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Syntheses and Cation Extraction Properties of Polycalixarenes from *p*-Hydroxycalix[6]arene

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ABSTRACT: A new polymer, polycalixarene, was prepared by the reaction of *p*-hydroxycalix[6]arene (HQ[6]) with paraformaldehyde under HCl acidic conditions. HQ[6] had two types of hydroxyl groups at the upper and lower rims and showed a conelike conformation. The conformation of the HQ[6] unit was maintained in the polymer chain. The extraction ability of poly(*p*-hydroxycalix[6]arene) (P-HQ[6]) for alkali metal cations was determined and compared with that of the monomeric HQ[6]. The extraction ability of P-HQ[6] was higher than that of HQ[6] due to new cation binding sites consisting of the aggregated HQ[6] units in the polymer. The affinity and selectivity of new binding sites depended on the aggregated state of HQ[6] units in the polymer chain. The aggregated state was controlled by the conformation of the polymer.

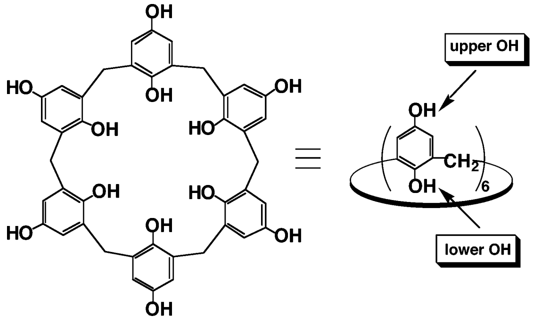
Introduction

Calixarenes are cyclic phenolic oligomers, and their selective cation extraction and transport properties are particularly attractive.[1] Calixarenes with some ligands (esters, ketones, and amines) showed the ionophoric abilities for alkali metal cations.[2] The influence of conformation[3] and size[4] of calixarenes on the selective extraction for alkali metal cations was discussed in detail by using the ethyl acetate derivatives.

Despite many studies concerning the synthesis and property of calixarenes, very few of the polymers containing calixarene units have been reported. Most of the polymers have calixarene units in the side chain as pendants,[5] and a few of the polymers contain them in the backbone.[6] The latter polymers were obtained by polymerization of the monomer having a calixarene unit. Since most of the polymers were obtained by copolymerization of difunctionalized calixarene-based monomers with comonomers, the content of monomer having a calixarene unit was not beyond a half. Therefore, the copolymers did not show the properties of the aggregated state of calixarene units so well.

To study the properties of the aggregated state of calixarene units, we attempted to synthesize polycalixarenes by the reaction of a reactive calixarene with formaldehyde, such as the synthesis of novolak resin using calixarene instead of phenol. In this paper, *p*-hydroxycalix[6]arene (HQ[6]) is proposed as a new reactive calixarene. HQ[6] has two types of hydroxyl groups at the upper (wide) and lower (narrow) rim in a molecule (Scheme 1). The reactive sites are the *ortho* positions to hydroxyl groups at the upper rim, so that HQ[6] plays a role of multifunctional monomer. Here, we report the syntheses and cation extraction properties of a new functional polymer based on *p*-hydroxycalix[6]arene units. Comparing the extraction result of the polycalixarene with that of the monomeric calixarene, the aggregated state of calixarene units is discussed.

Scheme 1. Structure of *p*-Hydroxycalix[6]arene (HQ[6])



Experimental Section

Materials. *p*-Methoxyphenol, 37% formalin, NaOH, BBr_3, and paraformaldehyde were used without further purification. $CHCl_3$ and tetrahydrofuran (THF) were distilled and then used. Other solvents were dried on molecular sieves (4A) and then used.

Sample Preparation. *p*-Hydroxycalix[6]arene was prepared by three reaction steps. The outline of the preparation process for *p*-hydroxycalix[6]arene from *p*-methoxyphenol and the polymer is shown in Schemes 2 and 3. The procedure is described in detail below.

Preparation of Linear *p*-Methoxyphenol Oligomer. 49.6 g (0.50 mol) of *p*-methoxyphenol, 40.6 mL (0.50 mol as formaldehyde) of 37% formalin, and 0.32 g (8 mmol) of NaOH were mixed, and then 100 mL of water was added to make the mixture homogeneous. The mixture was refluxed for 3 h. After cooling to room temperature, the oligomer was precipitated and filtered off on a glass filter. The oligomer was washed with water several times and then dried. Yield: 32.0 g.

