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Linear all-*ortho* oligomers of phenol-formaldehyde resins

II. Preparation and cation extraction properties of ester derivatives

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Summary

The ethyl acetate derivatives of all-*ortho* oligomers of *p-tert*-butylphenol-formaldehyde resins were prepared. The cation extraction properties were determined and were compared with those of the calixarene derivatives. The derivatives of linear oligomers showed the affinity toward alkali metal cations, arising from the cavity based on the pseudo-cyclic conformation. The same derivatives of *p-tert*-butylphenol resins also showed the affinity toward alkali metal cations.

Introduction

In our previous paper (1), linear all-*ortho* oligomers of phenol-formaldehyde resins were prepared, and the characterization and solution properties were investigated. These oligomers form cyclic conformation in an apolar solvent due to inter- and/or intramolecular hydrogen bonding, whose conformation must be the same as that of calix[*n*]arenes, phenol-formaldehyde cyclic oligomers. The calixarenes are produced by condensation of *p*-substituted phenols with formaldehyde, and whose selective extraction and transport properties based on the formation of host-guest complex are particularly interesting (2).

Consequently, the linear oligomers will be also expected to form host-guest complex in solutions, because the conformation in solution is stabilized by inter- and/or intramolecular hydrogen bonds and must contain inter- and/or intramolecular cavities sufficiently large to allow substrate inclusion.

In this paper, new phenolic oligomers, ethyl acetate derivatives of linear all-*ortho* oligomers with ion binding affinity toward alkali metal cations are prepared and the liquid-liquid extraction behavior for alkali metal cations is examined. And the affinity of the linear oligomer is compared with that of the derivative of calixarenes. If phenolic resin has the selective extraction property for metal cations, the application of phenolic resins will be wider as a functional polymer. Thus, the extraction ability of ethyl acetate derivative of *p-tert*-butylphenol resin toward alkali metal cations is also determined.

Experimental

Preparation

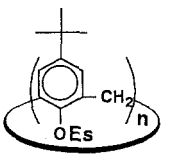
The ethyl acetate derivatives of calix[*n*]arenes (*n=4, 6* and *8*) were prepared according to the literature (3). The derivative was symbolized as *n*Es (*n=4, 6* and *8*).

Linear all-*ortho* oligomers of *p-tert*-butylphenol were prepared according to the previous paper (1). These oligomers were designed as *n*BP (*n=2-7*). The ethyl acetate derivatives of oligomers (*n*BP-Es) were prepared by the reaction of *n*BP with ethyl bromoacetate. A typical procedure was described below, as an example for 2BP-Es : *2*-BP (3.12 g, 0.01mol) was treated with NaH (4.0 g, 500 % molar excess) in dry THF (200mL), and then ethyl bromoacetate (16.7 g, 0.1mol) was added dropwise. The reaction mixture was stirred at room temperature for 24 h. The mixture was concentrated to syrupy liquid under reduced pressure. Excess NaH was decomposed with dil.HCl. The product was extracted with CH_2Cl_2 and then the extract was washed with distilled water. After removing water over Na_2SO_4, the extract was concentrated to dryness. The oily product was heated on the hot stage at 60 °C under reduced pressure to remove a trace of ethyl bromoacetate.

The products were identified to be *n*BP-Es on the basis of the following analyses :

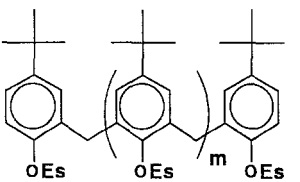
***2*BP-Es** : 95% yield; mp < r.t. ; IR (KBr disk) $\nu_{C=O}$ 1750cm^{-1}, no ν_{OH} ; ^{1}H-NMR (100 MHz, $CDCl_3$, 25 °C) δ 1.23 (*t*-Bu, s, 18H), 1.29 (CH_3, t, *J*=7.7Hz, 6H), 4.15 ($ArCH_2Ar$, s, 2H), 4.23 (CO_2CH_2, q, J=7.2Hz, 4H), 4.59 (OCH_2CO, s, 4H), 6.59 - 7.13 (ArH, m, 6H) . Anal. Calcd for $C_{29}H_{40}O_6$: C, 71.92; H, 8.26. Found : C, 70.94; H, 8.17.

