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Cyclopolymerization of Divinyl Ethers. Synthesis and the Cation-Binding Property of Poly(crown ether)s

Toyoji Kakuchi,* Osamu Haba, and Kazuaki Yokota*

Department of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

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ABSTRACT: Divinyl ethers capable of forming 16–25-membered rings (**1a–g**) were synthesized and polymerized with $SnCl_4$ in CH_2Cl_2 at 0 °C. All the polymers obtained were gel-free and did not contain any residual vinylic bonds. In order to confirm the cyclic units, 1,2-bis[2–(2–(vinyloxy)ethoxy)ethoxy]benzene (**1a**) was reacted with a HI/I_2 initiator and with MeOH as the terminator. The 19-membered cyclic unimer was isolated, and this result proved that cationic cyclopolymerization of **1a** gave poly(benzo-19-crown-6) (**2a**) through a head-to-tail addition. Polymer **2a** showed the same binding property toward alkali-metal picrates, regardless of its polymerization degrees. The extraction yields for **2a** were higher than those for benzo-19-crown-6, and their selectivities were different. For the polymers consisting of 16–25-membered rings, the cation-binding properties were discussed in connection with ring size, shape, and the number and electronic properties of oxygen.

Introduction

The synthesis of polymers with macrocyclic units through cyclopolymerization, which does not need a cyclic derivative as a monomer, is a direct method for producing rings and polymer chains at the same time. We have found that polymers with crown ether,[1] thia-crown ether,[2] crown lactone,[3] cryptand,[4] and hemispherand units[5] are synthesized through the cyclopolymerization of bifunctional monomers. The cyclopolymerization of divinyl ethers is a particularly facile method for preparing optically active poly(crown ether)s incorporating (*R*)- and (*S*)-1,1′-bi-2-naphthol, D-mannitol, L-threitol, and hexopyranosides.[6] These polymers exhibit the property of chiral recognition toward racemic amino acid and are used as agents for the optical resolution of racemates in the form of a column filling and a membrane.

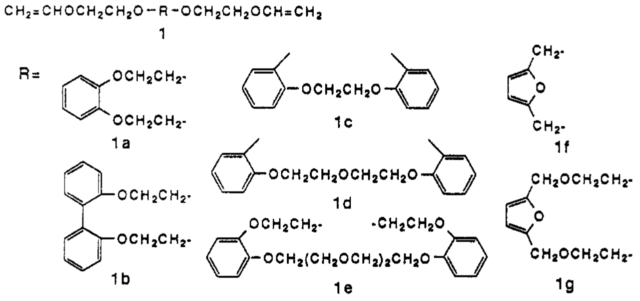
The present study aims at preparing polymers with various sizes of crown ether units by the cyclopolymerization of the divinyl ethers and at elucidating the cation-binding property of the prepared poly(crown ether)s. For these purposes, the structures of the crown ether units in the polymers need to be exactly determined because the number of donor atoms and the ring size of the crown ether are significantly affected by the host–guest complexation.

In this paper, we report the synthesis of poly(crown ether)s (**2**) by the cyclopolymerization of divinyl ethers **1**, the identification of the cyclic unit in polymer **2a** obtained from **1a** using the living cationic polymerization technique, and the binding property of poly(crown ether)s toward alkali-metal picrates. In addition, polymer **2a** is characterized by comparing its cation-binding property with that of crown ether **4**, which corresponds to the cyclic repeating units in polymer **2a**.