Preparation of *p*-Methoxycalix[6]arene. 10 g of linear *p*-methoxyphenol oligomer, 8.0 g (0.25 mol as formaldehyde) of paraformaldehyde, and 1.0 g (0.025 mol) of NaOH were dissolved in 100 mL of diphenyl ether. The mixture was gradually heated until 250 °C to remove condensed water from the mixture. The mixture was heated at 250 °C for 3 h. After cooling to room temperature, the mixture was neutralized with 10 mL of acetic acid, and the solution was poured to 300 mL of methanol to precipitate *p*-methoxycalix[6]arene. The calixarene was filtered off on a glass filter and washed with methanol and then hot water several times and dried in vacuo. Yield: 9.5 g.

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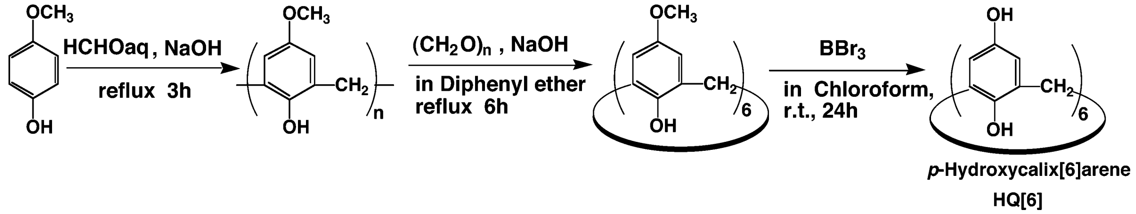
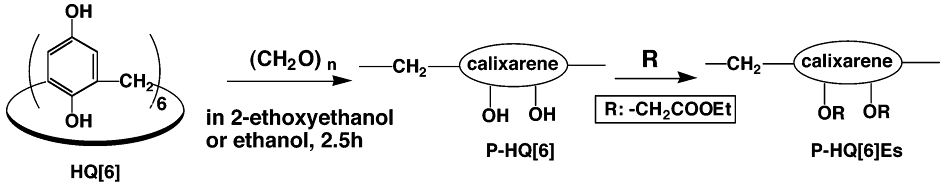
Scheme 2. Preparation of *p*-Hydroxycalix[6]arene (HQ[6])



Scheme 3. Outline of the Polymerization Process for HQ[6]



The compound was identified to be *p*-methoxycalix[6]arene on the basis of the following analyses: mp = 380 °C; IR (KBr disk) ν_{OH} 3200 cm^{-1}, ν_{C-O-C} 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$, 25 °C) $\delta = 3.73$ (CH_3, s, 18H), 3.80 ($ArCH_2Ar$, s, 12H), 6.69 (ArH, s, 12H), 10.08 (OH, s, 6H). Anal. Calcd for $C_{48}H_{48}O_{12}$: C, 70.57; H, 5.92. Found: C, 68.32; H, 5.86.

The molecular weight of *p*-methoxycalix[6]arene was confirmed by mass spectrometry of *p*-methoxycalix[6]arene hexamethyl ether derivative because the melting point of *p*-methoxycalix[6]arene was too high to ionize.

Preparation of *p*-Methoxycalix[6]arene Hexamethyl Ether. 0.5 g (0.61 mmol) of *p*-methoxycalix[6]arene was dissolved in 25 mL of DMF at room temperature. 0.96 g (20 mmol) of NaH was added, and the mixture was stirred at room temperature for 0.5 h. CH_3I was added, and the mixture was stirred at room temperature for 48 h. The reaction was quenched with 80 mL of 0.05 N HCl solution. Then the solvent was removed by reduced pressure; the resulting product was dissolved in 20 mL of $CHCl_3$ and washed with water several times. After removing the solvent slightly by reduced pressure, the concentrated $CHCl_3$ solution was poured into 100 mL of methanol to precipitate *p*-methoxycalix[6]arene hexamethyl ether. The product was filtered off on a glass filter and washed with methanol several times and dried in vacuo. Yield: 0.2 g (36%).