***3*BP-Es** : 80% yield; mp < r.t. ; IR (KBr disk) $\nu_{C=O}$ 1750cm^{-1}, no ν_{OH} ; ^{1}H-NMR (100 MHz, $CDCl_3$, 25 °C) δ 1.15 - 1.28 (*t*-Bu, CH_3, m, 36H), 4.11 - 4.33 ($ArCH_2Ar$ and CO_2CH_2, m, 12H), 4.59 (OCH_2CO, s, 4H), 6.71 - 7.26 (ArH, m, 8H) . Anal. Calcd for $C_{44}H_{60}O_9$: C, 72.15; H, 8.26. Found : C, 70.29; H, 8.13.



***4*Es (n=4), *6*Es (n=6), *8*Es (n=8)**

Es = -CH_2CO_2Et



***2*BP-Es (m= 0), *3*BP-Es (m= 1), *4*BP-Es (m= 2)**
***5*BP-Es (m= 3), *6*BP-Es (m= 4), *7*BP-Es (m= 5)**

***4*BP-Es** : 80% yield; mp < r.t. ; IR (KBr disk) $\nu_{C=O}$ 1750cm^{-1}, no ν_{OH}; ^{1}H-NMR (100 MHz, $CDCl_3$, 25 ℃) δ 1.13 - 1.39 (*t*-Bu and CH_3, m, 48H), 4.11 - 4.32 ($ArCH_2Ar$ and CO_2CH_2, m, 14H), 4.68 (OCH_2CO, s, 8H), 6.71 - 7.26 (ArH, m, 10H). Anal. Calcd for $C_{59}H_{80}O_{12}$: C, 72.26; H, 8.22. Found : C, 71.14; H, 8.14.

***5*BP-Es** : 78% yield; mp < r.t. ; IR (KBr disk) $\nu_{C=O}$ 1750cm^{-1}, no ν_{OH}; ^{1}H-NMR (100 MHz, $CDCl_3$, 25 ℃) δ 1.13 - 1.35 (*t*-Bu and CH_3, m, 60H), 4.13 - 4.32 ($ArCH_2Ar$ and CO_2CH_2, m, 18H), 4.59 (OCH_2CO, s, 10H), 6.89 - 7.26 (ArH, m, 12H). Anal. Calcd for $C_{74}H_{100}O_{15}$: C, 72.30; H, 8.20. Found : C, 70.82; H, 7.95.

***6*BP-Es** : 83% yield; mp < r.t. ; IR (KBr disk) $\nu_{C=O}$ 1750cm^{-1}, no ν_{OH}; ^{1}H-NMR (100 MHz, $CDCl_3$, 25 ℃) δ 1.13 - 1.33 (*t*-Bu and CH_3, m, 72H), 4.13 - 4.50 ($ArCH_2Ar$ and CO_2CH_2, m, 22H), 4.59 (OCH_2CO, s, 12H), 6.90 - 7.26 (ArH, m, 14H). Anal. Calcd for $C_{89}H_{120}O_{18}$: C, 72.37; H, 8.19. Found : C, 72.49; H, 8.62.

***7*BP-Es** : 86% yield; mp < r.t.; IR (KBr disk) $\nu_{C=O}$ 1750cm^{-1}, no ν_{OH}; ^{1}H-NMR (100 MHz, $CDCl_3$, 25 ℃) δ 1.12- 1.35 (*t*-Bu and CH_3, m, 84H), 4.15- 4.60 ($ArCH_2Ar$ and CO_2CH_2, m, 26H), 4.59 (OCH_2CO, s, 14H), 6.90 - 7.26 (ArH, m, 16H) . Anal.Calcd for $C_{104}H_{140}O_{21}$: C, 72.41; H, 8.18. Found : C, 72.90; H, 8.68.

p-tert-Butylphenol resin was prepared by condensation of *p-tert*-butylphenol with formaldehyde. *p-tert*-Butylphenol (30 g, 0.2 mol), 37 % formalin (32.5 g, 0.4 mol as a formaldehyde) and conc. HCl (23.4 mL, 0.3 mol) were stirred at 80 ℃ for 7 h. The reaction mixture was poured into a large amount of water and the product obtained was extracted with CH_2Cl_2. The extract was concentrated into dryness and then the residue was dissolved in CH_3OH. The soluble part in CH_3OH contained lower molecular weight resin and the insoluble part contained higher molecular weight one. The ethyl acetate derivatives of the resins were prepared according to the method described above.