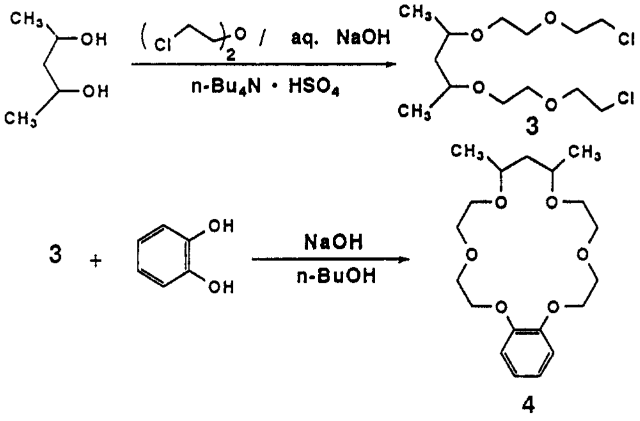
Experimental Section

Measurement. ^1H and ^{13}C NMR spectra were recorded using a Brucker MSL 400 instrument. IR and UV spectra were recorded on Jasco A-102 and Jasco 660 UV/vis spectrophotometers, respectively. The molecular weights of the resulting polymers were measured by gel permeation chromatography (GPC) in THF on a Waters M45 high-performance liquid chromatograph equipped with three polystyrene gel columns (Shodex KF-804L). The number-average molecular weight (M_n) was calculated on the basis of a polystyrene calibration.

Chart I



Scheme I



Materials. Tin(IV) chloride ($SnCl_4$) was purified by distillation of a commercial product under reduced pressure. Hydrogen iodide (HI) was obtained by dehydrating a 57% aqueous solution with phosphorus pentaoxide and stored as an *n*-hexane solution. Iodine (I_2) was sublimed over potassium iodide under reduced pressure and stored as an *n*-hexane solution. Dichloromethane, *n*-hexane, and toluene were purified by the usual methods and distilled over calcium hydride.

Monomers. The synthesis of 1,2-bis[2-(2-(vinyloxy)ethoxy)-ethoxy]benzene (**1a**) was reported in a previous paper.[1a] 1,2-Bis[2-(2-(vinyloxy)ethoxy)phenoxy]ethane (**1c**), 1,5-bis[2-(2-(vinyloxy)ethoxy)phenoxy]-3-oxapentane (**1d**), 1,8-bis[2-(2-(vinyloxy)ethoxy)phenoxy]-3,6-dioxaoctane (**1e**), and 2,5-bis(4-(vinyloxy)-2-oxabutyl)furan (**1f**) were prepared from the corresponding dihydroxy compounds and 2-chloroethyl vinyl ether, and 2,2′-bis[2-(2-(vinyloxy)ethoxy)ethoxy]biphenyl (**1b**) and 2,5-bis(7-(vinyloxy)-2,5-dioxaheptyl)furan (**1g**) from the diols and 2-(2-chloroethoxy)ethyl vinyl ether. Table I lists the syntheses and the properties of the divinyl ethers **1b–g**.

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Table I
Synthesis and Properties of Divinyl Ethers **1b–g**

divinyl ether	yield (%)	R_f, mp, and bp	molecular formula (M_w)	calcd (found) C, H	^{1}H NMR ($CDCl_3$/TMS) δ (ppm) [J (Hz)]
1b	60	0.25[a]	$C_{24}H_{30}O_6$ (414.48)	69.54 (96.32), 7.30 (7.33)	3.44–4.21 (m, 20 H), 6.44 (dd, 2 H, HC=, J_{cis} = 6.8, J_{trans} = 14.3), 6.88–7.38 (s, 8 H_{arom})
1c	55	70 °C (methanol)	$C_{22}H_{26}O_6$ (386.43)	68.38 (68.39), 6.78 (6.75)	3.95–4.29 (m, 12 H), 4.32 (s, 4 H), 6.50 (dd, 2 H, HC=, J_{cis} = 6.9, J_{trans} = 14.3), 6.94 (s, 8 H_{arom})
1d	51	46–48 °C (methanol)	$C_{24}H_{30}O_7$ (430.48)	66.96 (67.00), 7.02 (7.03)	3.88–4.28 (m, 20 H), 6.51 (dd, 2 H, HC=, J_{cis} = 6.9, J_{trans} = 14.3), 6.95 (s, 8 H_{arom})
1e	65	66–67 °C (methanol)	$C_{26}H_{34}O_8$ (474.53)	65.80 (65.76), 7.22 (7.23)	3.73–4.31 (m, 24 H), 6.52 (dd, 2 H, HC=, J_{cis} = 6.9, J_{trans} = 14.3), 6.91 (s, 8 H_{arom})
1f	59	138–140 °C (0.25 mmHg)	$C_{14}H_{20}O_5$ (268.30)	62.26 (62.67), 7.51 (7.51)	3.50–3.79 (m, 8 H), 3.87 (dd, 2 H, *cis*-CH_2=, J_{gem} = 2, J = 6.5), 4.04 (dd, 2 H, *trans*-CH_2=, J_{gem} = 2, J = 14), 4.37 (s, 4 H), 6.12 (s, 2 H_{furyl}), 6.32 (dd, 2 H, HC=)
1g	20	190–192 °C (0.4 mmHg)	$C_{18}H_{28}O_7$ (356.40)	60.66 (60.37), 7.92 (7.89)	3.52 (s, 8 H), 3.52–3.68 (m, 8 H), 3.85 (dd, 2 H, *cis*-CH_2=, J_{gem} = 2, J = 6.5), 4.04 (dd, 2 H, *trans*-CH_2=, J_{gem} = 2, J = 13.2), 4.35 (s, 4 H), 6.12 (s, 2 H_{furyl}), 6.3 (dd, 2 H, HC=)