The compound was identified to be *p*-methoxycalix [6]arene hexamethyl ether on the basis of the following analyses: MS: *m/z* = 900 (M+); mp = 173 °C. IR (KBr disk) no ν_{OH}, ν_{C-O-C} 1050 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C) $\delta = 3.65$ (CH_3, s, 36H), 3.85 ($ArCH_2Ar$, s, 12H), 6.49 (ArH, s, 12H). Anal. Calcd for $C_{54}H_{60}O_{12}$ (900): C, 71.98; H, 6.70. Found: C, 71.54; H, 6.73.

Preparation of *p*-Hydroxycalix[6]arene. 2.0 g (2.45 mmol) of *p*-methoxycalix[6]arene was dissolved in 100 mL of $CHCl_3$ at room temperature. 7.36 g (29.4 mmol) of BBr_3 was added, and the mixture was stirred at room temperature for 24 h. The reaction was quenched with 80 mL of 0.05 N HCl solution. Then the solvent was removed by reduced pressure; the resulting product was washed with water and then dried. The product was washed with $CHCl_3$ and dried in vacuo. Yield: 1.5 g (84%).

The compound was identified as *p*-hydroxycalix[6]arene on the basis of the following analyses: mp > 400 °C; IR (KBr disk) ν_{OH} 3200 cm^{-1} no ν_{C-O-C}; ^{1}H NMR (CD_3COCD_3, 25 °C) $\delta =$ 3.75 ($ArCH_2Ar$, s, 12H), 6.65 (ArH, s, 12H), 7.81 (OH_{upper}, s, 6H), 9.59 (OH_{lower}, s, 6H). Anal. Calcd for $C_{42}H_{36}O_{12}\cdot H_2O$: C, 67.24; H, 5.07. Found: C, 67.36; H, 5.22.

Preparation of *p-tert*-Butylcalix[6]arene and Calix[6]arene. *p-tert*-Butylcalix[6]arene and calix[6]arene were prepared according to the literature.[7] The characterization data of these calixarenes are in agreement with the literature.

Addition–Condensation of *p*-Hydroxycalix[6]arene with Paraformaldehyde. 1.22 g (1.67 mmol) of *p*-hydroxycalix[6]arene and 1.58 g (32 mmol as formaldehyde) of paraformaldehyde were dissolved in 50 mL of 2-ethoxyethanol (or ethanol), and then 0.46 mL (5.2 mmol) of concentrated HCl was added to the mixture at room temperature. The mixture was heated at 80 °C for 2.5 h. After cooling to room temperature, the polymer was precipitated in hexane. The polymer was washed with methanol to remove monomer and then dried in vacuo. Yield: 0.7 g.

The ethyl acetate derivatives of calixarenes and polycalixarenes were prepared according to the literature.[8] The derivatives were symbolized as HQ[6]Es and P-HQ[6]Es, respectively, as shown in Scheme 3.

Measurements. GPC measurements were carried out by a Shimadzu HPLC LC-6A equipped with two TSKgel GMHHR-M columns and a TOSOH UV-8011 spectrophotometer (270 nm) as a detector and THF as an eluent at 1.0 mL/min. The chromatograms were analyzed by a Shimadzu C-R4A data processor. Mass data were collected by a Hitachi M-80 spectrometer. ^{1}H NMR spectra were recorded on a JNM-EX-270 FT-NMR spectrometer at 270 MHz. $CDCl_3$ and CD_3COCD_3 were used as solvents, and tetramethylsilane (TMS) was used as a reference. FT-IR spectra were obtained by a Jasco FT/IR-3 spectrophotometer with a KBr disk.

Extraction Studies. The extraction ability toward alkali metal cations was evaluated following the Cram procedure.[9] 5 mL of aqueous alkali picrate solution ([picric acid] = 2.7×10^{-5} mol/L, [MCl] = 1.0×10^{-2} mol/L) and 5 mL of a 2.7×10^{-3} mol/L solution of calixarene unit in $CHCl_3$ were stored in a stoppered test tube immersed in a thermostated water bath at 25 °C. The extraction equilibrium was reached after 1 min vigorous shaking by automatic shaker, followed by standing for 12 h in the water bath. The absorption, *A*, of aqueous phase was measured at 355 nm, i.e., the wavelength of maximum absorption of the picrate ion. A blank experiment, without calixarene, was run under the same conditions, which yielded an absorbance, A_0, of the aqueous phase. The percentage extracted cation was calculated as the ratio $(A_0 - A)/A_0 \times 100$. In this work, a blank experiment showed no extraction for alkali cations.

