

Preparation and Ion-Binding Properties of Calix[4]crown-Containing Polyesters

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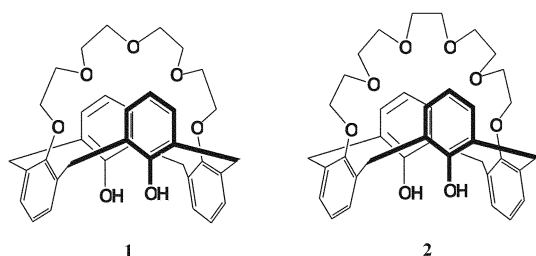
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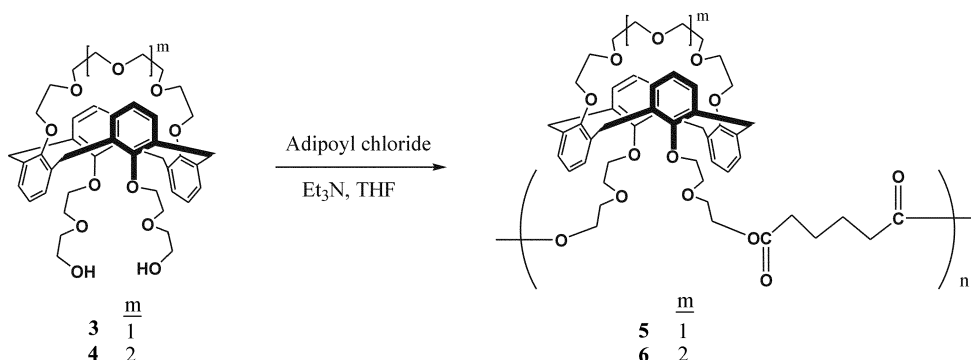
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The calix[4]arene macrocyclic structural framework has been shown to be an attractive building block which can be selectively functionalized both at the hydroxyl lower rim and at the upper rim for the coordination of neutral, cationic and more recently, anionic guest species.¹⁻⁹

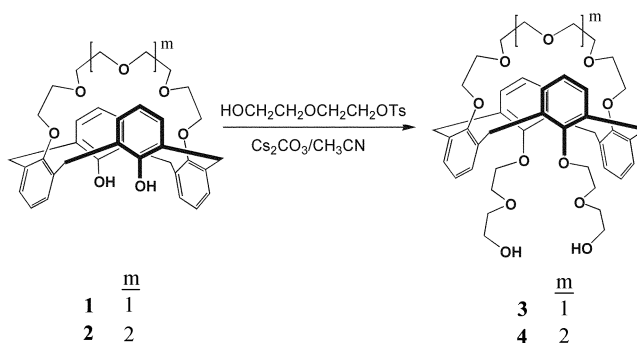
Although quite a large number of reports exist on the molecular calix[4]arenes, those on polymeric calix[4]arenes are limited. Polymeric inclusion membrane system has been recently developed taking advantage of easy set up, high selectivity and high durability. The measurement of the transport rate and permeability toward metal ions in polymeric inclusion membrane system using the polymeric calix[4]crown has been reported.^{10,11} However, calix[4]arene based polymers have just begun to receive attention, as these new polymers may then be processed into materials suitable for the chemical sensor devices such as ion selective electrodes and filtration/extraction membranes.^{12,13} It was recently reported that the copolymers containing pendent calix[4]arene and calix[4]crown units were prepared and the



Scheme 1



Scheme 3



Scheme 2

complexion studies were made by using liquid-liquid and solid-liquid extraction procedures.^{14,15}

In this work, calix[4]crown-5 and 6-containing monomers, calix[4]crown-5-2,4-bis[2-(2-hydroxyethoxy) ethyl ether] (3) and calix[4]crown-6-2,4-bis[2-(2-hydroxyethoxy) ethyl ether] (4), were prepared and then polymerized with adipoyl chloride to give polyesters 5 and 6. And also, we will discuss their ionophoric properties for some alkali and alkali earth metal cations.

Monomers 3 and 4 were prepared by reacting calix[4]crown-5 (1) and calix[4]crown-6 (2) with di(ethylene glycol) monotosylate in the presence of Cs_2CO_3 , respectively, as shown in Schemes 1 and 2.