[a] Silica gel 60 with hexane/ether (volume ratio, 7/3).

Polymerizations. (A) The polymerizations of the divinyl ethers **1a–g** were carried out with $SnCl_4$ in dichloromethane at 0 °C. At the end of the polymerization, the reaction mixture was poured into a large amount of methanol. The resulting polymers were purified by reprecipitation from chloroform–methanol.

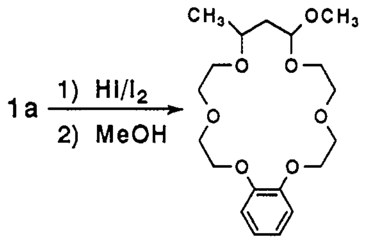
(B) A solution of HI in *n*-hexane was added to a solution of **1a** in dichloromethane at -72 °C, followed by addition of a solution of I_2 in *n*-hexane at -72 °C. After 5 h, the reaction mixture was poured into ammoniacal methanol, diluted with water, and extracted with dichloromethane. The extract was washed with 10% aqueous sodium thiosulfate solution, dried with anhydrous sodium sulfate, and evaporated in vacuum. The residue was purified by reprecipitation.

1,15-Dichloro-7,9-dimethyl-3,6,10,13-tetraoxapentadecane (3). A solution of 2,4-pentanediol (2.1 g, 20 mmol) and tetrabutylammonium hydrogen sulfate (6.8 g, 20 mmol) in bis(chloroethyl) ether (50 mL) was vigorously stirred with a 50% aqueous sodium hydroxide solution (50 mL) at 40 °C. After 24 h, the mixture was diluted with water and extracted with dichloromethane. The extracts were washed with water, dried, and concentrated under vacuum. The residual oil was distilled under vacuum to give a colorless oil having a boiling point of 155 °C/0.3 mmHg in 44.6% yield (2.8 g). The dichloride **3** was the diastereomeric mixture of the mesoisomer and racemate in a 2/3 molar ratio. ^{1}H NMR ($CDCl_3$): δ = 1.14 (d, racemic CH_3), 1.17 (d, meso CH_3), 1.54 (dd, racemic CH_2), 1.34 (dd, meso CH_2), 1.97 (dd, meso CH_2), and 3.49–3.86 (m, OCH_2).

Benzo[1,2-*a*]10,12-dimethyl-3,6,9,13,16,19-hexaoxa-1-cyclononadecene [Benzo-19-crown-6 (4)]. A solution of sodium hydroxide (0.39 g, 16 mmol) and catechol (0.88 g, 8 mmol) in 1-butanol (20 mL) was refluxed with stirring under nitrogen for 30 min. To the mixture was added a solution of dichloride **3** in 1-butanol (15 mL) and then refluxed for 8 h. After cooling, the reaction mixture was diluted with water and extracted with dichloromethane. The extracts were washed with water, dried, and evaporated. The residue was purified by column chromatography on silica gel with *n*-hexane/ethyl acetate (volume ratio, 1/1) to give a trans diastereoisomer in 26% yield (75 mg) and a cis isomer with a small amount of impurity. The trans isomer was used for the extraction experiment of alkali-metal picrates. ^{1}H NMR ($CDCl_3$): δ = 1.07 (d, 6 H, CH_3), 1.43 (t, 2 H, CH_2), 3.50–4.25 (m, 18 H, OCH and OCH_2), 6.88 (s, 4 H, aromatic). Anal. Calcd for $C_{19}H_{30}O_6$ (354.43): C, 64.38; H, 8.54. Found: C, 64.26; H, 8.91.

