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Anionic Polymerization of Macrocyclic α-(Alkoxymethyl)acrylates Leading to Novel Vinyl Polymer with Crown Ether Type Side Chain

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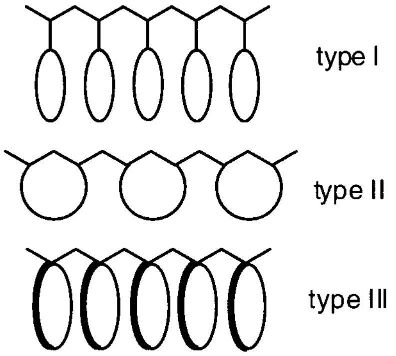
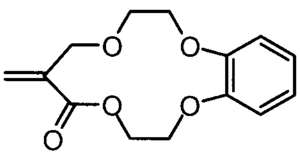
Introduction. Polymers bearing macrocycles, such as crown ethers, in the side chain are attractive because of their metal and molecular recognition abilities, and many studies have been reported on the syntheses and functions. The polymers with macrocyclic side chains have been generally synthesized by the polymerization of a monomer having a large ring as a substituent to produce a polymer with a "type I" structure[1,2] and the cyclopolymerization of a two-functional monomer to give the "type II" one.[3] In the former, macrorings flexibly attach to the main chain, whereas rings are linked and fixed through the main chain in the latter. We propose here a new type of polymer having macrocycles perpendicularly arranged on the main chain ("type III"), which is prepared by the polymerization of macrocyclic vinyl monomers.[4] Successful control of the stereoregularity and the placement of the macrorings in the "type III" polymer may generate a novel organic nanotube.



α-(Alkoxymethyl)acrylates are interesting monomers that have two different types of substituents on an olefin. We recently reported that the stereospecific polymerizations proceeded by controlling the intra- and intermolecular coordinations of α-substituents to a Lewis acid catalyst during the radical polymerization[5,6] as well as coordination to a countercation in the anionic method.[7,8] To produce a vinyl polymer with a "type III" structure, novel α-(alkoxymethyl)acrylates with a macrocyclic structure, 8,9-benzo-2-methylene-4,7,10-trioxa-8-dodecen-12-olide (**1**) and 9,10-benzo-2-methylene-4,8,-11-trioxa-9-tetradecen-14-olide (**2**) with 13- and 15-membered rings, respectively, were synthesized and anionically polymerized.[9]

Experimental Section. The solvents and reagents were purified or prepared as previously reported.[7,8] Monomers were synthesized from ethyl α-(bromomethyl)acrylate[10] as follows. Ethyl α-(bromomethyl)acrylate was reacted with the corresponding diol (3 equiv) using triethylamine in tetrahydrofuran (THF) to give the mono-2-(ethoxycarbonyl)allyl ether of the starting alcohol. After hydrolysis of ester group using sodium hydroxide, the hydroxy acid was cyclized using 2-chloro-1-methylpyridinium iodide and triethylamine in acetonitrile to afford the monomer.[9,11]



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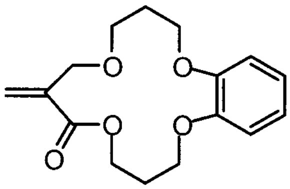

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8,9-Benzo-2-methylene-4,7,10-trioxa-8-dodecen-12-olide (**1**). Total yield in three steps: 28%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (m, 2H, $-OCH_2$), 4.11 (m, 2H, $-OCH_2$), 4.21 (m, 2H, $-OCH_2$), 4.32 (s, 2H, allylic CH_2), 4.57 (m, 2H, $-OCH_2$), 5.72 (m, 1H, vinyl), 6.25 (m, 1H, vinyl), 6.89 (m, 2H, aromatic), 7.00 (m, 2H, aromatic). IR (neat, cm^{-1}): 2960, 1719, 1640, 1595, 1503, 1454, 1247, 1168, 1087, 1035. Elemental analysis. Found: C, 63.63%; H, 6.12%. Calcd for $C_{14}H_{16}O_5$: C, 63.63%; H, 6.10%.