Results and Discussion

Synthesis of *p*-Hydroxycalix[6]arene and Its Polymerization. *p*-Hydroxycalix[6]arene (HQ[6]) was synthesized according to the procedure, as shown in Scheme 2. HQ[6] has two types of hydroxyl groups. One is the hydroxyl group derived from methoxy group at the upper rim of *p*-methoxycalix[6]arene. The other is the hydroxyl group at the lower rim, defined by the phenolic oxygen atoms in the calixarene. The *ortho* position to the hydroxyl group at the upper rim is able to react with formaldehyde under acidic conditions, like phenol. Poly(*p*-hydroxycalix[6]arene) (P-HQ[6]) was obtained by the HCl acidic condensation of HQ[6] with paraformaldehyde in ethanol (P-HQ[6]L) or 2-ethoxy-

Table 1. Addition−Condensation of HQ[6] with Paraformaldehyde for 2.5 h at 80 °C

polymer	solvent	molar ratio HQ	HCHO	HCl	yield [%][a]	M_n[b] (M_w/M_n)	degree of substitution[c]
P-HQ[6]L	EtOH	1	5	0.5	25	2500 (2.5)	1.5
P-HQ[6]B	EGMEE	1	5	0.5	11	3100 (3.0)	3.0

[a] MeOH-insoluble and acetone-soluble part. [b] Determined by GPC using polystyrene standards. [c] Determined by ^{1}H NMR analysis in CD_3COCD_3 at 25 °C.

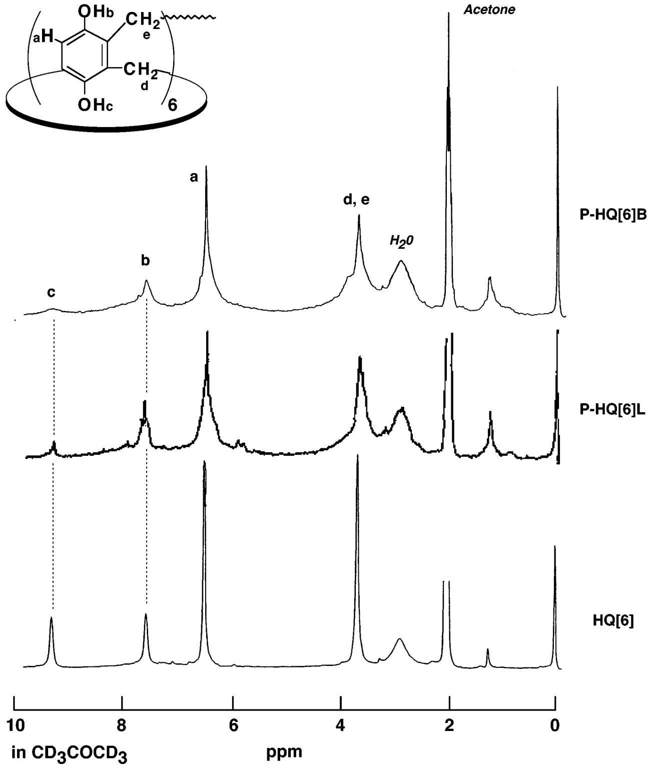


Figure 1. ^{1}H NMR spectra of HQ[6], P-HQ[6]L, and P-HQ[6]B.

ethanol (P-HQ[6]B), as shown in Scheme 3. The addition−condensation results are listed in Table 1. HQ[6] plays a role of multifunctional monomer. Gels were readily formed in the reaction. In this study, the soluble part in acetone and THF was prepared by lowing the extent of reaction of HQ[6]. Therefore, the polymer yield was not so high.

