

Synthesis and Properties of Calix[4]crown-6 Functionalized Polymers

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Abstract: Calix[4]crown-6-2,4-bis(4-aminobutyl ether), which has a crown-6 moiety at the 1,3-position and amino function at the 2,4-position, was prepared as an intermediate for the subsequent synthesis of calix[4]crown-6-containing polyamide and polyimide using adipoyl chloride and 1,2,4,5-benzenetetracarboxylic dianhydride. The chemical structures were characterized by IR, ¹H NMR spectroscopy and elemental analysis, and some of their physical properties, including their thermal behavior, were examined. The ion binding characteristics of the monomer and polymers for alkali metal and alkali earth metal ions were measured by liquid-liquid extraction from the aqueous phase into the organic phase. It has been observed that polyamide has a high binding ability towards various metal cations as compared to polyimide, which showed cesium ion selectivity.

Keywords: calix[4]crown-6, polyamide, polyimide, ion-binding.

Introduction

Several families of macrocyclic molecules are at the origin of the present wide development of supramolecular chemistry. Among them, calix[4]arene-crown ethers or calix[4]crowns are one of the most widely investigated classes of cation ligand based on calixarene.¹ They show considerable interest as selective ion transport agents for more particularly for the cesium cation.² Calix[4]arene 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 and cationic 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 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.¹⁴⁻¹⁷ It was reported that the copolymers containing pendant calix[4]arene and calix[4]crown units or polymer-supported calix[4]arenes were prepared and the cation ion-binding studies were performed using liquid-liquid and solid-liquid extraction methods.¹⁸⁻²⁴ Recently, in our previous work we have synthesized polyesters and polyurethane having calix[4]crown-5 and calix[4]crown-6 and have investigated their ionophoric properties for alkali and alkali earth metal cations.^{25,26}

In order to study the selectivity of polymeric calix[4]crown-metal ion complex, we prepared new polyamide and polyimide containing calix[4]crown-6 moiety by reacting calix[4]crown-6-2,4-bis(4-aminobutyl ether) with adipoyl chloride and 1,2,4,5-benzenetetracarboxylic dianhydride and performed liquid-liquid extraction experiments of various alkali and alkali earth metal.

Experimental

Materials and Measurements. Calix[4]crown-6 (1) was prepared by the method previously reported.² Cesium carbonate, adipoyl chloride, 1,2,4,5-benzenetetracarboxylic dianhydride, 4-bromobutyronitrile, picric acid and lithium aluminum hydride (Aldrich Chem. Co.) were used as received. Acetonitrile was 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]arene-1,3-bis(3-cyanopropyl ether) (2). Calix[4]arene (1, 2.04 g, 4.8 mmol), 4-bromobutyronitrile (1.42 g, 9.6 mmol), cesium carbonate (4.69 g, 15.3 mmol) and acetonitrile (60 mL) were refluxed for 4 days

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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 72%. Mp, 246 °C. IR (KBr, cm^{-1}): 3400 (OH), 3148 (aromatic C-H), 2922, 2875 (aliphatic C-H), 2215 ($\text{C} \equiv \text{N}$), 1584, 1452, 1357, 1298, 1249, 1210, 1151, 1084 (C-O), 1047, 842, 771. ^1H NMR (CDCl_3): 10.21 (s, 2H, -OH), 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), 3.66 (t, 4H, 2 $-\text{OCH}_2-$), 2.04 (t, 4H, 2 $-\text{CH}_2\text{CN}$), 1.63 (m, 4H, 2 $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CN}$). Anal. Calcd for $\text{C}_{36}\text{H}_{34}\text{O}_4\text{N}_2$ (M_w , 558.68); C, 77.40; H, 6.13; N, 5.01. Found: C, 77.22; H, 7.12; N, 5.05.

Synthesis of Calix[4]crown-6-2,4-bis(3-cyanopropyl ether) (3). Calix[4]arene-1,3-bis(3-cyanopropyl ether) (**2**) (2.68 g, 4.8 mmol), pentaerythritol di-*p*-toluenesulfonate (3.55 g, 7.1 mmol) and cesium carbonate (3.07 g, 10.0 mmol) were dissolved in acetonitrile (60 mL) and refluxed for 4 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.

