Macromolecular Ionophore II. Metal Cation-Binding Property of (1→6)-2,5-Anhydro-D-glucitol

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ABSTRACT: The cation-binding property has been studied for polymer **1** consisting of 3,4-di-*O*-methyl-D-glucitol units, (1→6)-2,5-anhydro-3,4-di-*O*-methyl-D-glucitol, and polymer **2** with a mole fraction of cyclized units of 0.52 synthesized by the polymerization of 1,2:5,6-dianhydro-3,4-*O*-isopropylidene-D-mannitol. Polymer **1** exhibited cation-binding selectivity in the order of $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$, which was estimated using both liquid–liquid extraction and liquid-membrane transport methods. On the other hand, **2** showed an extremely low cation-binding characteristic in both extraction yield and selectivity, and the yield of K^+ for **2** was *ca.* one-eighth of that for **1**. There was a need for *ca.* 21–25 and *ca.* 200–400 repeating units in the complexes of **1** and **2** with K^+ , respectively. The binding ability of **1** strongly depended on the radius of the metal cations, and the extraction yields were relatively low for a cation with a radius of 1.12 Å and below (Mg^{2+} , Li^+ , Ni^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Na^+ , Ca^{2+} , and Sr^{2+}) and high for a cation with a radius of 1.20 Å and above (Pb^{2+} , Ag^+ , K^+ , Ba^{2+} , Rb^+ , and Cs^+).

KEY WORDS D-Glucitol / Metal Cation / Liquid–Liquid Extraction / Liquid–Membrane Transport /

Macromolecular ionophores such as poly(cyclooxal-kane)diyl,¹ poly(7-oxanorbornene),² and (1→6)-2,5-anhydro-3,4-di-*O*-alkyl-D-glucitol (alkyl = CH_3 , **1**)^{3–6} recognize a metal cation and form a complex with it, as do naturally occurring acyclic ionophores. In the host–guest complexations, the molecular recognitions are supposed to realize that helical conformers of these polymers vary their pitch and cavity size for optimizing multidentate coordination with a given cation. Therefore, it is of interest to elucidate the effect of the structural regularity and number of repeating units in the host polymer on the molecular discrimination, when the polymer forms the complex with a cationic guest.

Previously, we reported the difference in the cyclo-polymerization tendency between 3,4-di-*O*-methyl and 3,4-*O*-isopropylidene-1,2:5,6-dianhydro-D-mannitols, *i.e.*, the former polymerization produced regio- and stereospecific polymer **1**,⁷ whereas the latter yielded polymer **2** consisting of cyclic and acyclic constitutional repeating units.⁸ Thus they are suitable polymers for

the fact that a naturally occurring acyclic ionophore transports a metal cation through a liquid membrane system.

In this paper, we report that the alkali metal cation-binding properties of **1** and **2** are characterized using a liquid–liquid extraction method and those for **1** using a liquid–membrane transport system. For the complexes with K^+ , the number of repeating units in **1** and **2** is estimated by changing the ratio of the units to K^+ . In addition, the relation between the metal cation radius and the binding property of **1** is clarified using various metal cations.

EXPERIMENTAL

Materials

The synthesis of polymers **1** and **2** was reported in previous papers.^{7,8} Dichloromethane and chloroform were washed three times with deionized water. Picric acid was recrystallized from methanol. All other reagents were commercially available and were used without further purification.

Measurements

UV spectra were measured using a JASCO UVDEC-660 UV/VIS spectrophotometer for the liquid–liquid extraction experiments. The concentration of metal cations was determined using a Varian Spectro AA-40 atomic absorption spectrometer for the liquid–membrane transport experiments.

Extraction Experiment

The extraction of alkali metal picrates was carried

investigating the effect of polymer structure on the molecular recognition toward a cationic guest. Moreover, the molecular recognition property of a macromolecular ionophore is of great interest in relation to

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Table I. Extraction of alkali-metal picrate by polymers **1** and **2**^a

Polymer	M_n (DP) ^b	Extraction yield/%				
		Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
1	2100 (12.1)	13	26	53	51	48
	2600 (14.9)	21	32	63	62	60
	3600 (20.7)	17	36	69	63	61
2	3500 (18.8)	9	8	8	9	8