The ^{1}H NMR spectra of P-HQ[6] polymers are shown and compared with that of HQ[6] monomer in Figure 1. The spectrum of HQ[6] shows the signals corresponding to the OH protons at the upper rim (δ = 7.83 ppm) and that at the lower rim (δ = 9.55 ppm), the aromatic protons (δ = 6.66 ppm), and also to the methylene linkages (δ = 3.75 ppm) at the lower rim in HQ[6]. The signal arising from the OH at the lower rim appears in lower field than that at the upper rim, indicating the formation of strong intramolecular hydrogen bonds in the lower rim. The signal pattern is identical with that of *p*-hydroxycalix[4]arene with cone conformation.[10] It is well-known that in a cone conformation the methylene linkage protons show a pair of doublets at lower temperature. In this study the signal of methylene protons of HQ[6] became broader with decreasing the temperature, but a pair of doublets pattern was not observed even at −70 °C. The conformation of HQ[6] was flexible on the NMR time scale. In ^{1}H NMR the signal pattern of HQ[6] was simple, indicating a highly symmetrical conformation. These results indicate that the fast ring inversion will occur and HQ[6] will not have a fixed conformation in the solution. On the other hand, the signal pattern of P-HQ[6]L or P-HQ[6]B is the same as that of monomeric HQ[6]. The signal of new methylene linkage protons between HQ[6] units in the polymer appears at δ = 3.70−3.80 ppm. Therefore, it is difficult to distinguish the signal of methylene linkage protons at the lower rim from that at the upper rim. It is worth noting that the chemical shifts of the signals arising from the OH protons at the upper and lower rims of HQ[6] units in the polymer are the same as that of monomeric HQ[6]. This indicates that the conformation of HQ[6] unit is maintained in the polymer chain.

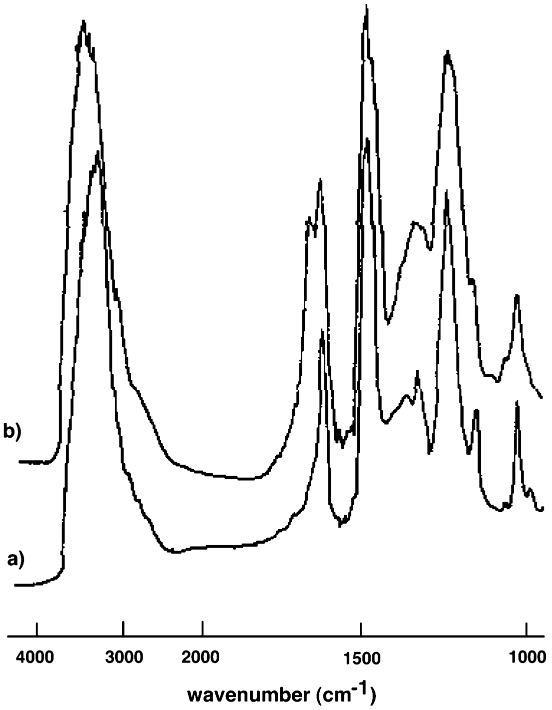


Figure 2. IR spectra of (a) HQ[6] and (b) P-HQ[6]L.

The degree of substitution (DS) was defined as the number of newly formed methylene linkages at the upper rim of a HQ[6] unit in the polymer, which was estimated from the signal area ratio of methylene protons at δ = 3.70−3.80 ppm to that of the aromatic protons at δ = 6.65−6.70 ppm. The DS of P-HQ[6]L was given to be about unity per HQ[6] unit. This result strongly supports that the P-HQ[6]L is a linear polymer. On the other hand, the DS of P-HQ[6]B was given to be about three per HQ[6] unit. This indicates that the P-HQ[6]B is a branched polymer. The NMR results show that the degree of aggregation of HQ[6] units in P-HQ[6]L is lower than that in P-HQ[6]B.

IR spectra of HQ[6] and P-HQ[6]L are shown in Figure 2. HQ[6] showed a sharp peak at 3200 cm^{-1} attributed to hydrogen-bonded O−H groups. On the other hand, P-HQ[6]L showed a peak at 3300 cm^{-1} attributed to hydrogen-bonded O−H groups. The peak was slightly shifted toward higher wavenumber and

