

Notes

Synthesis and Binding Properties of a Calix[4]crown-6-functionalized Polymeric Ion Acceptor

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Abstract: Calix[4]crown-6-2,4-bis(2-hydroxyethyl ether) (**2**), which has crown-6 moieties at the 1- and 3-positions and hydroxyethyl functions at the 2- and 4-positions, was prepared for the syntheses of polyester **3** and polyurethane **4** by reactions with adipoyl chloride and hexamethylene diisocyanate, respectively. The ion binding characteristics of monomer **2** and polymers **3** and **4** toward alkali and alkali earth metal ions were measured by liquid-liquid extraction from the aqueous phase into the organic phase. We observed that the polyurethane **4** has a higher binding affinity toward various metal cations when compared to polyester **3**, which exhibits cesium ion selectivity.

Keywords: calix[4]crown-6, polyester, polyurethane, ion-binding.

Introduction

The calix[4]crown 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 of para position of the phenol aryl moieties for the coordination of neutral, cationic and more recently, anionic guest species.¹⁻⁹

Although quite a large number of reports exists on the molecular calix[4]arenes and calix[4]crowns, those on polymeric calix[4]crowns are limited.¹⁰⁻¹³ Calix[4]arene based polymers, however, 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.¹⁴⁻¹⁷ It was reported that the copolymers containing pendant calix[4]arene and calix[4]crown units were prepared and the cation ion-binding studies were performed using liquid-liquid and solid-liquid extraction methods.¹⁸⁻²¹ In our previous work, we have synthesized polyesters containing calix[4]crown-5 and calix[4]crown-6 and their ionophoric properties have been investigated for alkali and alkali earth metal cations.²²

In this work, new polyester and polyurethane containing calix[4]crown-6 were prepared by reacting calix[4]crown-6-2,4-bis(2-hydroxyethyl ether) with adipoyl chloride and hexamethylene diisocyanate and their liquid-liquid extraction experiments were performed.

Experimental

Materials and Measurements. Calix[4]crown-6 (**1**) was prepared by the method previously reported.² Cesium carbonate, adipoyl chloride, hexamethylene diisocyanate, 2-bromoethanol, picric acid (Aldrich Chem. Co.) were used as received. Acetonitrile and chloroform were dried from molecular sieves (4 Å) and distilled over phosphorus pentoxide. Tetrahydrofuran and triethylamine (Aldrich Chem. Co.) were distilled over sodium and calcium hydride.

FT-IR spectra were obtained with a Biorad Excaliber 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. 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.

Synthesis of Calix[4]crown-6-2,4-bis(2-hydroxyethyl ether) (2**).** Calix[4]crown-6 (3.0 g, 4.8 mmol), 2-bromoethanol (1.50 g, 12 mmol), cesium carbonate (4.69 g, 15.3 mmol) and acetonitrile (60 mL) were refluxed for 3 days under nitrogen at 80 °C. The solvent was evaporated under reduced pressure. The crude residue was dissolved in methylene chloride and acidified with aqueous hydrochloric acid. The organic layer was washed with deionized water several times and dried with anhydrous magnesium sulfate. Recrystallization was performed using diethyl ether.

2: Yield 57%. Mp, 302-304 °C. IR (KBr, cm⁻¹): 3400, 3148, 2922, 2875, 1584, 1452, 1357, 1298, 1249, 1210,

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1151, 1084, 1047, 842, 771. $^1\text{H NMR}$ (CDCl_3): δ 7.02-6.98 (d, 8H, 4 ArH_m), 6.84-6.78 (d, 4H, 4 ArH_p), 3.76 (d, 8H, 4 ArCH_2Ar), 3.71-3.34 (m, 28H, 5 $-\text{CH}_2\text{CH}_2\text{O}-$ and 2 $-\text{CH}_2\text{CH}_2\text{OH}$), 3.52 (br, 2H, $-\text{CH}_2\text{CH}_2\text{OH}$). Anal. Calcd for $\text{C}_{42}\text{H}_{50}\text{O}_{10}$ (M_w , 714.85); C, 70.57; H, 7.05. Found: C, 70.22; H, 7.02.

Synthesis of Polyester (3) Containing Calix[4]crown-6. In a three-necked flask were placed a solution of **2** (3 g, 4.2 mmol) and triethylamine (0.79 g) dissolved in THF (30 mL). Adipoyl chloride (0.76 g, 4.2 mmol) was added dropwise slowly through a dropping funnel under nitrogen. The mixture was stirred at 60°C and maintained for 24 h. After the solvent was evaporated, the crude product was washed with deionized water several times. The resulting polymer was reprecipitated in hexane and dried *in vacuo* at 60°C .

