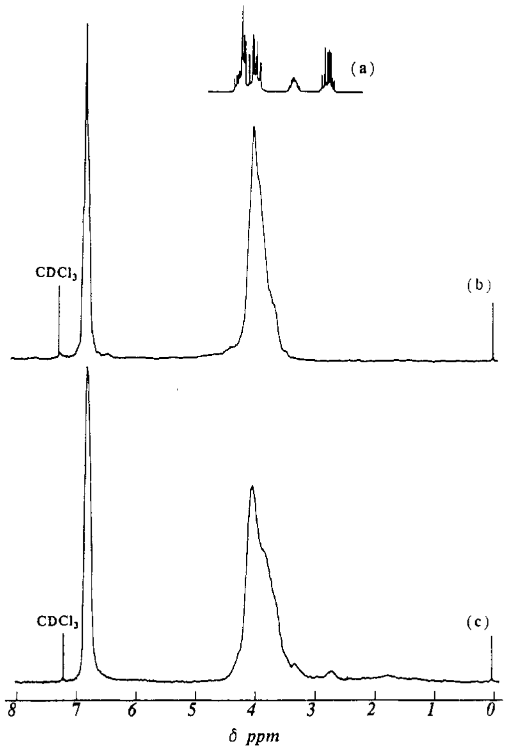

Figure 1. ^{1}H NMR spectra of (a) (*R*,*R*)-(−)-1, (b) polymer 7 obtained from (*R*,*R*)-(−)-1 with KOH, and (c) polymer 3 obtained from (±)-1 with SnCl$_4$.

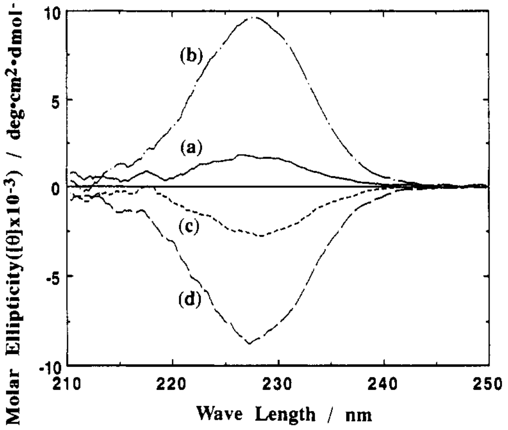

Figure 2. X-ray diffraction profiles of polymers 7 (a) and 9 (b) obtained from (*R*,*R*)-(−)-1 and (±)-1 with KOH, respectively.

of the polymers obtained from the cationic polymerization of (±)-1 (polymers 3 and 6) showed residual epoxy groups, and the mole fractions of cyclic units in polymers 3 and 6 were 95 and 82%, respectively. These results indicate that the cyclopolymerization tendency differs between the meso and the racemic compounds of 1, but this problem must be further investigated.

Figure 2 shows the X-ray diffraction profiles of the polymers obtained from (*R*,*R*)-(−)- and (±)-1 with KOH (polymers 7 and 9). The profile of polymer 7 shows a relatively sharp reflection at $2\theta = 19.5°$ and small ones at $2\theta = 14.0°$ and 22.5°, which could be overlaid on an amorphous halo center at $2\theta = 20.5°$ observed for polymer 9. The weight-average crystallinity in polymer 7, which is calculated on the basis of the ratio between the integral intensities of the crystalline and amorphous scatterings, was found to be 21 wt %. The crystallinity in polymer 7 was also confirmed by the differential scanning calorimetry measurement in which a sharply endothermic peak corresponding to a melting point was observed at 129 °C.

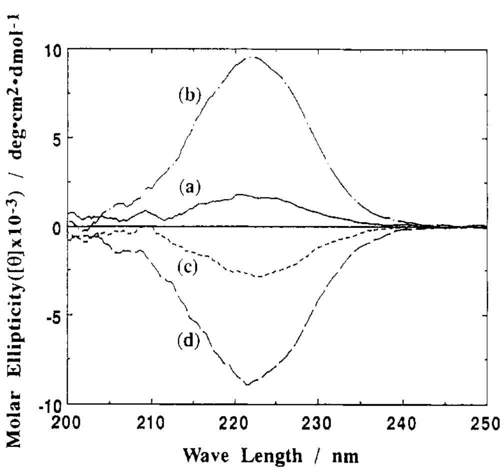

Figure 3. CD spectra of polymers 1 (a) and 7 (b) obtained from (*R*,*R*)-(−)-1 with SnCl$_4$ and KOH, respectively, and polymers 4 (c) and 8 (d) obtained from (*S*,*S*)-(+)-1 with SnCl$_4$ and KOH, respectively.

These results indicate that (*R*,*R*)-(−)- and (*S*,*S*)-(+)-1 with KOH undergo a regio- and stereospecific ring-opening polymerization to produce stereoregular polymers, i.e., mesodiisotactic polymers.