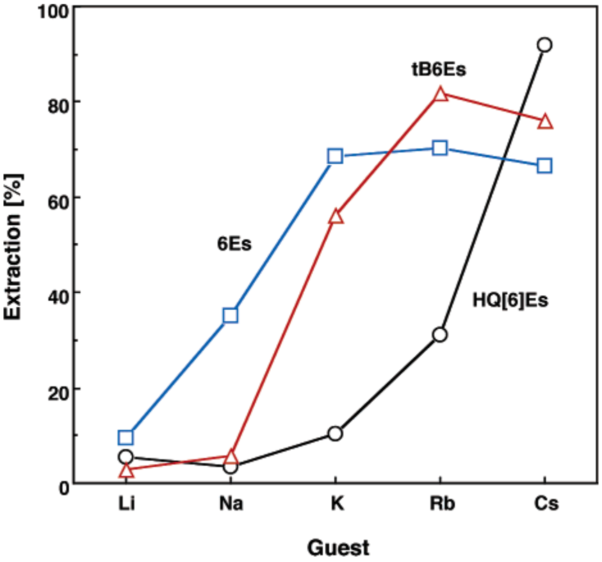


Figure 3. Extraction ability of alkali metal picrates by 6Es, tB6Es, and HQ[6]Es ([picric acid] = 2.7 × 10^{-5} mol/L, [MCl] = 1.0 × 10^{-2} mol/L, [calixarene] = 2.7 × 10^{-3} mol/L).

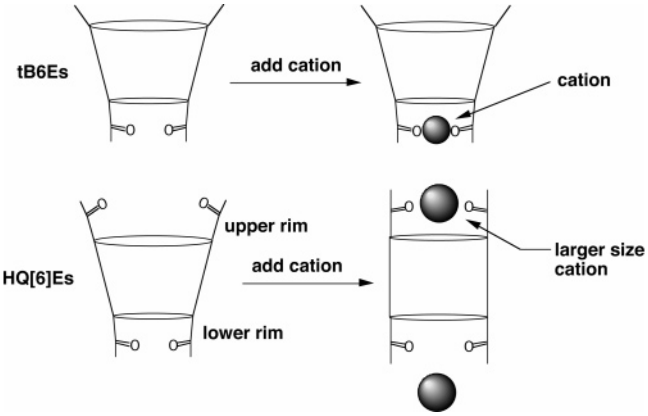


Figure 4. Proposed conformation of calixarene–cation complex.

broadened due to lower flexibility of calixarene unit in P-HQ[6]L.

Extraction Properties. The selective extraction properties of calixarenes and polycalixarenes for alkali metal cations were determined according to Pederson's technique of picrate extraction,[11] which is semiquantitative means of assessing ion transfer ability from aqueous solution into an apolar organic solvent (chloroform in this study) as a convenient. For details of the extraction condition the Cram procedure[9] was referred to. The extraction result for ethyl acetate derivative of HQ[6] (HQ[6]Es) is shown in Figure 3, compared with ethyl acetate derivatives of calix[6]arene (6Es) and *p-tert*-butylcalix[6]arene (tB6Es). 6Es showed high affinity for K^+, Rb^+, and Cs^+. tB6Es exhibited high extraction ability toward Rb^+ and Cs^+. On the other hand, HQ[6]Es showed high extraction ability and high selectivity for Cs^+. The extraction behavior of HQ[6]Es is different from that of 6Es and tB6Es, even though the size of lower rim is the same one another. The difference in their affinity is considered to arise from the cation binding mechanism of each calixarene. The complex conformation of HQ[6]Es with cations is proposed in Figure 4. HQ[6]Es will have two cation binding sites at both upper and lower rims in a molecule. The size of cavity at the upper rim is larger than that at the lower rim because the OH groups at the lower rim formed stronger hydrogen bonds than that at the upper rim. The cavity at the lower rim will spread, when a cation binds to the cavity at the upper rim in HQ[6]Es. Accordingly, HQ[6]Es shows much higher affinity for Cs^+ than Rb^+ and K^+, for which 6Es and tB6Es showed sufficient affinity. The same mechanism has been reported for the partial cone type derivative of *p-tert*-butylcalix[4]arene.[3]