The polyesters 5 and 6 containing calix[4]crown were prepared by condensation polymerization of 3 and 4 with adipoyl chloride in tetrahydrofuran using acid acceptor, respectively, as shown in Scheme 3. The results of polymeri-

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Table 1. Physical properties of calix[4]crown 5- and 6-containing polymers

	Mw ^a	MWD ^b	η_{inh} ^c	Yield (%)	Solubility					
					Hexane	EE ^d	EA ^e	Acetone	Chloroform	THF ^f
3	757	–	–	43	⊙	⊙	⊙	⊙	⊙	⊙
4	801	–	–	57	⊙	⊙	⊙	⊙	⊙	⊙
5	6800	1.2	0.29	74	⊙	⊙	⊙	⊙	⊙	⊙
6	8200	1.3	0.34	52	⊙	⊙	⊙	⊙	⊙	⊙

⊙: Soluble, ⊖: Insoluble. ^aMw, weight average molecular weight; ^bMWD, molecular weight distribution; ^c η_{inh} , inherent viscosities were measured using 1 g/dl in chloroform at 25 °C; ^dEE, ethyl ether; ^eEA, ethyl acetate; ^fTHF, tetrahydrofuran.

zation were summarized in Table 1.

The chemical structure of the polymers was characterized by IR and ¹H-NMR spectroscopy, and elemental analysis. In the infrared spectra, the polymers **5** and **6** showed characteristic absorption bands at 1735 cm⁻¹ corresponding to the ester linkage. In the NMR spectrum of polymers **5** and **6**, the ethylene protons in crown ether and alkylene protons in adipoyl moiety appear at 3.90-3.50 ppm and 2.44-1.50 ppm as multiplets, respectively. The elemental analysis data of the monomer and polymers gave satisfactory results.

The solubility of the polymers was evaluated in various solvents such as ethyl ether, ethyl acetate, acetone, methylene chloride and tetrahydrofuran at 5 mg/mL. The incorporation of aliphatic ester linkage into the polymer backbone enhances the solubility in common organic solvents to a high degree. The polymers show good solubility in common organic solvents such as acetone, ethyl acetate, chloroform and THF, while they display virtually no solubility in toluene, *n*-hexane and ethyl ether.

This condensation polymerization gave the polymers of somewhat small molecular weight judging from the data of viscosity and GPC data as shown in Table 1. The inherent viscosities of polymers **5** and **6** possessed 0.29 dL/g and 0.34 dL/g, respectively. The average molecular weights of polymers **5** and **6** were 6800 and 8200 g/mole, respectively. The relatively low molecular weights of the present polymers were presumably due to the bulky calix[4]-crown moiety.

The recognition properties of polyesters **5** and **6** were studied by liquid-liquid and solid-liquid extraction experi-

ments. Selective extraction experiments were then performed to see the transference of some alkali metals and alkali earth metals (Na, K, Rb, Cs, Mg, Ca, Sr, Ba) from aqueous phase to organic phase by the present polymeric calix[4]crowns.

In the control experiments, it was confirmed that no metal ion transport was observed in the absence of the carrier. To measure the selectivity and efficiency of ligands **5** and **6** for metal ions, the concentration of picrate anions extracted from the aqueous phase into the organic phase were measured at equilibrium.

The results of two phases extraction experiment of metal picrate with **5** and **6** are summarized in Table 2.

Although both the polymer **5** and **6** possess the same 1,3-alternate conformation, they display different selectivity characteristics. The polymer **5**, where crown-5 was incorporated into the calix[4]arene, shows high selectivity to potassium ion due to the size agreement between calix-crown-5 and K⁺. But the cavity size of the calixcrown-5 framework is less suitable to rubidium ion. It has been shown that except K⁺, Rb⁺, Mg⁺ and Ca⁺ neither Li⁺, Na⁺ and Cs⁺ nor Sr²⁺ and Ba²⁺ used in the extraction experiments were significantly extracted by the polymer **5**.

In the case of polymer **6**, high cesium ion extraction was observed. It has been reported that the calix[4]crown-6 in which the pentaethylene glycol unit connects with the 1,3-dialkoxy framework within the 1,3-alternate type, was known to show high cesium ion selectivity over other alkali metal ions.¹⁷ This is ascribed not only to the size agreement of the crown ether moiety based on electrostatic interaction between the electron donor atom and the metal cation, but

Table 2. Extraction^a of picrate salts with various concentration of calix[4]arene crown ether polymer