3: Yield 61%. Mp, 144 °C. IR (KBr, cm^{-1}): 3120 (aromatic C-H), 2920-2880 (aliphatic C-H), 2217 ($\text{C} \equiv \text{N}$), 1582, 1491, 1296, 1250-1052 (C-O). ^1H NMR (CDCl_3): 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, 20H, 5 $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.68 (t, 4H, 2 $-\text{OCH}_2-$), 2.04 (t, 4H, 2 $-\text{CH}_2\text{CN}$), 1.63 (m, 4H, 2 $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CN}$). Anal. Calcd for $\text{C}_{46}\text{H}_{52}\text{O}_8\text{N}_2$ (M_w , 760.94); C, 72.61; H, 6.89; N, 3.68. Found: C, 72.22; H, 6.92; N, 3.65.

Synthesis of Calix[4]crown-6-2,4-bis(4-aminobutyl ether) (4). Lithium aluminum hydride (0.38 g, 10.0 mmol) was suspended in anhydrous THF (40 g) for 20 min under nitrogen atmosphere. Calix[4]crown-6-2,4-bis(3-cyanopropyl ether) (**3**) (3.80 g, 4.8 mmol) was added drop-wise slowly through dropping funnel. The reaction mixture was continuously stirred at 40 °C for 24 h. The reaction mixture was destroyed with THF/ H_2O (9/1) and the reaction product was extracted with methylene chloride. The organic layer was dried with anhydrous magnesium sulfate. Recrystallization was performed using diethyl ether.

4: Yield 75%. Mp, 72 °C. IR (KBr, cm^{-1}): 3400-3100 ($-\text{NH}_2$), 3148 (aromatic C-H), 2922, 2875 (aliphatic C-H), 1584, 1452, 1357, 1298, 1249, 1210, 1151, 1084, 1047 (C-O), 842, 771. ^1H NMR (CDCl_3): 9.21 (br, 4H, NH_2), 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, 20H, 5 $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.67 (t, 4H, 2 $-\text{OCH}_2-$), 2.64 (t, 4H, 2 $-\text{CH}_2\text{NH}_2$), 1.65 (m, 8H, 2 $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$). Anal. Calcd for $\text{C}_{46}\text{H}_{60}\text{O}_8\text{N}_2$ (M_w , 769.00); C, 71.85; H, 7.86; N, 3.64. Found: C, 71.72; H,

7.92; N, 3.65.

Synthesis of Polyamide (5) Containing Calix[4]crown-6. In a three-necked flask were placed a solution of **4** (3.23 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.

5: Yield 94%. IR (KBr, cm^{-1}): 3220 (amide N-H), 3120 (aromatic C-H), 2920-2880 (aliphatic C-H), 1685, 1679 (amide C=O), 1584, 1490, 1298, 1250-1050 (C-O). ^1H NMR (CDCl_3): 9.89 (br, 2H, amide N-H), 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, 20H, 5 $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.67 (t, 4H, 2 $-\text{OCH}_2-$), 2.76 (t, 4H, 2 $-\text{CH}_2\text{NH}-$), 2 $-\text{CH}_2\text{CH}_2\text{O}-\text{CO}$), 2.48 (t, 4H, $-\text{NHCO}-\text{CH}_2-$), 1.65 (m, 8H, 2 $-\text{OCH}_2\text{CH}_2\text{CH}_2-\text{CH}_2\text{NH}-$), 1.97-1.52 (m, 4H, $-(\text{CH}_2)_2-$). Anal. Calcd for $\text{C}_{52}\text{H}_{66}\text{O}_{10}\text{N}_2$ (M_w , 879.14); C, 71.05; H, 7.57; N, 3.19. Found: C, 71.12; H, 7.52; N, 5.14.

Synthesis of Polyimide (6) Containing Calix[4]crown-6. In a three-necked flask were placed a solution of **3** (3.23 g, 4.2 mmol) was dissolved in NMP (30 mL). 1,2,4,5-Benzenetetracarboxylic dianhydride (0.92 g, 4.2 mmol) was added dropwise slowly and the mixture was continuously stirred at 20 °C for 2 h and 80 °C for 2 days. The resulting solution was precipitated in water and dried *in vacuo* at 60 °C.

6: Yield 92%. IR (KBr, cm^{-1}): 3100 (aromatic C-H), 2920 (aliphatic C-H), 1659, 1688 (imide C=O), 1584, 1495, 1250-1050 (C-O), 1107. ^1H NMR (CDCl_3): δ =8.02 (s, 2H, fragment of pyromellitic anhydride) 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, 20H, 5 $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.67 (t, 4H, 2 $-\text{OCH}_2-$), 2.72 (t, 4H, 2 $-\text{CH}_2\text{N}=\text{O}$), 1.65 (m, 8H, 2 $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$). Anal. Calcd for $\text{C}_{56}\text{H}_{58}\text{O}_{12}\text{N}_2$ (M_w , 991.09); C, 70.72; H, 6.15; N, 2.95. Found: C, 70.67; H, 6.12; N, 2.89.