Preparation of Unimer 5 Corresponding to the Cyclic Unit of Polymer 2a. The reaction of **1a** with HI/I_2 ([**1a**] = [HI] = 2[I_2]) was carried out using the same procedure as for the polymerization. The crude product was purified by column chromatography on aluminum oxide with *n*-hexane/ethyl acetate (volume ratio, 1/1) to give benzo[1,2-*a*]10-methoxy-12-methyl-3,6,9,13,16,19-hexaoxa-1-cyclononadecene (**5**) which was a diastereomeric mixture consisting of cis and trans isomers. ^{1}H NMR ($CDCl_3$): δ = 1.16 and 1.31 (d and d, J = 6.22 Hz and J = 5.3 Hz, 3 H, CH_3), 1.42–2.34 (m, 2 H, CH_2), 3.31 and 3.35 (s and s, 3 H, OCH_3), 3.42–4.03 (m, 12 H, OCH_2), 4.16–4.18 (m, 4 H, $ArOCH_2$), 4.67–4.72 (m, 1 H, OCHO), 6.89–6.91 (m, 4 H, aromatic). Anal. Calcd for $C_{19}H_{30}O_7$ (370.45): C, 61.60; H, 8.16. Found: C, 61.60; H, 8.35.

Scheme II



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Cation-Binding Property. The extraction of alkali-metal picrates was carried out using a procedure similar to the one developed by Pedersen.[7] A solution of polymer in dichloromethane ([crown ether units] = 3.5 × 10^{-3} mol·L^{-1}) was vigorously shaken in a culture tube with the aqueous solution of alkali-metal hydroxide and picric acid ([picric acid] = 7 × 10^{-5} mol·L^{-1}, [metal hydroxide] = 0.1 mol·L^{-1}). After the resulting two phases were separated, the alkali-metal picrate extracted into the dichloromethane was indirectly determined by measuring the absorbance of picrate in the aqueous phase at 357 nm using a UV spectrophotometer.

Results and Discussion

Synthesis of Poly(crown ether)s. The polymerization of divinyl ether **1a** was attempted with $BF_3{\cdot}OEt_2$, $SnCl_4$, and I_2 in CH_2Cl_2 and $C_2H_5NO_2$ at 0 °C, with $AlEtCl_2$ and $AlEt_2Cl$ in toluene at 0 °C, and with $TiCl_4$ in $C_2H_5NO_2$ at 40 °C to form soluble polymers. For $BF_3{\cdot}OEt_2$ and $SnCl_4$ in CH_2Cl_2 and $C_2H_5NO_2$, gel-free polymers were obtained even when the polymer yield was 90% or greater. The polymers, however, contained residual vinylic bonds or the polymerization was accompanied by gelation at the monomer concentration ([M]) of 0.5 mol·L^{-1} or above. Little or no polymerization occurred at a [M] of 0.1 mol·L^{-1} or below.

The syntheses of poly(crown ether)s through the cyclopolymerization of divinyl ethers **1a–g** were carried out with $SnCl_4$ in CH_2Cl_2 at 0 °C as the most suitable condition. The polymerization results are listed in Table II. All the polymerizations proceeded homogeneously. The obtained polymers were semisticky or powdery and soluble in benzene, chloroform, and THF. Figurel shows the ^{1}H and the ^{13}C NMR spectra of polymer **2a**. The characteristic absorptions at 6.36–6.59 ppm due to the vinyloxy protons and at 86.7 and 151.6 ppm due to the vinyl carbons had completely disappeared. This means that polymer

Table II
Synthesis of Poly(crown ether)s via Cyclopolymerization of Divinyl Ethers 1a–g with $SnCl_4$ in CH_2Cl_2 at 0 °C[a]

monomer	time (h)	polymer	yield (%)	$10^{-3}M_n$[b]	P_n[b]
1a	1.0	**2a**	84	12.6	37.2
1b	0.3	**2b**	70	11.2	27.0
1c	1.0	**2c**	58	19.3	49.9
1d	1.0	**2d**	61	14.0	32.5
1e	0.2	**2e**	53	9.4	19.8
1f	0.5	**2f**	85	12.4	46.2
1g	0.2	**2g**	33	8.9	25.0

[a] [M] = 0.3 mol·L^{-1}; [cat.] = 0.06 mmol·L^{-1}. [b] Determined by GPC (polystyrene standard).