9,10-Benzo-2-methylene-4,8,11-trioxa-9-tetradecen-14-olide (**2**). Total yield in three steps: 22%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03 (m, 2H, $-CH_2$), 2.18 (m, 2H, $-CH_2$), 3.69 (t, 2H, $J = 5.6$ Hz, $-OCH_2$), 4.11 (t, 2H, $J = 5.6$ Hz, $-OCH_2$), 4.17 (t, 2H, $J = 6.0$ Hz, $-OCH_2$), 4.26 (s, 2H, allylic CH_2), 4.42 (t, 2H, $J = 5.6$ Hz, $-OCH_2$), 5.73 (s, 1H, vinyl), 6.25 (s, 1H, vinyl), 6.86−6.98 (m, 4H, aromatic). IR (neat, cm^{-1}): 2956, 1721, 1640, 1595, 1499, 1470, 1392, 1255, 1115, 1049. Elemental analysis. Found: C, 65.78%; H, 6.92%. Calcd for $C_{16}H_{20}O_5$: C, 65.74%; H, 6.90%.

Anionic polymerization was carried out in the same way as reported previously.[7,8] Extraction experiments of alkali metal picrate salts were conducted using a solution of the crown ether compound (3.5 mM/unit) in 1,2-dichloroethane (3.0 mL) and a mixture of picric acid (3.9×10^{-2} M) and alkali metal hydroxide (1.0×10^{-2} M) in H_2O (3.0 mL). The UV value observed for the aqueous layer after extraction using 1,2-dichloroethane (3.0 mL) without including crown ether compounds was used as a reference.[3] Cobalt ion transport of the polymers using dihexadecyl phosphate (DHP) vesicle incorporated 4-(2-pyridylazo)resorcinol monosodium salt (PAR) was examined according to the procedure reported.[2,12]

^{1}H NMR spectra were measured on a Varian Gemini-2000 (400 MHz) spectrometer in $CDCl_3$. Infrared (IR) spectra were recorded on a JASCO FT/IR-620 spectrometer. Ultraviolet (UV) absorption spectra were taken on JASCO V-570 spectrometer. The size exclusion chromatographic (SEC) analyses were performed on a Shodex GPC-System-21 equipped with Shodex UV-41 and Shodex RI-71S detectors using columns (pore and bead sizes = 100 Å, 6 μm and 1000 Å, 10 μm) connected in series and THF was used as eluent (temperature = 40 °C, flow rate = 1.0 mL/min). Calibration was carried out using standard polystyrenes.

Results and Discussion. The anionic polymerization of **1** and **2** was carried out in THF at −78 °C using various initiator systems, and the results are sum-

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Table 1. Anionic Polymerization of 1 and 2 in THF at −78 °C for 48 h[a]

entry	monomer	initiator	yield[b] (%)	$M_n \times 10^{-3}$ (M_w/M_n)	tacticity (m/r)
1	**1**	*n*-BuLi	11	6.9 (3.7)[e]	82/18
2	**1**	Ph_2NLi−TMEDA	9	7.1 (3.0)[e]	87/13
3	**1**	Na−biphenylide	16	6.1 (1.7)	
4	**1**	K−biphenylide	93	12.2 (6.3)	
5	**2**	*n*-BuLi	>99	13.2 (5.4)	88/12
6	**2**	Ph_2NLi−TMEDA	1	3.8 (−)	92/8
7	**2**	K−biphenylide	>99	12.9 (4.0)	

[a] [Monomer] = 0.5 M (entries 1−4), 1.0 M (entries 5−7), [monomer]/[initiator] = 20. [b] MeOH-insoluble part. [c] Determined by SEC (polystyrene standard). [d] Determined by ^{1}H NMR analysis ($CDCl_3$, 60 °C). [e] $CHCl_3$-soluble part.

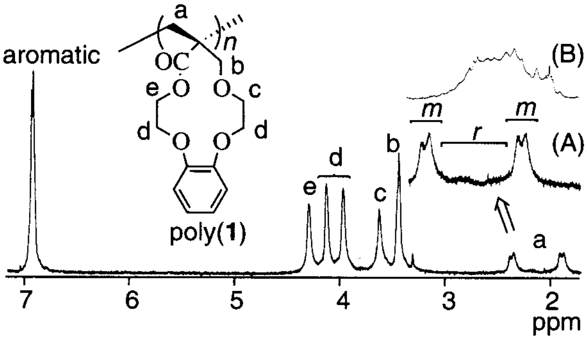


Figure 1. ^{1}H NMR spectra of (A) poly(**1**) obtained with *n*-BuLi and (B) with K-biphenylide (in $CDCl_3$, 60 °C).