Liquid-Liquid Extraction. Picrate extraction experiments were performed using Pedersons procedure.²³ Aqueous picrate solution (10 mL, 3.5×10^{-5} M) and solution of polymer (**3**, 10 mL, 7.0×10^{-4} , 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 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 solution of metal hydroxide.

Results and Discussion

Monomer calix[4]crown-6-2,4-bis(4-aminobutyl ether) (**4**) was synthesized via three steps-reaction as illustrated in Scheme I. Calix[4]crown-6-2,4-bis(3-cyanopropyl ether) was prepared by reacting **1** and 4-bromobutyronitrile in the presence of K_2CO_3 and followed by reacting pentaethylene glycol di-*p*-toluenesulfonate as shown in Scheme I. Monomer **4** was finally obtained by reducing calix[4]crown-6-2,4-bis(3-cyanopropyl ether) (**3**) with lithium aluminum hydride.

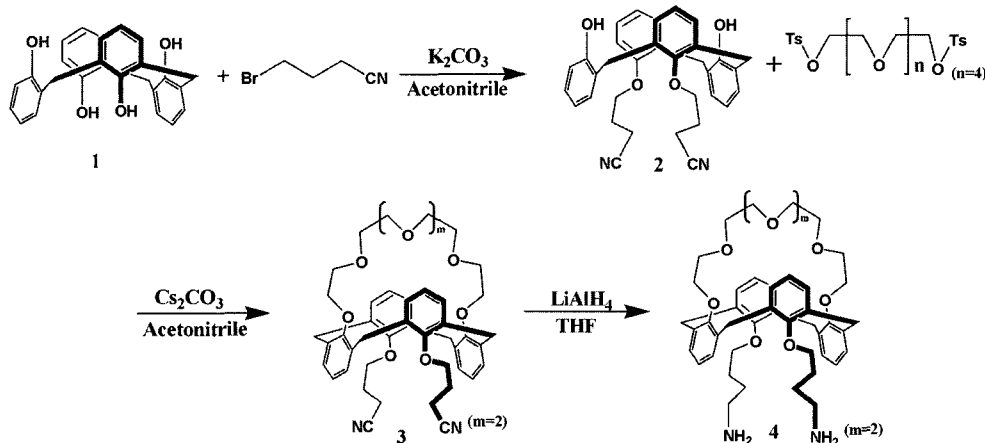
Polyamide **5** and polyimide **6** containing calix[4]crown-6 moiety were prepared by polymerization of **4** with adipoyl chloride and 1,2,4,5-benzenetetracarboxylic dianhydride by condensation polymerization, respectively, as shown in Scheme II. Total yields of polymers were found to be moderately high.

Table I summarizes the yields and some physical properties

of polymers in this study. The chemical structure of resulting polymers was characterized through the data from FT-IR and ^1H NMR. The CHN elemental analysis values matched well with the expected chemical structure. In the infrared spectra, the polymers **5** and **6** showed characteristic absorption bands around 1680 and 1659–1688 cm^{-1} corresponding to C=O stretching band of the amide and imide linkage, respectively. In the NMR spectrum of polymer **5**, the alkylene protons in adipoyl moiety appeared at 2.44–1.52 ppm as a multiplets, whereas polymer **6** showed singlet peak around 8.02 ppm corresponding to the aromatic protons of pyrromellitic anhydride.

The solubility of the polymers was measured in various solvents such as ethyl ether, ethyl acetate, acetone, methylene chloride, tetrahydrofuran and *N*-methyl-2-pyrrolidinone at 5 mg/mL as shown in Table I. The incorporation of aliphatic amide linkage into the polymer backbone enhances the