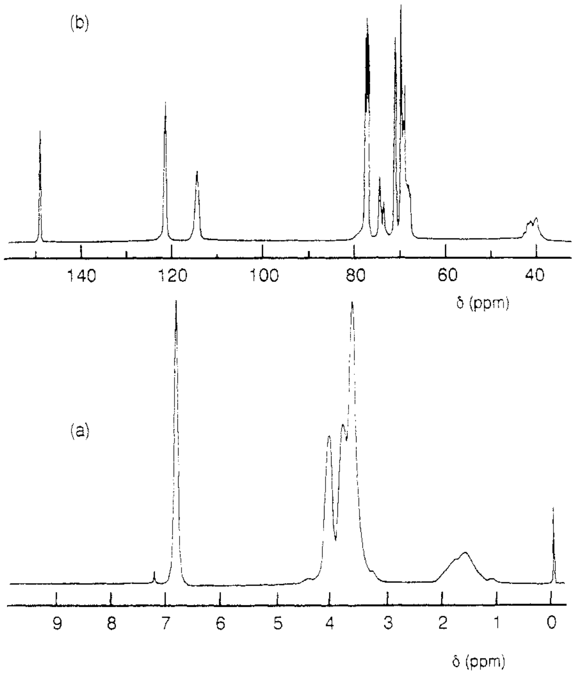
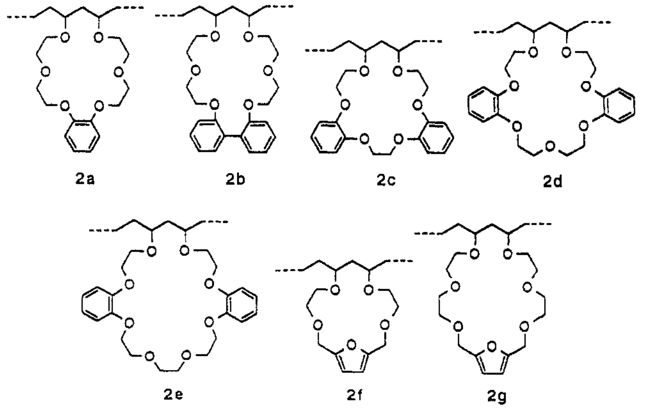


Figure 1. ^1H (a) and ^{13}C (b) NMR spectra of polymer **2a** obtained by the cyclopolymerization of 1,2-bis[2-(2-(vinyloxy)ethoxy)ethoxy]benzene (**1a**) with $SnCl_4$ in CH_2Cl_2 at 0 °C.

Chart II



2a essentially consists of cyclic constitutional repeating units caused by the cyclopolymerization mechanism. Also, polymers **2b–g** consist of only the cyclic units as well, because of the disappearance of absorption due to the vinyloxy groups in their ^1H NMR spectra. The cyclic structure of the polymer prepared from the cationic polymerization of divinyl ether has been theorized on the basis of the study reported by Butler et al.; the cyclopolymerization of 1,2-bis(vinyloxy)benzene with a cationic initiator proceeded through a head-to-tail addition because of the agreement of the ^{13}C NMR spectra between the polymers obtained and 2,4-dimethylbenzo[1,5]dioxepane.[8]

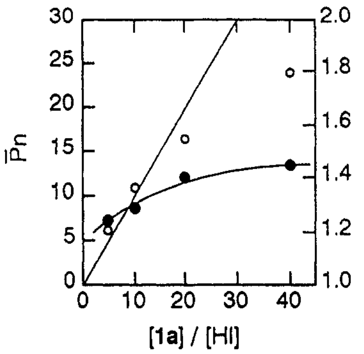


Figure 2. Polts of P_n and the M_w/M_n ratio vs the [**1a**]/[HI] ratio for the cyclopolymerization of 1,2-bis[2-(2-(vinyloxy)ethoxy)ethoxy]benzene (**1a**) with HI/I_2 in CH_2Cl_2 at -72 °C.