Ligands ^b	Picrate salt extracted (%)									
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺	
5	a	0	<1	40.43	19.26	0	2.42	0.72	<1	0
	b	0	<1	57.45	35.34	0	4.73	1.51	<1	0
	c	0	<1	78.72	69.08	0	6.21	3.58	<1	0
6	a	0	0	<1	<1	18.06	0	0	<1	1.22
	b	0	0	<1	3.98	36.48	0	0	1.43	3.65
	c	0	0	<1	12.50	51.94	0	0	2.62	7.21
5^c	–	<1	28.12	13.32	0	2.72	<1	–	–	–
6^c	–	–	<1	5.76	35.79	–	–	<1	<1	4.86

^aH₂O/CHCl₃ = 50/50 (v/v). ^bConcentration of calix[4]crown ether polymer; [a] = 3.5 × 10⁻⁴ M, [b] = 7.0 × 10⁻⁴ M, [c] = 1.4 × 10⁻³ M. ^cLiquid-solid extraction

also to π -metal interaction between two 1,3-alternate phenyl rings and the metal ion. The calix[4]crown-5 and 6-containing polymers studied were polyester bearing oxygen atoms as hard donor sites and similar to those presented in calix[4]crown-5 and 6-2,4-bis[2-(2-acyloxyethoxy) ethyl ether]. Other functional groups with other types of donor sites have been introduced on calix[4]crowns, which result in the influence on the complexing behavior and the selectivity.

The solid-liquid, batchwise adsorption extraction experiments of polymers were carried out in the aqueous solutions of selected metal picrates. The extractability behaviors of the polymers are described in Table 2. It has been observed that there is a significant decrease in the extraction ability is weak in solid state, but showed more or less the same affinity toward the metal cation.

In conclusion, new polyesters were prepared and their liquid-liquid and solid-liquid extraction experiments were performed. As a result of ion binding properties using picrate extraction method, the polyester **5** showed more than 70% selectivity for potassium and rubidium ion and the polyester **6** showed high selectivity to cesium ion generally. Calix[4]crown-containing polyesters are applicable for polymeric ion acceptor to extract potassium, rubidium, cesium and some alkali earth metal ion.

Other experiments on the transport rate and permeability toward metal ions in polymeric inclusion membrane system using calix[4]crown-containing polyesters **5** and **6** are now in progress.

Experimental Section

Calix[4]crown-5 (**1**) and calix[4]crown-6 (**2**) were prepared by the method previously reported.² Cesium carbonate, adipoyl chloride, di(ethylene glycol) monotosylate and picric acid (Aldrich Chem. Co.) were used as received. Acetonitrile and chloroform were dried by distillation over phosphorus pentoxide. Tetrahydrofuran and triethylamine were distilled over sodium and calcium hydride.

FT-IR spectra were obtained with a Biorad exaliber FTS-3000MX spectrophotometer and ¹H NMR spectra were recorded on a Varian Unity Inova (200 MHz) spectrometer. Elemental analyses were performed using a Yanaco MT-3 CHN instrument. UV/vis spectra were obtained on a Shimadzu 1601PC spectrophotometer. Gel-permeation chromatography (GPC) data were obtained with a Waters HPLC using three columns (μ -Stryragel 10², 10³ and 10⁴ Å) in THF and calibrated with polystyrene standards at 20 °C.

Preparation of calix[4]crown-5-2,4-bis[2-(2-hydroxyethoxy)ethyl ether] (3). **1** (3.0 g, 5.1 mmol), di(ethylene glycol) monotosylate (3.32 g, 1.3 mmol), and cesium carbonate (4.99 g, 15.3 mmol) were dissolved in acetonitrile (100 mL) and refluxed for 24 h under nitrogen at 85 °C. The solvent was evaporated and the crude residue was washed with distilled water several times. The crude residue was dissolved in methylene chloride and acidified with 5% aqueous hydrochloric acid. Recrystallization was performed