Scheme I



Scheme II

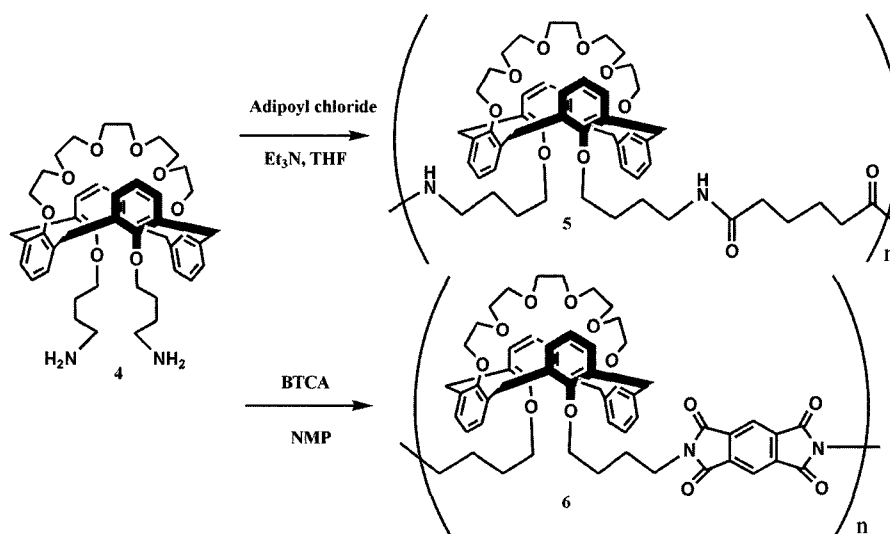


Table I. Physical Properties of Calix[4]crown-6 Derivatives and Polymers

	m.p °C	M_w^a	MWD ^b	η_{inh}^c	Yield (%)	Solubility					
						Hexane	EE ^d	EA ^e	Acetone	MC ^f	THF ^g
3	144	760.94	-	-	61	-	-	+	+	+	+
4	72	769.00	-	-	75	-	-	+	+	+	+
5	-	17,800	1.87	0.39	94	-	-	+	+	+	+
6	-	15,200	2.01	0.35	92	-	-	-	+	+	+

+: Soluble -: Insoluble.

^a Weight average molecular weight. ^b Molecular weight distribution. ^c Inherent viscosity. ^d Ethyl ether. ^e Ethyl acetate.

^f Methylene chloride. ^g Tetrahydrofuran.

solubility in common organic solvents to a high degree. The polymers show good solubility in common organic solvents such as acetone, ethyl acetate, chloroform, methylene chloride and THF, while they display virtually no solubility in toluene, *n*-hexane, benzene and ethyl ether.

The condensation polymerization gave the polymers with somewhat small molecular weight judging from the data of viscosity and GPC. The polymers possessed inherent viscosity 0.39 dL/g for **5** and 0.35 dL/g for **6** using chloroform at 25 °C. The weight average molecular weights, which were determined by gel permeation chromatography using polystyrene standards, of polymers **5** and **6** were 17,800 and 15,200 g/mole with a polydispersity index of 1.87 and 2.01. However, these are somewhat high molecular weights, judging from viscosity and GPC data. Calix[4]crown-6 moiety often prevents the growing of the molecular weight due to the bulkiness. When films were cast by allowing the solvent of the polymers **5** and **6** to evaporate on a glass, hard and brittle films were obtained. These polymers were incorporated into polymer inclusion membrane composed of cellulose acetate as a support and tris(2-butoxyethyl)phosphate as a plasticizer. Tough films were obtained from them.

The thermal behaviors were examined by DSC at 10 °C/min under nitrogen. Figure 1 shows the dynamic scan of the **5** and **6**. The small signal at 17 °C and large endotherm starting 100 °C in the DSC curve of polyamide **5** may be related to the glass transition temperature and softening temperature, respectively, as shown in Figure 1(a). In the case of DSC traces of polymer **5**, endothermic peak around 110 °C was coincident with the resulting temperature determined in a capillary tube. Polymer **6** showed different DSC curve which exhibited two large endothermic peak at 125 and 160 °C attributing to melt transition as shown in Figure 1(b). Other endothermic transition shown at higher temperature than melting was ascribed to the change of conformation of rigid chain and calix[4]crown moiety.

