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Synthesis of polymers with cryptand-like units via radical cyclopolymerization of diacrylate and dimethacrylate derived from diaza-12-crown-4, and the binding property for lithium ion

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Summary

Polymers with cryptand-like units have been obtained by the radical cyclopolymerization of 4,10-bis(acryloyloxyethyl)- and 4,10-bis(methacryloyloxyethyl)-1,7-dioxa-4,10-diazacyclododecane. The polymers consist of only bicyclic constitutional units, though having fairly low molecular weight. In the complexation with alkali-metal ions, the participation of the cavity effect for Li^+ ion and the cooperative effect of neighbouring ligands for the larger ions is a characteristic of the polymers, thereby giving high binding ability for every ion, but low selectivity.

Introduction

Several macrocycles, such as macrocyclic diamines(1), pentaazabicycles(2), cryptands(3), and crown ethers(4-7), act as lithium ionophores. In particular, [2.1.1]-cryptand, the smallest macrocycle in the homologs, has the highest ability for complexing with Li^+ ion(3). Therefore, it is interesting to produce the lithium-selective, polymeric materials with cryptand units. The polymers with [2.2.2]cryptand units have been synthesized by several methods consisting of chain- and step-growth polymerizations(8-10), and polymer analogous reactions(11-13). Cryptand derivatives as starting material are essential in the synthesis of these polymers. On the other hand, the cationic cyclopolymerization of divinyl ether(**5**) derived from diaza-12-crown-4 has produced the polymer with [2.1.1]cryptand units, polymer which possesses a high binding ability for every ion of alkali metals(14). This paper reports on the radical cyclopolymerization of diacrylate(**1**) and dimethacrylate(**2**) also derived from the diazacrown and the binding ability of the resulting polymers for Li^+ ion.

Experimental

Materials

*4,10-Bis(2-acryloyloxyethyl)-1,7-dioxa-4,10-diazacyclododecane (**1**):* To a mixture of 4,10-bis(2-hydroxyethy)-1,7-dioxa-4,10-diazacyclododecane(6.6g; 0.025mol) and triethylamine (7ml; 0.05mol) in benzene(100ml) was gradually added acryloyl chloride (4.5g; 0.05mol) under ice-cooling. After stirring at room temperature for 2h, the precipitate was filtered off, and the filtrate was washed with 1% $NaHCO_3$ solution and dried over potassium carbonate. Then the benzene was distilled off and the residual oil was purified by column chromatograph on alumina with chloroform/ethyl acetate (volume ratio 1:1), giving a pale yellow oil. Yield: 5.2g (56.2%).
Distillation via "Kugelrohr-apparatus" also gave a purified product with b.p. 232°C ($8 \cdot 10^{-4}$ mbar). Yield: 3.0g.
^1H NMR ($CDCl_3$): $\delta=2.77$ (t, 8H, $J=4.8$Hz, *N*-methylene), 2.82 (t, 4H, $J=6.4$Hz, *N*-methylene), 3.59 (t, 8H, $J=4.8$Hz, *O*-methylene), 4.24 (t, 4H, $J=6.4$Hz, *O*-methylene), 5.81 and 5.84 (each t, 2H), and 6.1-6.5 (m, 4H).

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$C_{18}H_{30}N_2O_6$(370.44)	Calc.	C 58.36	H 8.16.	N 7.56
	Found	C 58.21	H 8.22	N 7.41

4,10-Bis(2-methacryloyloxyethyl)-1,7-dioxa-4,10-diazacyclododecane (**2**): This was obtained by a reaction of diaza-12-crown-4 with methacryloyl chloride, following a procedure similar to that used for monomer **1**.