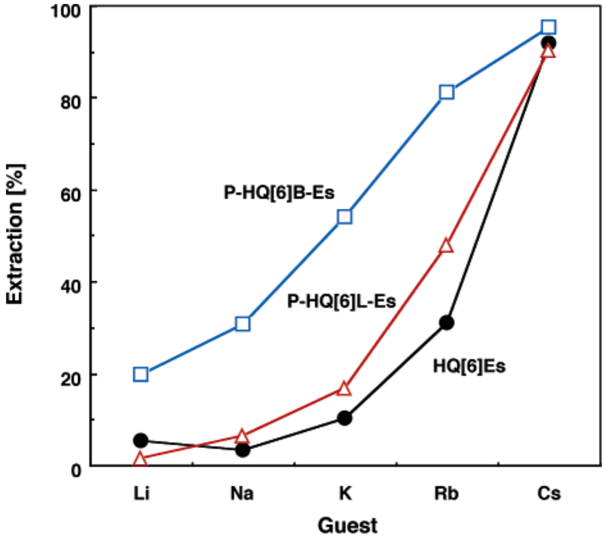


Figure 5. Extraction ability of alkali metal picrates by HQ-[6]Es, P-HQ[6]L-Es and P-HQ[6]B-Es ([picric acid] = 2.7 × 10^{-5} mol/L, [MCl] = 1.0 × 10^{-2} mol/L, [calixarene unit] = 2.7 × 10^{-3} mol/L).

The ability of polycalixarene derivatives to extract alkali metal cations was compared with the monomeric calixarene HQ[6]Es. The results are shown in Figure 5. The extraction ability of P-HQ[6]L-Es for alkali metal cations was slightly higher than that of monomeric HQ-[6]Es. On the other hand, the ability of P-HQ[6]B-Es to extract Na^+, K^+, and Rb^+ became much higher, and the extraction ability for Li^+ was higher than that of 6Es and tB6Es. These results indicate that new cation binding sites are formed in P-HQ[6]L-Es and P-HQ[6]B-Es by the polymerization of HQ[6]. P-HQ[6]B-Es exhibited higher levels of extraction abilities toward alkali metal cations except Cs^+ than P-HQ[6]L-Es. Since the aggregation state of P-HQ[6]B is denser than that of P-HQ[6]L, the size of binging sites in the aggregation state of P-HQ[6]B is smaller than that of P-HQ[6]L. Thus, the new binding sites are consisted of aggregated HQ[6] units, and the size strongly depends on the degree of aggregation of HQ[6] units. The extraction selectivity of P-HQ[6]L-Es and P-HQ[6]B-Es is lower than that of monomeric HQ[6]Es. However, the order of extraction ability of the polycalixarenes is the same as that of HQ-[6]Es in most favor of Cs^+. Therefore, the extraction mechanism of the polycalixarenes will be mainly governed by the cavity in monomeric HQ[6]Es unit. From these results, the polycalixarene derivatives are estimated to have two kinds of cation binding sites: one is the cavity of HQ[6]Es unit in the polycalixarene chain, which is a main cation binding site, and the other is the cavity-like site consisted of the aggregated HQ[6]-Es units, whose size is smaller than the cavity of HQ-[6]Es.

A similar extraction behavior was observed for P-HQ-[6]L-Es and P-HQ[6]B-Es, although the reduction in extraction percentages of all alkali metal cations, when the concentration of polycalixarenes decreased ([calixarene unit] = 2.7×10^{-4}). This indicates that the cation extraction mechanism of the aggregated state of HQ[6] units was independent of the polymer concentration. Accordingly, the aggregation of HQ[6] units will occur intramoleculary in a polymer chain and the polymer assists the aggregation to cooperatively bind cations.

The complexation of P-HQ[6]L-Es with alkali metal cations was examined by ^{1}H NMR spectra. When a stable complex of P-HQ[6]L-Es with Cs^+ is formed, signals of cation binding sites must change and remain unchanged after the molar ratio of HQ[6] unit in P-HQ[6]L-Es to Cs^+ has reached the stoichiometric value of the complex composition. The shape of signals in ^{1}H NMR spectra of P-HQ[6]L-Es determined in $CDCl_3$ at room temperature were changing by adding Cs^+ in CD_3OCD_3. In particular, the signals of methylene protons in the ligand ($-CO_2CH_2CH_3$: $\delta = 3.9-4.3$ ppm; $ArOCH_2CO_2-$: $\delta = 4.6-4.7$ ppm) were changing. This shows an electrostatic interaction between ligands and Cs^+. However, since the interaction is not so strong, the observed change in ^{1}H NMR spectra is too small to decide the complex composition. This fact indicates that the complexing ability and stability of P-HQ[6]L-Es with Cs^+ are not so high.