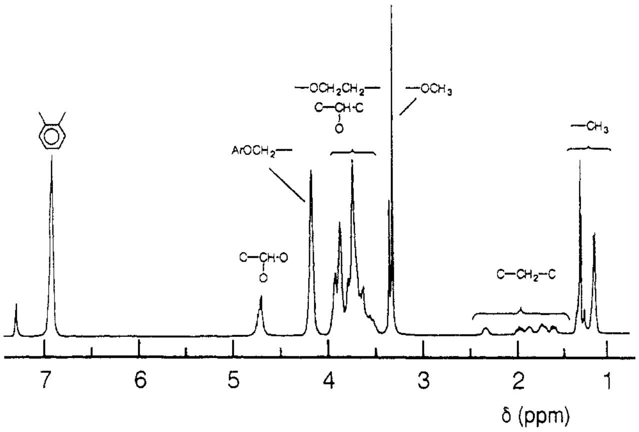


Figure 3. ^1H NMR spectrum of benzo[1,2-*a*]10-methoxy-12-methyl-3,6,9,13,16,19-hexaoxa-1-cyclononadecene, the cyclic unimer **5**, obtained by the equimolar reaction of 1,2-bis[2-(2-(vinyloxy)ethoxy)ethoxy]benzene (**1a**) and HI following with I_2 and MeOH in CH_2Cl_2 at -72 °C.

The crown ether units in polymers **2a–g**, however, have to be characterized exactly because the number of donor atoms and the ring size of the crown ether are significantly affected by the host–guest complexation.

Hydrogen iodide/iodine (HI/I_2), which is a useful initiating system for the living polymerization of vinyl ether,[9] was used for the cyclopolymerization of **1a**.[10] Figure 2 shows the plots of P_n and the M_w/M_n ratio as a function of the monomer–initiator ratio ([**1a**]/[HI]) in CH_2Cl_2 at -72 °C. The P_n's agreed with the calculated values and their molecular weight distributions (MWD) were narrow at the [**1a**]/[HI] ratios of 5 and 10, but above this ratio, P_n became smaller than the calculated value and the MWD was somewhat broad. These results indicate that the cyclopolymerization of **1a** with the HI/I_2 initiator proceeds through a long-lived intermediate for the [**1a**]/[HI] ratio ≤ 10. The livinglike polymerization of **1a** with HI/I_2 can be employed for characterization of the cyclic constitutional unit in polymer **2a**. The reaction of **1a** with equimolar HI was carried out in CH_2Cl_2 at -72 °C. The cyclization was promoted by the addition of I_2 and terminated with ammoniacal MeOH. After purification by column chromatography on aluminum oxide, a compound with m/z = 370 was isolated in 8% yield, which is expected from the equimolar reaction of **1a** with HI/I_2 using MeOH as the terminator. Figure 3 shows the ^1H NMR spectrum of the isolated product. The absorptions at 1.16 and 1.31, 1.42–2.34, 3.31 and 3.35, and 4.65–4.89 ppm are attributed to the methyl, the methylene, the methoxy, and the acetal methine protons, respectively. The resulting compound is benzo[1,2-*a*]10-methoxy-12-methyl-3,6,9,13,16,19-hexaoxa-1-cyclononadecene, namely the cy-

Table III
Effect of the Number of Crown Ether Units (P_n) in Polymer 2a on the Extraction of Alkali-Metal Picrates[a]

		extraction yield (%) of the picrates				
crown ether	P_n	Li^+	Na^+	K^+	Rb^+	Cs^+
crown 4	1	0	45.8	51.7	37.4	20.6
polymer 2a	6.0	12.2	35.5	82.0	90.6	82.4
	10.9	9.1	40.0	83.3	91.5	83.6
	16.3	10.0	36.8	82.6	91.4	82.5
	23.9	8.4	36.3	81.6	91.2	82.5