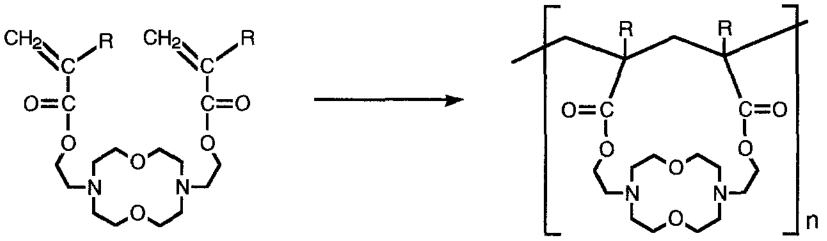
^{1}H NMR ($CDCl_3$): δ=1.98 (s, 6H), 2.80 (t, 8H, J=4.8Hz), 2.88 (t, 4H, J=6.4Hz), 3.66 (t, 8H, J=4.8Hz), 4.32 (t, 4H, J=6.4Hz), 5.63 (s, 2H, *cis*-vinyl methylene), and 6.21 (s, 2H, *trans*-vinyl methylene).

$C_{20}H_{34}N_2O_6$ (398.49)	Calc.	C 60.28	H 8.60	N 7.03
	Found	C 60.11	H 8.45	N 6.96

Polymerizations

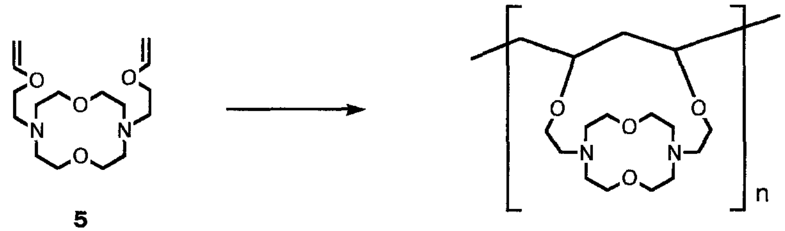
Radical polymerization was performed in a Pyrex glass ampoule at 60°C in benzene using AIBN as initiator. After introducing the reaction components and several freeze-thaw cycles, the ampoule was sealed under nitrogen. When placed in a thermostat for a given time, the solution was poured into an excess of hexane to precipitate the polymer, which was purified by the reprecipitation using chloroform and hexane as solvent and precipitant.

*Polymer **3**:*				
$(C_{18}H_{30}N_2O_6)_n$ $(370.44)_n$	Calc.	C 58.36	H 8.16	N 7.56
	Found	C 58.34	H 8.32	N 7.51
*Polymer **4**:*				
$(C_{20}H_{34}N_2O_6)_n$ $(398.49)_n$	Calc.	C 60.28	H 8.60	N 7.03
	Found	C 58.40	H 8.40	N 6.79



1: R=H
2: R=CH$_3$

3: R=H
4: R=CH$_3$



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6

Cation binding ability

The extraction of metal picrates was carried out by the procedure described in a previous paper(14). The overall extraction constant, *Ke*, was estimated according to the method of Smid(15), assuming a 1:1 stoichiometry for the complexation.

Measurements

^{1}H NMR spectra were recorded on a Hitachi R90H and a Bruker MSL-400 spectrometer. IR spectra were measured on a JASCO A-102 spectrometer. Gel permeation chromatography (GPC) in tetrahydrofuran was performed on a WATERS M45 high performance liquid chromatograph equipped with three columns (Shodex KF-804F). UV spectra were recorded with a Shimadzu UV-210 spectrometer.

Results and Discussion

Monomers **1** and **2** are so reactive that the storage in neat state brings about gelation even at -20°C, which are eliminated any tendency to gelation in solution. The polymerization with *n*-BuLi in THF yielded insoluble gels.

Some results of radical polymerization are given in Table 1. The reaction proceeded homogeneously, but gelation took place when a monomer concentration more than 0.5M was used. The resulting polymers were colorless or pale yellow powders and soluble in benzene, chloroform, and THF. Polymer **4** that was obtained at the monomer concentration of 0.25M was converted to the insoluble gel, when purified by reprecipitation. The molecular weight (Mn) of polymers **3** and **4** was 1500 and 3800 corresponding to the degree of polymerization of 4.0 and 9.5, respectively, and thus chain transfer should frequently occur. The diazacrown moieties in the monomers are concerned with the transfer, because tertiary amines have a large tendency to chain transfer reactions.