3: Yield 88%. Mp, 197-198. IR (KBr, cm^{-1}): 3120 (aromatic C-H), 2920-2880 (aliphatic C-H), 1735 (ester C=O), 1584, 1490, 1298, 1250-1050 (C-O). $^1\text{H NMR}$ (CDCl_3): 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 ArCH_2Ar), 3.87-3.52 (m, 28H, 5 $-\text{OCH}_2\text{CH}_2\text{O}-$ and 2 $-\text{CH}_2\text{CH}_2\text{O}-\text{CO}$), 2.44 (t, 4H, $-\text{O}-\text{CO}-\text{CH}_2-$), 1.97-1.52 (m, 4H, $-(\text{CH}_2)_2-$). Anal. Calcd for $\text{C}_{48}\text{H}_{56}\text{O}_{12}$ (M_w , 824.96); C, 69.89; H, 6.84. Found: C, 70.12; H, 6.79.

Synthesis of Polyurethane (4) Containing Calix[4]crown-6. In a three-necked flask were placed a solution of **2** (3 g, 4.2 mmol) and triethylamine (0.84 g) dissolved in THF (30 mL). Hexamethylene diisocyanate (0.70 g, 4.2 mmol) was added dropwise slowly and the mixture was continuously stirred at 40°C for 24 h. The solvent was evaporated and washed with deionized water several times. The resulting polymer was precipitated in hexane and dried *in vacuo* at 60°C .

4: Yield 92%. Mp, 167-168 $^\circ\text{C}$. IR (KBr, cm^{-1}): 3410 (N-H), 3100 (aromatic C-H), 2920 (aliphatic C-H), 1715 (urethane C=O), 1584, 1495, 1250-1050 (CO), 1107. $^1\text{H NMR}$ (CDCl_3): δ = 7.12-7.01 (d, 8H, 4 ArH_m), 6.87-6.82 (d, 4H, 4 ArH_p), 4.02-3.87 (d, 8H, 4 ArCH_2Ar), 3.96-3.36 (m, 28H, 5 $-\text{OCH}_2\text{CH}_2\text{O}-$ and 2 $-\text{CH}_2\text{CH}_2\text{O}-\text{CO}$), 3.25 (t, 4H, 2 $-\text{O}-\text{CO}-\text{NH}-\text{CH}_2-$), 1.50 (m, 8H, $-(\text{CH}_2)_4-$). Anal. Calcd for $\text{C}_{50}\text{H}_{62}\text{N}_2\text{O}_{12}$ (M_w , 883.48): C, 68.01%; H, 7.01%; N, 3.18%. Found: C, 68.84%; H, 6.96%; N, 3.28%.

Liquid-Liquid Extraction. Picrate extraction experiments were performed using Pederson's procedure.²³ Aqueous picrate solution (10 mL, 3.5×10^{-5} M) and solution of polymer (**3**, 10 mL, 3.5×10^{-4} and 1.4×10^{-3} M) in chloroform were vigorously agitated in a stopped glass tube with a homogenizer for 2 min, then magnetically stirred in a thermostated water-bath at 25°C for 30 min, and finally left standing for 30 min. The concentration of picrate ion remaining in the organic phase was then determined spectrophotometrically. Blank experiments showed that no picrate extraction occurred in the absence of polymer. The alkali picrates were prepared by stepwise addition of a 7×10^{-5} M aqueous picric acid solution to a 1×10^{-2} M aqueous solu-

tion of metal hydroxide.

Results and Discussion

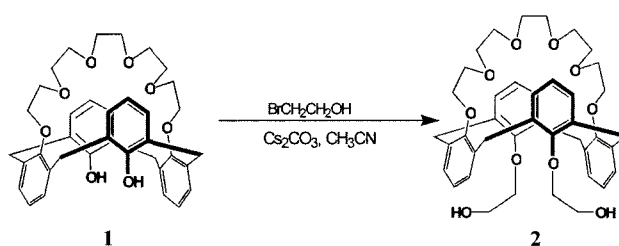
Monomer calix[4]crown-6-[2,4-bis(2-hydroxyethyl ether)] (**2**) was synthesized by reacting **1** and 2-bromoethanol in the presence of Cs_2CO_3 as shown in Scheme I. Polyester **3** and polyurethane **4** containing calix[4]crown-6 moiety were prepared by polymerization of **2** with adipoyl chloride and hexamethylene diisocyanate, respectively, as shown in Scheme II. Total yields of copolymers were found to be moderately high.