^a Temp, 20°C; [metal ion] = 1.0×10^{-2} mol L⁻¹; [picric acid] = 7.0×10^{-5} mol L⁻¹; [repeating unit in polymer] = 5.75×10^{-3} mol L⁻¹.
^b M_n , number average molecular weight; DP, average degree of polymerization.

out using a procedure similar to that developed by Pedersen.⁹ A solution of polymer **1** in dichloromethane (2.5 mL, [polymer unit] = 5.75×10^{-3} mol L⁻¹) was vigorously shaken with an aqueous solution (2.5 mL) containing alkali metal chloride and picric acid ([picric acid] = 7.0×10^{-5} mol L⁻¹ and [alkali metal chloride] = 0.1 and 0.01 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-spectrometer. The extraction of alkaline earth metals and transition metals was carried out under the same conditions for alkali metals, except for Cd²⁺, Pb²⁺, and Ag⁺ using an aqueous phase containing metal nitrate and picric acid ([picric acid] = 7.0×10^{-5} mol L⁻¹ and [metal nitrate] = 0.01 mol L⁻¹). The extraction experiment with varying molar ratio of the repeating units in the polymer to potassium cation ([P]/[K⁺]) was carried out by the same procedure using a dichloromethane solution of polymer **1** or **2** (2.5 mL) and an aqueous solution (2.5 mL) containing potassium hydroxide (KOH) and picric acid. The mole concentration of KOH and picric acid was kept constant ([picric acid] = 1.0×10^{-3} mol L⁻¹ and [KOH] = 0.1 mol L⁻¹), and the concentration of the polymer unit was changed from 1.0×10^{-4} mol L⁻¹ to 5.0×10^{-3} mol L⁻¹.

Liquid-Membrane Transport

In an "H-tube" with a 14-mm internal diameter was placed 10 mL of chloroform with 1 g L⁻¹ of **1**. An aqueous solution (10 mL) of picric acid (4.0 mM), NaCl (1.0 mM), KCl (1.0 mM), RbCl (1.0 mM), and CsCl (1.0 mM) was placed in the source phase. Water was used as the receiving phase. The aqueous and organic phases were stirred at 250 rpm. Samples of the receiving phase were withdrawn at an appropriate time and the concentration of cations was determined by atomic absorption spectrometry.

RESULTS AND DISCUSSION

Metal cation-binding properties were estimated by the liquid-liquid extraction method. Table I lists the results of extraction yields of alkali metal picrates using **1** with a number-average degree of polymerization (DP) of 12.1, 14.9, and 20.7 and **2** with a DP of 18.8. Extractions were carried out under the condition that the ratio of repeating units in the polymer to metal picrate was *ca.* 82. Every

Figure 1. Plots of $[P]_{\text{org.}}/[K^+]_{\text{initial aq.}}$ in the feed vs. $[P]_{\text{org.}}/[K^+]_{\text{final org.}}$ in the extraction equilibrium for (a) polymer **1** and (b) polymer **2** ([potassium hydroxide] = 0.10 mol L⁻¹, [picric acid] = 1.0×10^{-3} mol L⁻¹, $[P]_{\text{org.}}$ = 1.0×10^{-4} – 5.0×10^{-3} mol L⁻¹).

specimen of **1** was similar in cation-binding selectivity in the order of $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$, regardless of its DP, though the extraction yields increased with increasing DP. For **1** with a DP of 20.7, the extraction yield of K⁺ was 69%. On the other hand, **2** showed an extremely low cation-binding characteristic in both extraction yield and selectivity. For instance, the yield of K⁺ for **2** was *ca.* one-eighth of that for **1**. The difference in ability between **1** and **2** arises from the fact that both polymers consist of different fractions of cyclized units. Thus, the apparent amounts of repeating units participating in complexation with a metal cation are estimated from the extraction experiment with varying the molar ratio of the repeating units in the polymer to the metal cation ([P]/[K⁺]).