[a] [Crown ether unit] = 3.3×10^{-3} mol·L^{-1}, [picric acid] = 7×10^{-5} mmol·L^{-1}, [metal hydroxide] = 0.1 mol·L^{-1}.

clic unimer **5**, which is a diastereomeric mixture consisting of cis and trans isomers. It was proved that the cyclopolymerization of **1a** with a cationic initiator proceeded through a head-to-tail addition. The structure of the cyclic repeating units, therefore, is benzo-19-crown-6 for polymer **2a**, diphenyl-21-crown-6 for **2b**, dibenzo-19-crown-6 for **2c**, dibenzo-22-crown-7 for **2d**, dibenzo-25-crown-8 for **2e**, furodimethyl-16-crown-5 for **2f**, and furodimethyl-22-crown-7 for **2g**.

Cation-Binding Property of Poly(crown ether). The cation-binding property of poly(crown ether) was estimated by the one-plate extraction experiment using lithium, sodium, potassium, rubidium, and cesium picrates. Table III lists the results of the extraction of alkali-metal picrates by poly(benzo-19-crown-6) (**2a**) and benzo-19-crown-6 (**4**) which corresponds to the cyclic repeating unit in polymer **2a**. In order to confirm the effect of the polymerization degree (P_n) on cation-binding, polymers **2a** with different P_n's were used, which were obtained from the polymerization with HI/I$_2$, as indicated in Figure 2. Each of the polymers showed the same cation-binding property, regardless of its P_n. The yields of picrates for polymer **2a** were higher than those for crown ether **4** except for Na^+. The yields increased in the order $K^+ > Na^+ > Rb^+ > Cs^+ >>> Li^+$ for crown ether **4** and $Rb^+ > K^+, Cs^+ > Na^+ > Li^+$ for polymer **2a**. Crown ether **4** shows the highest selectivity for K^+, which agrees with the fact that the diameter of the 18-crown-6 cavity corresponds to that of K^+. On the other hand, polymer **2a** is considerably more efficient than crown ether **4** in binding K^+, Rb^+, and Cs^+ which have diameters larger than the crown cavity. This result can be explained by cooperative coordination effects, where two neighboring crown ether rings combine with a single cation. The cation-binding property of polymer **2a** is similar to that of polymeric crown ethers prepared by other synthetic methods. Smid et al. reported that poly(vinylbenzo-18-crown-6) is more efficient in complexing cations than methylbenzo-18-crown-6, especially in this case where the diameter of the crown ether units is smaller than that of the cation, and tends to form 2/1 crown–cation complexes; the yield of cesium picrate complexed with poly(vinylbenzo-18-crown-6) is 4 times larger than that with methylbenzo-18-crown-6.[11]

Table IV
Extraction of Alkali-Metal Picrates by Poly(crown ether)s 2a–g[a]

		extraction yield (%) of the picrates				
polymer	crown ether units	Li^+	Na^+	K^+	Rb^+	Cs^+
2a	19-crown-6	8.4	36.3	81.6	91.2	82.5
2b	21-crown-6	4.3	5.3	6.8	9.2	7.2
2c	19-crown-6	18.5	21.7	57.9	68.7	60.2
2d	22-crown-7	17.9	18.7	53.0	61.0	60.9
2e	25-crown-8	5.6	51.5	67.3	60.5	72.2
2f	16-crown-5	0	1.2	6.9	8.2	10.5
2g	22-crown-6	5.2	20.5	50.7	67.3	72.3

[a] [Crown ether unit] = 3.3×10^{-3} mol·L^{-1}, [picric acid] = 7×10^{-5} mmol·L^{-1}, [metal hydroxide] = 0.1 mol·L^{-1}.