Table I summarizes the yields and some physical properties of the polymers synthesized in this study. The chemical structure of resulting polymers was characterized by using the data from IR and $^1\text{H NMR}$ spectroscopies. The CHN elemental analysis values matched well with the expected chemical structure. In the infrared spectra, the polymers **3** and **4** showed characteristic absorption bands at 1735 and 1715 cm^{-1} corresponding to the C=O stretching band of the ester and urethane linkage, respectively. In the NMR spectrum of polymer **3**, the alkylene protons in adipoyl moiety appeared at 2.44-1.52 ppm as a multiplets, whereas those of hexamethylene diisocyanate fragment appeared at 3.25-1.50 ppm.

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

The condensation polymerization gave the polymers somewhat small molecular weight judging from the data of viscosity and GPC. The polymers possessed the inherent viscosities of 0.32 dL/g for **3** and 0.38 dL/g for **4** using chloroform at 25°C . The average molecular weights, which were determined by gel permeation chromatography using polystyrene standards, of polymers **3** and **4** were 12,000 and 13,200 g/mole with a polydispersity index of 1.42 and 1.57. This result was presumably due to the bulkiness of

Scheme I



Scheme II

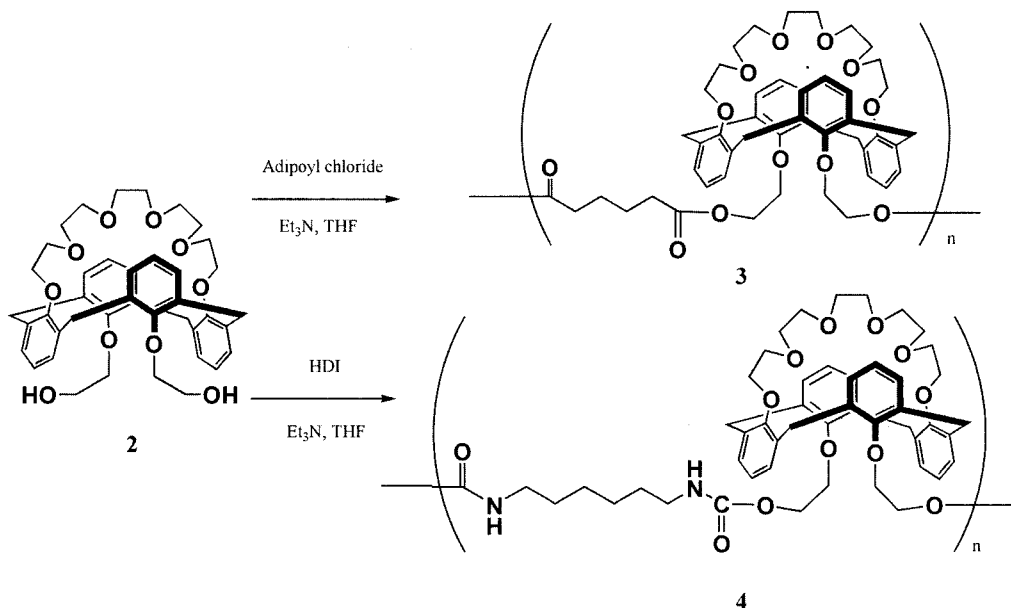


Table I. Physical Properties of Calix[4]crown-6 Derivatives 1-4

	m.p (°C)	M_w^a	MWD^b	η_{inh}^c	Yield (%)	Solubility					
						Hexane	EE ^d	EA ^e	Acetone	MC ^f	THF ^g
1	275-276	626.72	-	-	27	-	-	+	+	+	+
2	302-304	714.85	-	-	64	-	-	+	+	+	+
3	197-198	12,500	1.42	0.32	88	-	-	+	+	+	+
4	167-168	13,200	1.57	0.38	92	-	-	+	+	+	+

+: Soluble. -: Insoluble.

^a M_w , weight average molecular weight. ^bMWD, molecular weight distribution. ^c η_{inh} , inherent viscosities were measured using 1 g/dL in chloroform at 25°C. ^dethyl ether. ^eethyl acetate. ^fmethylene chloride. ^gtetrahydrofuran.

calix[4]crown-6 moiety.