from diethyl ether. Calix[4]crown-6-2,4-bis[2-(2-hydroxyethoxy) ethyl ether] (**4**) was also prepared by the similar procedures described above. **3**: Yield 43%, IR (KBr, cm⁻¹): 3150, 2926, 2865, 1594, 1459, 1411, 1204, 1084, 839, 753. ¹H NMR (CDCl₃): δ 7.03-7.02 (d, 4H, 4 ArH_m), 6.93-6.92 (d, 4H, 4 ArH_m), 6.64 (q, 4H, 4 ArH_p), 4.47-4.05 (d, 8H, ArCH₂Ar), 3.87 (m, 24H, -CH₂CH₂O-), 3.52 (m, 8H, -CH₂CH₂OH), 3.27 (d, 4H, ArCH₂Ar). Anal. Calcd for C₄₄H₅₂O₁₁ (Mw, 756.89); C, 69.82; H, 6.93. Found: C, 70.12; H, 6.79. **4**: Yield 57%. IR (KBr, cm⁻¹): 3152, 2920, 2865, 1592, 1460, 1410, 1205, 1082, 840, 754. ¹H NMR (CDCl₃): δ 7.02-7.02 (d, 4H, 4 ArH_m), 6.92-6.92 (d, 4H, 4 ArH_m), 6.65 (q, 4H, 4 ArH_p), 4.46-4.02 (d, 8H, ArCH₂Ar), 3.86 (m, 28H, -CH₂CH₂O-), 3.50 (m, 8H, -CH₂CH₂OH), 3.25 (d, 4H, ArCH₂Ar). Anal. Calcd for C₄₆H₅₆O₁₂ (Mw, 800.94); C, 68.98; H, 7.04. Found: C, 69.02; H, 7.06.

Synthesis of polyester (5) containing calix[4]crown-5. **3** (3.00 g) and triethylamine (0.10 g) were dissolved in THF (40 g) for 20 min under nitrogen atmosphere. Adipoyl chloride (0.72 g, 0.039 mmol) was added dropwise slowly through dropping funnel. The reaction mixture was continuously stirred at 40 °C for 36 h. The solvent was evaporated and the crude residue was washed with distilled water. The solid product was redissolved in methylene chloride and acidified with 5% aqueous HCl. The organic layer was dried with anhydrous magnesium sulfate. The resulting polymer was precipitated in hexane and dried in vacuo at 60 °C. Polyester (**6**) containing calix[4]crown-6 moiety was also prepared by the similar method described above. **5**: Yield 82%. IR (KBr, cm⁻¹): 3120, 2920-2880 (aliphatic C-H), 1735 (ester C=O), 1584, 1490, 1298, 1250-1050 (C-O). ¹H NMR (CDCl₃): δ 7.13-7.02 (d, 8H, 4 ArH_m), 6.87-6.82 (d, 4H, 4 ArH_p), 4.05-3.86 (d, 8H, 4 ArCH₂Ar), 3.87-3.52 (m, 24H, -OCH₂CH₂O- and 2 -CH₂CH₂O-CO), 2.44 (t, 4H, -O-CO-CH₂-), 1.97-1.52 (m, 4H, -(CH₂)₂-). Anal. Calcd for C₅₀H₅₈O₁₃ (Mw, 867.00); C, 69.27; H, 6.74. Found: C, 69.12; H, 6.78. **6**: Yield 88%. IR (KBr, cm⁻¹): 3120, 2920-2880 (aliphatic C-H), 1735 (ester C=O), 1582, 1491, 1296, 1250-1052 (C-O). ¹H NMR (CDCl₃): δ 7.12-7.00 (d, 8H, 4 ArH_m), 6.88-6.80 (d, 4H, 4 ArH_p), 4.04-3.84 (d, 8H, 4 ArCH₂Ar), 3.88-3.52 (m, 28H, 5 -OCH₂CH₂- and 2 -CH₂CH₂O-CO), 2.44 (t, 4H, -O-CO-CH₂-), 1.98-1.50 (m, 4H, -(CH₂)₂-). Anal. Calcd for C₅₂H₆₂O₁₄ (Mw, 911.05); C, 68.56; H, 6.86. Found: C, 68.49; H, 6.89.

Liquid-liquid extraction. Aqueous picrate solution (10 mL, 3.5 × 10⁻⁵ M) and solution of polymer (**5**, 10 mL, 3.5 × 10⁻⁴, 7.0 × 10⁻⁴, 1.4 × 10⁻³ M) in chloroform were vigorously agitated in a stopped glass tube with a homogenizer for 2 min, then magnetically stirred at 25 °C for 30 min, and finally left standing for 30 min. The concentration of picrate ion remaining in the aqueous phase was then determined by UV-vis spectrophotometer. Blank experiments showed that no picrate extraction occurred in the absence of calix[4]crown. The alkali picrates were prepared by stepwise addition of 3.5 × 10⁻⁵ M aqueous picric acid solution to 1 × 10⁻² M aqueous solution of metal hydroxide.¹⁶

Solid-liquid extraction. Copolymer (**5**, 30 mg) was

shaken with an aqueous solution (10 mL, 2.5×10^{-5} M) of metal picrate in a vial (50 mL) at 25 °C for 1 h and finally filtered off. The concentration of picrate ion remaining in the aqueous phase after the adsorption was then determined spectrophotometrically.

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