(*R*,*R*)-(−)-1 yielded polymers with negative optical rotations ($[\alpha]^{25}{}_{435} = -4.4°$ and −4.7°) by cationic polymerization (polymers 1 and 4) and polymers with positive ones ($[\alpha]^{25}{}_{435} = +5.0°$) by anionic polymerization (polymer 7). The reverse is the case of (*S*,*S*)-(+)-1, which yielded the polymers with optical rotations of the same absolute values and the reverse sign for each polymerization.

The chiroptical property of the polymeric chain is determined using the CD spectral measurement (Figure 3). The CD spectra of polymers from (*R*,*R*)-(−)-1 (polymers 1 and 7) show a positive Cotton effect with a maximum at 228 nm, while the polymers from (*S*,*S*)-(+)-1 (polymers 4 and 8) present nearly a mirror image CD curve with a negative Cotton effect. Taking the same sign of the Cotton effect, both polymers, which were obtained by cationic and anionic polymerizations of one enantiomer, should consist of the constitutional units with the same configuration. The absolute values of the molar ellipticity ($[\theta]^{25}{}_{228}$) for polymers 7 and 8 were 3–5 times larger than those for polymers 1 and 4. This means that the polymers obtained with KOH have a higher stereoregularity than those with cationic initiators.

The polymerization of monosubstituted epoxides proceeds through ring opening at the CH–O and/or the CH$_2$–O bonds (α- and β-bonds).[10] During the polymerization of 1 the intramolecular cyclization with α,α- and β,β-scissions of the two epoxides forms 19-membered rings (I), whereas α,β- and β,α-scissions lead to the formation of 18- and 20-membered rings (II and III), respectively. The ring-opening polymerization with an anionic initiator occurs almost exclusively at β, thereby retaining the configuration of the asymmetric carbon atom and producing pure head-to-tail polymers. The polymer prepared with KOH, therefore, contains essentially dibenzo-19-crown-6 (I) as cyclic constitutional units. The stereochemistries of polymers from (*R*,*R*)-(−)-1 and (*S*,*S*)-(+)-1 are mesodiisotactic polymers with high optical activity, namely, poly[(*R*,*R*)-dibenzo-19-crown-6] and poly[(*S*,*S*)-dibenzo-19-crown-6], respectively, as shown in Scheme III.

On the other hand, the cationic catalyst cleaves at α and β to yield the polymers having a mixture of three possible cyclic units, I–III. The random orientation of ring opening forms the main constitutional units with at least 50% of I. The polymers obtained with cationic initiators, in fact,

Scheme III

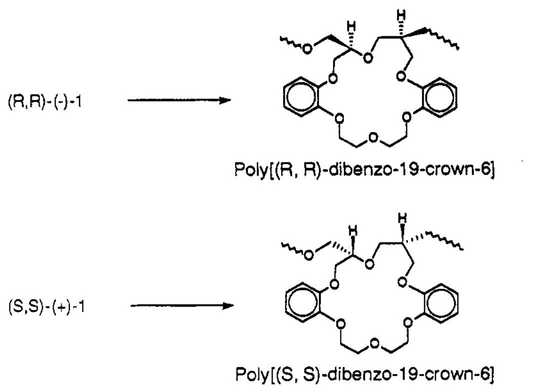

Table II
Chiral Recognition Ability of Host Polymers 2 and 8 toward Racemic Guest $RCH(CO_2CH_3)NH_3^+PF_6^-$ [a]

	polymer 2			polymer 8		
	guest in CH_2Cl_2 phase			guest in CH_2Cl_2 phase		
R	optical purity, %	dominant confign	EDC[b]	optical purity, %	dominant confign	EDC[b]
Ph	1.6	D	1.04	5.4	D	1.19
$PhCH_2$	0.5	D	1.06	1.8	D	1.08
CH_3SCH_2-CH_2	2.0	D	1.07	4.7	D	1.17

[a] [Host] = 0.2 mol·L^{-1} in CH_2Cl_2. [Guest] = 1.0 mol·L^{-1} in H_2O. [Guest]/[Host] = 3. Temp, 0 °C. [b] The enantiomer distribution constant (EDC) is defined as EDC = $([G_A]_{CH_2Cl_2}/[G_A]_{H_2O}/([G_B]_{CH_2Cl_2}/[G_B]_{H_2O})$, where $[G_A]_{CH_2Cl_2}$ and $[G_B]_{CH_2Cl_2}$ and $[G_B]_{H_2O}$ and $[G_A]_{H_2O}$ are the concentrations of the more (A) or less (B) soluble guest enantiomers in the CH_2Cl_2 phase and the concentrations in the water phase, respectively.

possessed an optical activity, although lower than that for polymers with KOH. This means that the ring opening occurs predominantly at the β-bond to form (*R*,*R*)-dibenzo-19-crown-6 or (*S*,*S*)-dibenzo-19-crown-6 as the main cyclic units.