The recognition properties of polymers **3** and **4** were studied by liquid-liquid extraction experiment. Extraction experiments were then carried out to see transference of some alkali metal and alkali earth elements (Na, K, Rb, Cs, Mg, Ca, Sr, Ba) from aqueous phase to organic phase by the polymeric calix[4]crown-6. In control experiments, it was confirmed that no metal ion transfer was observed in the absence of the carrier.

When a ligating agent complexes with specific metal ion, the major factors which influence the complexation are the radius of metal ion, the oxidation state of metal ion, the identity of the donor atoms, the solvent effect, the anion effect, and the dipolar interaction between the organic ligand and the metal ion.²

The results of two phases extraction experiment of metal picrate with model compound **2**, polymers **3** and **4** are summarized in Table II. Although both the polymers **3** and **4** possessed a similar chemical structure, they displayed dif-

Table II. Extraction of Picrate Salts with Various Concentration of Calix[4]crown Monomer and Polymers

Ligand	2		3		4	
	a	b	a	b	a	b
Na ⁺	< 1	< 1	< 1	< 1	11.67	42.29
K ⁺	< 1	4.31	< 1	3.63	11.14	54.35
Rb ⁺	3.79	41.53	3.09	35.31	12.69	71.17
Cs ⁺	6.58	74.89	8.17	72.55	13.90	79.26
Mg ²⁺	< 1	< 1	< 1	< 1	4.26	14.21
Ca ²⁺	< 1	< 1	< 1	< 1	12.31	46.36
Sr ²⁺	< 1	2.11	< 1	2.35	9.82	51.28
Ba ²⁺	1.74	3.41	< 1	4.33	13.02	56.33

H₂O/CHCl₃ = 50/50(V/V); picric acid = 3.5×10^{-5} M; metal hydroxide = 0.01 M.

Calix[4]crown ether polymer; a = 3.5×10^{-4} M, b = 1.4×10^{-3} M.

erent behaviors and characteristics. In the case of polymer **3**, high cesium ion extraction was observed with undetectable transport of sodium and potassium ions. Some of rubidium ion was extracted because of an increase of the ion size relative to sodium and potassium. 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 also to π -metal interaction between two 1,3-alternate phenyl rings and the metal ion. It has been reported that the calix[4]crown-6 was known to give high cesium ion selectivity over other alkali metal ions.²

Interestingly, polymer **4** prefers all the cations of alkali metal and alkali earth metal in the extraction experiment. And its extraction level was higher than that of polymer **3** as shown in Table II. But the maximum cesium extraction was observed with significant extraction of sodium, potassium, rubidium, strontium and barium ions, which have smaller ion radius. This indicates that the 2-alkylaminocarbonyloxyethyl ether unit fits in a wrapping around fashion and two urethane nitrogen atoms are enough to make the ligand-metal complex soluble in the organic layer. The calix[4]crown-6-containing polyurethane **4**, bearing nitrogen atoms as hard donor sites, was similar to those present in calix[4]crown-6-2,4-bis(2-alkylaminocarbonyloxyethyl ether).

These trends were confirmed by transport results of monomeric ligand **2**. The extraction results were similar to that of polyester **3** toward K^+ , Rb^+ and Cs^+ . Such differences can be explained by the effect of pseudo-cyclic conformation of the polymer **4**, the urethane unit fits metal ion to give maximized ion and electrostatic interaction as illustrated in Figure 1.^{6,24,25}

In conclusion, it has been observed that the polymer **4** has high binding ability towards various metal cations as compared to the polymer **3**, which showed the cesium ion selectivity. As a result, the metal transfer ability of polymers

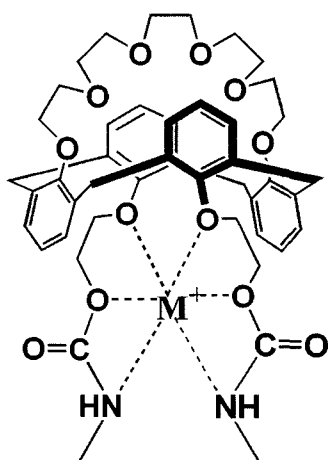


Figure 1. Ion binding structure of the polyurethane(**4**) containing calix[4] crown-6.

depends upon the size of calix[4]crown and the conformation of spacer chain in the polymer skeleton.

Other experiments on the transport to metal ions in polymeric inclusion membrane system using calix[4]crown-containing polyurethane **4** are in progress.

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