marized in Table 1. The polymerization of **1** using lithium and sodium initiators such as *n*-BuLi, the lithium diphenylamide with *N,N,N′N′*-tetramethylethylenediamine (TMEDA) complex, and sodium biphenylide resulted in low yields, whereas the potassium reagent gave a polymer as a methanol-insoluble part in a good yield. The polymerizations of **2** with *n*-BuLi and potassium biphenylide proceeded quantitatively. The polymers were soluble in THF and $CHCl_3$ except for poly(**1**)s obtained with lithium reagents, which were partially insoluble in these solvents.

Figure 1A shows the ^{1}H NMR spectra of poly(**1**) obtained using *n*-BuLi. Each peak is assigned as shown in the figure, indicating that the polymer has a normal vinyl polymer structure. In addition, the spectral pattern of the main chain methylene protons around 2.1 ppm shows a typical AB quartet. The polymers prepared with the lithium reagents are rich in isotacticity; for example, is m:$r \approx 82$:18 for poly(**1**) obtained using *n*-BuLi. The polymers prepared with potassium biphenylide mainly have a vinyl polymer structure according to ^{1}H NMR analysis, although there are some small undefined peaks due to the olefinic protons.[8] In addition, the stereoregularity is quite different from that of the polymers obtained with the lithium reagents and may be atactic judging from the much broader peaks and pattern of the main-chain methylene protons (Figure 1B). The countercation strongly affects the polymer yield and tacticity of the obtained polymer, probably due to the difference in the interaction ability for the alkali metals with the macrocyclic side chain of the crown ether.

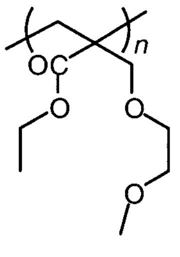
The alkali metal ion complexing abilities of poly(**1**) and poly(**2**) were examined. Extraction was carried out with a 1,2-dichloroethane solution of a polymer from aqueous solution containing alkali metal picrate under dark conditions (Table 2). In general, polymers bearing a crown ether side chain show a strong extraction ability in a less selective manner than those of the monomeric crown ether due to the polymer effect.[1,3] Monomer **1** preferentially extracted Li^+. Poly(**1**)s obtained with the lithium, sodium, and potassium reagents showed selective extraction abilities of Li^+, which were lower than that of **1** and different from one another. On the other hand, poly(**2**) obtained with the lithium reagent extracted in the order of $Na^+ \approx Rb^+ \approx K^+ > Cs^+ > Li^+$, and Na^+ was selectively extracted by poly(**2**) prepared by potassium biphenylide, although monomer **2** exhibited almost no extraction ability. These results demonstrate that the alkali metal ion extraction abilities of the polymers are significantly affected by the stereoregularity as well as their ring size and structure. Although some polymer effects should be considered for the alkali metal ion complexing abilities of poly(**1**) and poly(**2**), they are quite different from the other typical polymers bearing a crown ether side chain.[1,3]

Table 2. Extraction Ratio of Alkali Metal Picrates by Poly(1) and Poly(2) into the 1,2-Dichloroethane Phase[a]

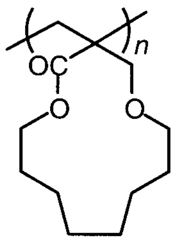
polymer	extraction ratio of the picrates[b]				
	Li^+	Na^+	K^+	Rb^+	Cs^+
1	14	1	3	<1	<1
poly(**1**)[c]	12	7	8	3	<1
poly(**1**)[d]	7	6	1	*e*	*e*
poly(**1**)[f]	13	9	6	5	<1
2	<1	2	2	1	<1
poly(**2**)[g]	<1	12	9	11	4
poly(**2**)[f]	5	13	5	4	<1
12-crown-4	15	5	2	2	2

[a] Extraction was carried out for 15 min in the dark. [b] Determined by UV absorption intensity at 356 nm. [c] Obtained with Ph_2NLi−TMEDA (Table 1, entry 2, $CHCl_3$-soluble part). [d] Obtained with Na−biphenylide (Table 1, entry 3). [e] Not measured. [f] Obtained with K−biphenylide (Table 1, entries 4 and 7). [g] Obtained with *n*-BuLi (Table 1, entry 5).