The thermal stability of polyamide **5** and polyimide **6** containing calix[4]crown-6 moiety was evaluated by thermogravimetric analyses (TGA) under nitrogen. Figure 1(c) and 1(d) also shows the TGA thermograms of polymer **5** and **6**. While being heated under nitrogen, the calix[4]crown

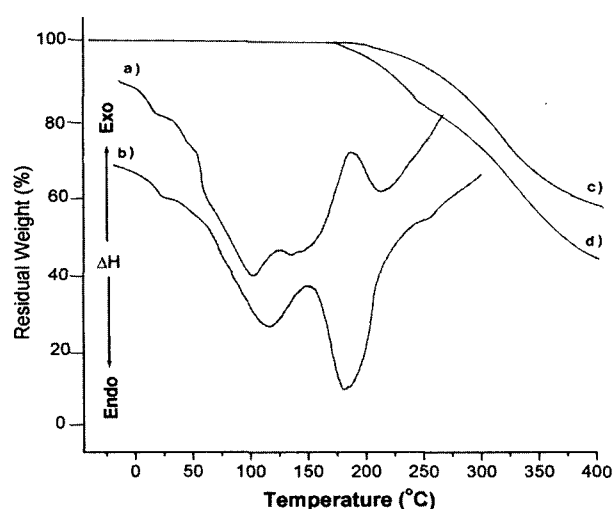


Figure 1. DSC thermograms and thermogravimetric trace of polymer **5** (a and d) and polymer **6** (b and c).

containing polymers showed a one-stage weight loss behavior. All the polymers showed residual weight percent 44% and 58% at 400 °C, which corresponded to the content of thermally stable rigid aromatic moiety of the polymers **5** and **6**. Weight loss of polyamide and polyimide begun at around 200 °C and then gives a rapid weight loss up to 400 °C to result in an one-stage weight loss. Although the initial weight loss temperature of polyimide **6** was a little lower than that polyamide **5**, 10% weight loss and residual weight indicate the increase in thermal stability of polyimide **6**. The lower thermal stability of **5** was due to the aliphatic amide moiety.

The recognition properties of polymers **5** and **6** 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 the control experiments it was confirmed that no metal ion transport was observed in the absence of the carrier.

When the ligand complexes with specific metal ion, the

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

Ion	Ligand	4		5		6	
		a	b	a	b	a	b
Na ⁺		< 1	< 1	3.06	4.93	1.45	2.17
K ⁺		< 1	4.31	5.71	7.23	2.31	4.10
Rb ⁺		3.79	41.53	21.01	25.82	15.69	17.13
Cs ⁺		6.58	74.89	68.37	70.55	29.40	57.96
Mg ²⁺		< 1	< 1	< 1	< 1	< 1	1.27
Ca ²⁺		< 1	< 1	1.40	5.72	< 1	8.81
Sr ²⁺		< 1	2.11	< 1	5.16	6.92	14.67
Ba ²⁺		1.74	3.41	1.82	5.55	13.02	16.33

H₂O/CHCl₃ = 50/50(V/V); picric acid = 3.5×10^{-5} M; hydroxide = 0.01 M. Calix[4]crown ether polymer; a = 3.5×10^{-4} M, b = 1.4×10^{-3} M.

major factors 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 ligand and the metal ion.²

The results of two phase's extraction experiment of metal picrate with model compound **4**, polymers **5** and **6** are summarized in Table II. Although both the polymer **5** and **6** possessed the different chemical structure, they displayed similar behaviors and selectivity characteristics. In the case of polymer **5**, high cesium ion extraction was observed with undetectable transport of sodium and potassium ions. Some of the 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 And extraction level of **5** was higher than that of polymer **6** as shown in Table II. But the maximum cesium extraction was observed with trace of extraction of sodium, potassium, magnesium and calcium, which have smaller ion radius. But the cavity size of the calix[4]crown-6 framework is less suitable to Na⁺, K⁺, Mg⁺, Ca⁺, Sr²⁺, and Ba²⁺ used in the extraction experiments were somewhat extracted by the polymer **6** at a higher concentration of ligand, which is comparable to rubidium ion. There is no large difference in the ion-binding properties between polyamide **5** and polyimide **6**. The rigidity of polymer chain and conformation of the polymer chain in the solvent affected the ion-binding properties.

In conclusion, polyamide and polyimide containing crown-6 moiety were newly prepared by reacting calix[4]crown-6-2,4-bis(4-aminobutyl ether) (**4**) with adipoyl chloride and 1,2,4,5-benzenetetracarboxylic dianhydride. It has

been observed that the polyamide **5** and polyimide **6**, which have ion-binding ability of calix[4]crown in the polymer backbone towards various metal cations, showed cesium ion selectivity. As a result, the metal transfer ability of polymers depends upon the size of calix[4]crown. Other experiments on the transport to metal ions in polymeric inclusion membrane system using calix[4]crown-containing polyamide **5** and polyimide **6** are in progress.

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