Chiral Poly(dibenzo-19-crown-6)s in the Host–Guest Complexation. Table II lists the results of the chiral recognition property of host polymers 2 and 8 which were prepared from (*S*,*S*)-(+)-1 with $SnCl_4$ and KOH, respectively, toward methyl esters of phenylglycine ($PhGlyOCH_3$), phenylalanine ($PhAlaOCH_3$), and methionine ($MetOCH_3$) as guests. For estimating the chiral recognition ability, the enantiomer distribution constant (EDC) is defined as EDC = $([G_A]_{CH_2Cl_2}/[G_A]_{H_2O})/([G_B]_{CH_2/Cl_2}/[G_B]_{H_2O})$, where $[G_A]_{CH_2Cl_2}$ and $[G_B]_{CH_2Cl_2}$ and $[G_B]_{H_2O}$ and $[G_A]_{H_2O}$ are the concentrations of the more (A) or less (B) soluble guest enantiomers in the CH_2Cl_2 phase and the concentrations in the water phase, respectively.[11]

The excess enantiomer of guest extracted into the CH_2Cl_2 phase was the D-isomer for every host–guest system, which means that (*S*,*S*)-dibenzo-19-crown-6, the main unit in both polymers, forms the complex predominantly with D-enantiomer. The optical purities of guests were quite low, with values ranging from 0.5 to 5.4%, and the maximum value of the enantiomer distribution constant (EDC) was obtained as 1.19 for the polymer 8–PhGly-OCH_3 system. The EDC values for every guest were higher for polymer 8 than for polymer 2. This result is reflected by the fact that the stereoregularity, i.e., the molar ratio of the (*S*,*S*)-19-crown-6 units, is higher for polymer 8 than for polymer 2.

Although many studies have been reported on the enantioselective polymerization of racemic epoxides and on the stereoselective polymerization of one enantiomer, the chiral polymers obtained have not found application as agents for the optical resolution of racemates. Optically active glycidole and its derivatives, which are commercially available and are useful for chiral building blocks in organic synthesis, have great potential importance as monomers for producing functional polymers. In the present study, the regio- and stereospecific polymerizations of chiral diepoxides, (*R*,*R*)-(−)- and (*S*,*S*)-(+)-1, successfully react to yield poly[(*R*,*R*)-dibenzo-19-crown-6] and poly[(*S*,*S*)-dibenzo-19-crown-6], respectively, which exhibit chiral recognition ability toward racemic α-amino acids.

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References and Notes

(1) (a) Sousa, L. R.; Sogah, G. D. Y.; Hoffmann, D. H.; Cram, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 4569. (b) Sogah, G. D. Y.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3035. (c) Manecke, G.; Winter, H.-J. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 569. (d) Fyles, T. M.; McGavin, C. A.; Thompson, D. E. *J. Chem. Soc., Chem. Commun.* **1982**, 924.

(2) Kakuchi, T.; Sasaki, H.; Yokota, K. *Makromol. Chem.* **1988**, *189*, 1279.

(3) Kakuchi, T.; Takaoka, T.; Yokota, K. *Makromol. Chem.* **1988**, *189*, 2007.

(4) Kakuchi, T.; Takaoka, T.; Yokota, K. *Makromol. Chem.* **1989**, *190*, 2449.

(5) Kakuchi, T.; Haba, O.; Yokota, K. *Makromol. Chem.* **1991**, *192*, 1601.

(6) Ciardelli, F. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Kroschwitz, J. I., Ed.; Wiley-Interscience: New York, 1985; Vol. 10, p 463.

(7) Yokota, K.; Hashomoto, H.; Kakuchi, T. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 115.

(8) Bartulin, J.; Parra, M.; Pamirez, A.; Zunza, H. *Polym. Bull.* **1989**, *22*, 33.

(9) Hashimoto, H.; Kakuchi, T.; Yokota, K. *Polym. Bull.* **1991**, *25*, 153.

(10) Parker, R. E.; Isaac, N. S. *Chem. Rev.* **1959**, *59*, 758.

(11) Peacock, S. C.; Walba, D. M.; Gaeta, F. C. A.; Helgeson, R. C.; Cram, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 2043.

Registry No. (*R*,*R*)-(−)-1, 138835-21-9; (*R*,*R*)-(−)-1 (homopolymer), 138835-23-1; (*S*,*S*)-(+)-1, 138835-22-0; (*S*,*S*)-(+)-1 (homopolymer), 138835-24-2; **3**, 23116-94-1; $BF_3{\cdot}OEt_2$, 109-63-7; $SnCl_4$, 7646-78-8; KOH, 1310-58-3; (±)-$PhCH(CO_2Me)NH_3^+Pr_6^-$, 54486-82-7; (±)-$PhCH_2CH(CO_2Me)NH_3^+PF_6^-$, 60389-74-4; (±)-$CH_3S(CH_2)_2CH(CO_2Me)NH_3^+PF_6^-$, 60389-73-3.