In conclusion, the polycalixarenes, P-HQ[6]L and P-HQ[6]B, were prepared from the reactive calixarene HQ[6] as a monomer, and the extraction ability for alkali metal cations was compared with the monomeric HQ[6]. The extraction ability of P-HQ[6]L-Es and P-HQ[6]B-Es was higher than that of monomeric HQ[6]Es due to new cation binding sites consisting of the aggregated HQ[6] units. The affinity and selectivity of new sites depended on the aggregated state of HQ[6] units in the polymer chain. The aggregated state was controlled by the conformation of P-HQ[6]. The synthesis and properties of polycalixarenes with various structures are under study in our laboratory.

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References and Notes

(1) (a) Gutsche, C. D. In *Calixarene*; The Royal Society of Chemistry: Cambridge, 1989. (b) Vicens, J., Bömer, V., Eds. In *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Kluwer Academic Publishers: Dordrecht, 1991.

(2) For example: Schwing-Weill, M.-J.; Arnaud-Neu, F.; Mckervey, M. A. *J. Phys. Org. Chem.* **1992**, *5*, 496−501.

(3) Iwamoto, K.; Shinkai, S. *J. Org. Chem.* **1992**, *57*, 7066−7073.

(4) Mckervey, M. A.; Seward, E. M.; Ferguson, G.; Ruhl, B.; Harris, S. J. *J. Chem. Soc., Chem. Commun.* **1985**, *5*, 388−390.

(5) (a) Harris, S. J.; Barrett, G.; McKervey, M. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1224−1225. (b) Arrigan, D. W. M.; Svehla, G.; Harris, S. J.; McKervey, M. A. *Anal. Proc.* **1992**, *29*, 27−29. (c) Kawabata, H.; Aoki, M.; Murata, K.; Shinkai, S. *Supramol. Chem.* **1993**, *2*, 33−39. (d) Deligöz, H.; Tavasli, M.; Yilmaz, M. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1994**, *32*, 2961−2964. (e) Deligöz, H.; Yilmaz, M. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1995**, *33*, 2851−2853. (f) Gravett, D. M.; Guillet, J. E. *Macromolecules* **1996**, *29*, 617−624. (g) Klok, H.-A.; Eibeck, P.; Möller, M.; Reinhoudt, D. N. *Macromolecules* **1997**, *30*, 795−802. (h) Blanda, M. T.; Adou, E. *Polymer* **1998**, *36*, 3821−3826. (i) Nishikubo, T.; Kameyama, A.; Tsutsui, K.; Iyo, M. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1999**, *37*, 1805−1814. (j) Wang, L.; Shi, X.; Jia, P.; Yang, Y. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **2004**, *42*, 6259−6266.

(6) (a) Dondoni, A.;. Ghiglione, C.;. Marra, A.; Scoponi, M. *Chem. Commun.* **1997**, 673−674. (b) Blanda, M. T.; Adou, E. *Chem. Commun.* **1998**, 139−140. (c) Kim, S. I.; Shin, T. J.; Ree, M.; Hwang, G. T.; Kim, B. H.; Han, H.; Seo, J. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1999**, *37*, 2013−2026. (d) Dondoni, A.; Marra, A.; Rossi, M.; Scoponi, M. *Polymer* **2004**, *45*, 6195−6206.

(7) Nakamoto, Y.; Yamagishi, T.; Ishida, S. PHENOLICS (Linear and Cyclic Phenolic Oligomers). In *Polymeric Materials Encyclopedia*; CRC Press: Boca Raton, FL, 1996.

(8) For example: (a) Yamagishi, T.; Tani, K. Ishida, S.; Nakamoto, Y. *Polym. Bull. (Berlin)* **1994**, *33*, 281−287. (b) Yamagishi, T.; Shirano, K.; Tani, K.; Nakamoto, Y.; Ishida, S.-i. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1996**, *34*, 687−693.

(9) Helgeson, R. C.; Weisman, G. R.; Toner, J. L.; Tarnowski, T. L.; Chao, Y.; Mayer, J. M.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 4928−4941.

(10) (a) Morita, Y.; Agawa, T.; Nomura, E.; Taniguchi, H. *J. Org. Chem.* **1992**, *57*, 3658−3662. (b) Reddy, P. A.; Kashyap, R. P.; Watson, W. H.; Gutsche, C. D. *Isr. J. Chem.* **1992**, *32*, 89−96.

(11) Pedersen, C. J. *Fed. Proc., Fed. Am. Soc. Expl. Biol.* **1968**, *27*, 1305−1309.

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