Table IV lists the results of the extraction yields of alkali-metal picrate by polymers **2a–g**. For polymer **2f** containing five oxygens, the selectivity and the extraction yields are very low, which is caused by the rigidity of the furodimethyl-16-crown-5 units. Polymers **2a**, **2b**, and **2c**, which have different ring sizes with six oxygens, exhibit similar selectivity in the order $Rb^+ > Cs^+, K^+ > Na^+ > Li^+$, and the extraction ability is in the order polymer **2a** > polymer **2c** $\gg$ polymer **2b**. Since the basicity of oxygen in Ph–O–CH$_2$ is lower than that in CH$_2$–O–CH$_2$, **2c** having four Ph–O–CH$_2$ units diminishes the extraction yields relative to **2a** having two Ph–O–CH$_2$ units. The lowest property of polymer **2b** is caused by the fact that the diphenyl unit disturbs the regulated arrangement of oxygen in the crown ether units. For polymers **2d** and **2g** consisting of the 22-crown-7 units, the selectivities are in the order Rb^+, $Cs^+ > K^+ > Na^+$, Li^+ and $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$, respectively. The crown ether units in **2g** contain one oxygen of low basicity in the furan ring, and those in **2d** have four oxygens from the Ph–O–CH$_2$s, and this is the reason for the higher extraction yields of **2g** compared to **2d**. Polymer **2e**, poly(dibenzo-25-crown-8), shows selectivity in the order $Cs^+ > K^+ > Rb^+ > Na^+ > Li^+$, which obviously differs from the cation-binding properties for poly(dibenzo-crown ether)s **2a** and **2c**. Because the diameter of dibenzo-25-crown-8 is almost equal to that of Cs^+, polymer **2d** shows the highest selectivity for Cs^+.

Conclusion

Polymers involving crown ethers as an integral part of the polymer are prepared by the step-growth polymerization of crown derivatives. Addition polymerization of vinyl derivatives of crown ethers gives polymers with crown ethers in the pendent form. Crown ethers are also bound to polymeric supporting materials, such as polystyrene resin. Compared with these conventional methods, the cyclopolymerization method is characterized by a simple design for monomer and cyclic units forming in polymers. In the case of divinyl ethers, monomers incorporating various designed units are easily synthesized and polymerized by a conventional cationic initiator to form gel-free polymers consisting of only the crown ether units in high yields. Such a cyclopolymerizability of divinyl ethers must be produced by the solvation of a growing carbocation with intramolecular oxygens in the cyclization process. This kind of solvation also plays an important role in the chirality induction in the cyclopolymerization of divinyl ethers derived from chiral 3,3′-disubstituted-1,1′-bi-2-naphthol.

The cation-binding property of poly(crown ether)s synthesized by the cyclopolymerization method depends on ring size and shape and the number and electronic properties of oxygen. Poly(benzo-19-crown-6) (**2a**) exhibits the highest selectivity for Rb^+ by forming a 2:1 crown–cation complex whose property is very similar to that of poly(vinylbenzo-18-crown-6).

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References and Notes

(1) (a) Yokota, K.; Matsumura, M.; Yamaguchi, K.; Takada, Y. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 721. (b) Hashimoto, H.; Kakuchi, T.; Yokota, K. *Polym. Bull.* **1991**, *25*, 153.
(2) Yokota, K.; Hashimoto, H.; Kakuchi, T.; Takada, Y. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 767.

(3) Yokota, K.; Kakuchi, T.; Taniguchi, Y.; Takada, Y. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 155.

(4) Yokota, K.; Kakuchi, T.; Yamanaka, M.; Takada, Y. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 633.

(5) Kakuchi, T.; Haba, O.; Harada, Y.; Hashimoto, H.; Yokota, K. *Polym. Bull.* **1992**, *27*, 599.

(6) Kakuchi, T.; Haba, O.; Yokota, K. *Makromol. Chem.* **1991**, *192*, 1601 and references cited therein.

(7) Pedersen, C. J. *Fed. Proc.* **1968**, *27*, 1305.

(8) Butler, G. B.; Lien, Q. S. *Cyclopolymerization and Polymer with Chain Ring Structure*; ACS Symposium Series 195; American Chemical Society: Washington, DC, 1982; p 145.

(9) Higashimura, T.; Sawamoto, M. In *Comprehensive Polymer Science*; Allen, G., Bevington, J., Eds.; Pergamon Press: Oxford, U.K., **1989**; Vol. 3, p 684.

(10) Kakuchi, T.; Kobayashi, O.; Nakaya, D.; Yokota, K. *Polym. J.* **1989**, *21*, 649.

(11) Kopolow, S.; Machacek, Z.; Takagi, U.; Smid, J. *J. Macromol. Sci. Chem.* **1973**, *A7*, 1015.