Table 1

Radical polymerizations of 4,10-bis(2-acryloyloxyethyl)- and 4,10-bis(2-methacryloyloxyethyl)-1,7-dioxa-4,10-diazacyclododecane(**1** and **2**)[a]

Monomer (M)	[M] (mol•l^{-1})	Time (h)	Conv. (%)	fc[b] (%)	Mn[c]	Mw/Mn[c]
1	0.05	72	55	100		
	0.1	24	66	100	1500	1.30
	0.25	12	74	100		
	0.5	12	gelation			
2	0.05	72	51	100		
	0.1	24	51	100	3800	1.42
	0.25	2	gelation			

[a] [AIBN]/[M] molar ratio, 0.05 ; solvent, benzene ; temp, 60°C.
[b] Extent of cyclization.
[c] Estimated by GPC using poly(styrene) as standard.

Both the infrared and the ^{1}H NMR spectra of the polymers showed that almost all the vinyl groups are consumed, while the diazacrown units are preserved. The polymerization according to a cyclization mechanism, then, led to the polymers with bicyclic constitutional units. The cyclic units should be 5,9-dioxo-4,10,16,21-tetraoxa-1,13-diazabicyclo[11.5.5]tricos-6,8-ylene, as shown in the reaction scheme. The spectroscopic data, however, had so far afford no clue to the confirmation of the end groups produced by chain transfer.

Divinyl ether **5**, which was derived from diaza-12-crown-4 in the similar manner as monomers **1** and **2**, partly remained the vinyl group to give the polymer with the extent of cyclization of 71% in the cationic polymerization(14). On the other hand, the cyclopolymerization to produce the polymers consisting of only cyclic units is the marked characteristic of monomers **1** and **2.**

Table 2 represents the cation-binding abilities of monomers **1** and **2**, and polymers **3** and **4**. From these data the overall extraction constant, *Ke*, of the monomers and the polymers was calculated to be compared with those of the related compounds (Figures 1 and 2). It is known that side chains on the nitrogen pivot of monoaza-15-crown-5 and 18-crown-6, so-called lariat ethers, have a notable effect on complexing with Na^+ and K^+ ions (16 - 19). Until recently, however, little attention was given to the substiluent effects on lithium-selectivity of monoaza-15-crown-5.

Table 2

Extraction of picrate salts by monomers **1** and **2**, and polymers **3** and **4** from aqueous into the methylene chloride phase$^{a)}$

Ligand		Extraction yield in mol-% of the picrates				
		Li^+	Na^+	K^+	Rb^+	Cs^+
Monomer	**1**	79.1	23.4	8.4	5.5	4.9
	2	64.0	4.9	2.7	1.9	2.3
Polymer	**3**	71.7	71.4	44.7	32.4	30.6
	4	60.8	30.7	61.0	11.5	11.8
		Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	
Monomer	**1**	81.2	79.1	80.2	80.8	
	2	78.1	72.1	79.9	77.9	
Polymer	**3**	86.4	86.8	86.4	86.5	
	4	91.1	87.5	90.9	91.0	

$^{a)}$ [Picric acid] = $7.0 \cdot 10^{-5}$ $mol \cdot l^{-1}$; [Monomeric units] = $3.5 \cdot 10^{-3}$ $mol \cdot l^{-1}$; [Metal ion] = 0.1 $mol \cdot l^{-1}$

The substituents influence the selectivity for Li^+ ion in the diaza-12-crown-4 as well (Figure 2). *N,N'*-Dibutyl and -bis(2-hydroxyethyl) derivatives(**8**,**9**) are slightly inferior to *N,N'*-dimethyl one(**7**) in the binding ability and selectivity for Li^+ ion. The binding abilities of *N,N'*-bis(2-methoxyethyl) and -bis(methoxycarbomethyl) derivatives(**10**,**11**) are remarkably enlarged for alkali-metal ions, other than Li^+ ion. As having the acyl group in the side chain, compound **11** shows slightly lower ability than compound **10**.