Figures 1a and 1b show the plots of the $[P]_{\text{org.}}/[K^+]_{\text{initial aq.}}$ in the feed vs. the ratio of $[P]_{\text{org.}}/[K^+]_{\text{final org.}}$ in the extraction equilibrium. When the ratio of $[P]_{\text{org.}}/[K^+]_{\text{initial aq.}}$ was varied from 0.5 to 5.0, the ratio $[P]_{\text{org.}}/[K^+]_{\text{final org.}}$ gave a constant value, 21–25, for **1** (DP = 20.7) but gradually increased from 200 to 400 for **2**. For the complexation, **2** needed a greater quantity of the repeating units than **1** of which one molecule binds one K⁺ ion. An appropriate amount of the repeating units, *i.e.*, the number of oxygen atom, for coordination to K⁺ may be independent of the polymer structure, and thus the greater part of repeating units in **2** does not use for the complex formation. These results indicate that the regularity of the polymer structure is substantially important for the molecular recognition.

In order to elucidate the molecular recognition property of **1** as a function mimicking that of a naturally occurring acyclic ionophore, the binding selectivity of **1** toward an alkali metal cation was carried out using an

Figure 2. Competitive transport of Na^+ , K^+ , Rb^+ , and Cs^+ with polymer **1** (source phase, an aqueous solution (10 mL) of picric acid (4.0 mM), NaCl (1.0 mM), KCl (1.0 mM), RbCl (1.0 mM), and CsCl (1.0 mM); organic phase, 10 mL of chloroform with 1 g L^{-1} of **1**; receiving phase, 10 mL of water).

Figure 3. Plots of extraction yield vs. metal cation radii.

H-type apparatus for liquid–membrane transport. Figure 2 shows the result of the competitive transport of Na^+ , K^+ , Rb^+ , and Cs^+ . The transport rate increases in the order of $\text{K}^+ > \text{Rb}^+ > \text{Cs}^+ > \text{Na}^+$, which closely agrees with the result using the liquid–liquid extraction method. The ratio of transport rates between Na^+ and K^+ , K^+/Na^+ was 9.0, which was half the value of that using dibenzo-18-crown-6 as a synthetic cyclic ionophore.

The effects of the metal cation radius on the extraction yield were clarified using picrates of alkali metal ions (Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+), alkaline earth metal ions (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}), heavy metal ions (Zn^{2+} , Cd^{2+} , and Pb^{2+}), and transition metal ions (Ni^+ , Co^{2+} , Cu^{2+} , and Ag^+). Figure 3 shows the plots of extraction yields vs. metal cation radii. The highest yield, 72%, was obtained for Ag^+ with a radius of $1.26 \text{ \AA}$. The metal cation-binding property of **1** strongly depends on the metal cation radius and was entirely different below and above $1.15 \text{ \AA}$, *i.e.*, relatively low and high yields were observed for the radius of Sr^{2+} , $1.12 \text{ \AA}$, and below and for the radius of Pb^{2+} , $1.20 \text{ \AA}$, and above, respectively.

Previously, we reported that the oxygens attached to

the C3, C4, and C6 carbons acted as a donor atom for the host–guest complexation on the basis of the NMR spectral study for the enantioselective transport of racemic amino acid using **1**. Though the apparent difference before and after the complex formation could not be observed for the NMR spectral measurement, the similar complexation should be deduced for the metal cation. Thus the higher regularity of **1** than **2** was suitable for the host–guest complexation and **1** preferably formed a complex with a metal cation whose radius is $1.20 \text{ \AA}$ and above, indicating that the conformer of **1** varied its pitch and cavity size for forming a complex with a given metal cation. However there is a possibility that the difference in substituent between **1** and **2**, *i.e.*, the methyl and isopropylidene groups, affects the cation-binding property, and thus the complexation mechanism involving the complex structure is obscure and more detailed studies are needed.

CONCLUSIONS

The cation-binding property of macromolecular ionophores, **1** and **2**, was characterized using liquid–liquid extraction and liquid–membrane transport methods. Polymer **1** formed the complex with a selectivity in the order of $\text{K}^+ > \text{Rb}^+ > \text{Cs}^+ > \text{Na}^+ > \text{Li}^+$ and exhibited higher cation-binding characteristic in both extraction yield and selectivity than **2**. The repeating units of *ca.* 21–25 for **1** and those of *ca.* 200–400 for **2** were needed for the formation of a complex with K^+ . These results indicated that the regularity of the polymer structure is substantially important for the molecular recognition. In addition, the molecular recognition property of **1** toward metal cations strongly depended on the metal cation radius, *i.e.*, **1** preferably formed a complex with a metal cation whose radius is $1.20 \text{ \AA}$ and above, regardless of the kind of metal cations.

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