Because poly(**1**) and poly(**2**) have a structure with the perpendicularly fixed macrorings on the main chain, they may act as an artificial pore. The ion transport ability as a synthetic ion channel was investigated for these polymers according to the method reported by Nolte et al.[2] DHP vesicles containing PAR were prepared using poly(**1**) and poly(**2**) obtained with the potassium reagent and poly[ethyl α-(methoxyethoxymethyl)acrylate] [poly(**3**)][6,13] and poly(2-methylene-4-oxa-12-dodecanolide) [poly(**4**)][14,15] as reference compounds. These polymers were incorporated into the bilayers of the vesicles.



poly(**3**)



poly(**4**)

The Co^{2+} transport was measured by a UV absorption increase at 510 nm (Figure 2).[12] The vesicle prepared without the polymers showed almost no ion permeability, and the formation of the cobalt−PAR complex was observed by adding a surfactant (Triton X-100) ($\Delta A = 0.049$) after 50 min. A small UV absorption

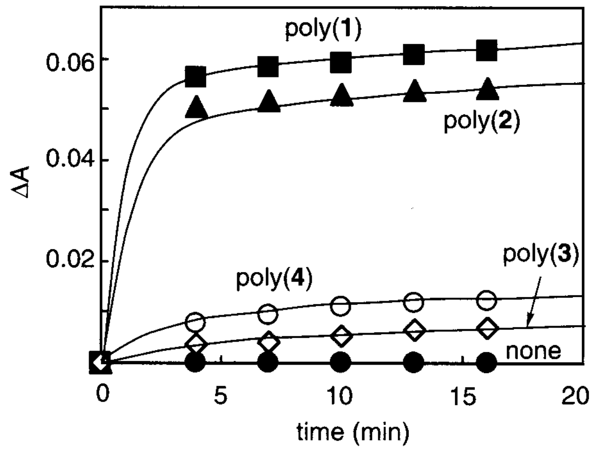


Figure 2. Plots of the change in UV absorption at 510 nm vs time using vesicles prepared with poly(**1**) (Table 1, entry 4): ■; poly(**2**) (Table 1, entry 7): ▲; poly(**3**):[6,13] ◇; poly(**4**):[14,15] ○; and without a polymer: ●.

increase was observed for the vesicles including poly(**3**) and poly(**4**), suggesting that the cobalt ion was quite slowly transported through the bilayer. In contrast, the DHP−poly(**1**) and −poly(**2**) vesicles showed a significantly pronounced effect on the ion permeability, and the effect for the former was better than that for the latter polymer. These results suggest that the polymers may have a structure with a pore or shaped like a nanotube.

In conclusion, novel types of vinyl polymers with macrocycles as a side chain were synthesized and demonstrated to have selective alkali ion extraction and ion transport abilities. Further investigations of the polymerization of various macrocyclic α-(alkoxymethyl)-acrylates and functions of the obtained polymers are now in progress.

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(12) Typical procedure for cobalt ion transport experiment: DHP (27.0 mg, 50 μmol), H_2O (5 mL), NaOH (0.1 M, 0.25 mL), and aqueous solution of PAR (5 mM, 5 mL) were added to a solution of a polymer (1.0 mg) in THF (0.2 mL) at 80 °C. The mixture was sonicated for 55 min and then washed by dialysis. The total volume of the resulting dispersion was adjusted to 10−11 mL. The cobalt ion transport measurement was carried out in a 2.0 mm UV cell filled with the prepared vesicles in water (0.6 mL) by adding a solution of $Co(NO_3)_2$ (1.17 mM, 10 μL), and the increase in absorbance at 510 nm was recorded.

(13) Poly(**3**) was prepared by the radical polymerization with (i-$PrOCO_2)_2$ in toluene at 30 °C: $M_n = 1.4 \times 10^4$, $M_w/M_n = 7.0$.

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(15) Poly(**4**) with a vinyl polymer structure was prepared by the anionic polymerization with Ph_2NLi−TMEDA in THF at −78 °C: $M_n = 7.4 \times 10^3$, $M_w/M_n = 1.5$.

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