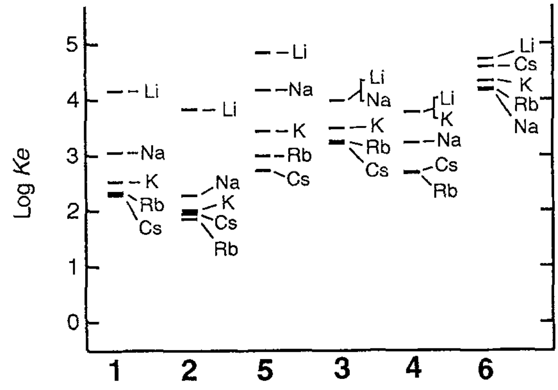


Figure 1:
Selective extraction of alkali-metal picrates by monomers **1**,**2**, and **5** and polymers **3**,**4**, and **6**. [Picric acid] = $7 \cdot 10^{-5}$ mol•l^{-1}; [Monomeric unit] = $3.5 \cdot 10^{-3}$ mol•l^{-1}; [Metal ion] = 0.1 mol•l^{-1}

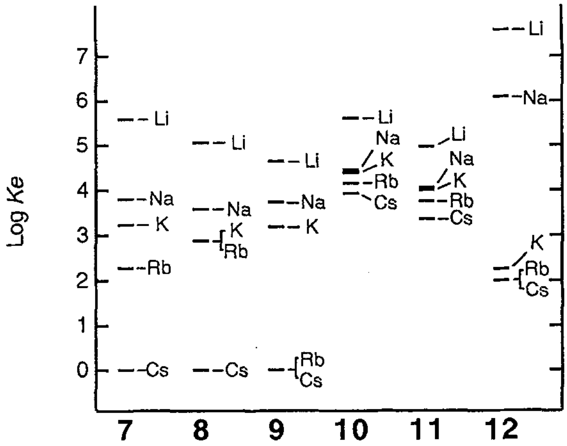
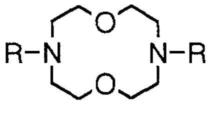


Figure 2:
Selective extraction of alkali-metal picrates by diazacrowns **7** - **11** and [2.1.1]cryptand **12**. [Picric acid] = $7 \cdot 10^{-5}$ mol•l^{-1}; [Ligand] = $7 \cdot 10^{-5}$ mol•l^{-1}; [Metal ion] = 0.1 mol•l^{-1}



7: R= methyl
8: R= n-butyl
9: R= $-CH_2CH_2OH$
10: R= $-CH_2CH_2OCH_3$
11: R= $-CH_2COOCH_3$

Each of the monomers **1**, **2**, and **5** retains the high selectivity for Li^+ ion, and notably monomer **5** is characteristic of the lariat ether (Figure 1). Monomer **1** slightly lowers the binding ability in comparison with monomer **5**, in the same manner as the relation between crowns **10** and **11**. A disadvantage of steric strain of complexation occurs to lower the binding ability for the ions, other than Li^+, resulting in the increased selectivity for Li^+ ion. In the polymers the highest binding ability for Li^+ ion remains unaltered, but the selectivity is lowered by the increase of binding ability for other alkali-metal ions: the marked tendency is observed in polymer **6**. A slight variety of components on the bicycles as ligand unit sensitively reflects the binding affinity for the ions, and thus the binding ability for Li^+ ion equals to that for Na^+ ion in polymer **3**, for K^+ ion in polymer **4**, and for Cs^+ ion in polymer **6**. The polymers are endowed with the binding ability for the larger alkali-metal ions by the cooperative effect of neighbouring ligands, in addition to that for Li^+ by the cavity effect, thereby losing the selectivity in contrast to cryptand **12**(3).

In the case of alkaline-earth ions, the binding ability of the polymers is comparable to that of the monomers and further polymers **3** and **4** to that of polymer **6**. The binding of polymers **3** and **4**, therefore, should be due to the chelation effect of the amino group in addition to the cavity effect. The amino group does not participate in binding alkali-metal ions which have a lower stability than alkaline-earth ions in the chelation. There is scarcely any selectivity for the alkaline-earth ions, however.

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