Measurements

^{1}H-NMR spectra were recorded on a JEOL FX-100S FT-NMR spectrometer at 100 MHz. Molecular weights and molecular weight distributions were determined by GPC using a Shimadzu HPLC LC-6A with a TOSOH UV-8011 spectrophotometer (270 nm) as a detector and two TSKgel G2000H8 and one TSKgel G3000H8 columns connected in series, and THF as an eluent.

Extraction studies

5 mL of aqueous alkali picrate solution ([Pic]=2.7×10^{-5} *M*, [MCl]=1.0×10^{-2} *M*) and 5 mL of a 2.7×10^{-3}- 2.7×10^{-2} *M* solution of ionophore in CH_2Cl_2 were stored in a stoppered test tube immersed in a thermostated water bath at 25 ℃. 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 ionophore, was run under the same condition which yielded an absorbance, A_0, of the aqueous phase. The percentage cation extracted 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

The selective extraction properties of *n*BP-Es for alkali metal cations were determined according to Pederson's technique (4) of picrate extraction that is semi-quantitative means

of assessing ion transfer ability from aqueous solution into an apolar organic solvent (CH_2Cl_2 in this study) as a convenient. The resulting extraction data were shown in Figure 1. Though *2*BP-Es and *3*BP-Es have a little extraction ability, *4*BP-Es, *5*BP-Es, *6*BP-Es and *7*BP-Es show the affinity toward alkali metal cations. The affinity becomes higher as the size of oligomer is larger. In particularly, *5*BP-Es shows Na^+ selectivity. Furthermore, the affinity of *6*BP-Es and *7*BP-Es are more preferable toward larger alkali cations, K^+, Rb^+ and Cs^+ than Na^+, but they show less selectivity. This result indicates that the alkali metal selectivity and affinity of *n*BP-Es are dependent on the size, as well as that of ester derivatives of calix[*n*]arene for alkali metal cations.

The affinity of *n*BP-Es toward alkali metal cations were compared with those of *4*Es, *6*Es and *8*Es. The typical result was illustrated in Figure 2. The extraction selectivity of *5*BP-Es resembles that of *4*Es in favor of Na^+, though the affinity of *5*BP-Es is lower than that of *4*Es. On the other hand, the affinity of *6*BP-Es and *7*BP-Es are similar to those of *6*Es and *8*Es, which show higher selectivity and affinity for K^+, Rb^+ and Cs^+. This indicates that these affinity of *n*BP-Es is considered to arise from the cavity present in *n*BP-Es based on the pseudo-cyclic conformation as shown in Scheme 1. The *n*BP-Es seems to form a complex with alkali metal cations by winding around alkali cations. The size of cavity formed by *5*BP-Es is equal to that of *4*Es, just fitting to Na^+ ion. The less extraction selectivity and affinity of *n*BP-Es than that of *n*Es may be due to the conformational flexibility.

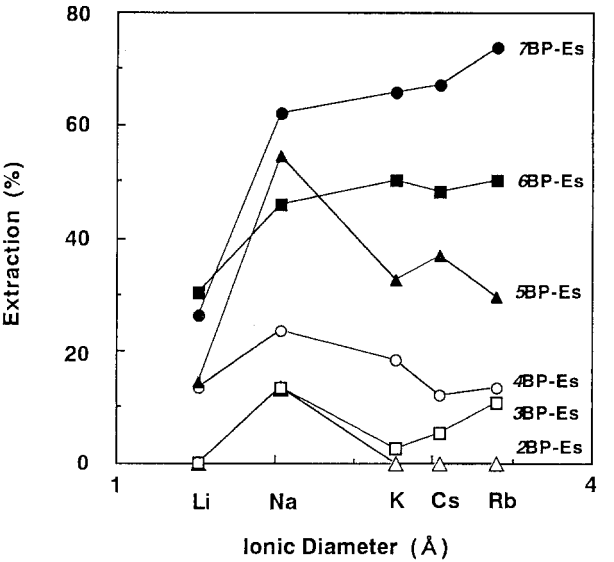


Figure 1. The extraction percentages of alkali metal picrates by *n*BP-Es from a neutral aqueous solution ([Pic]=2.7×10^{-5} *M*, [MCl]=1.0×10^{-2} *M*) into CH_2Cl_2 solution ([*n*BP-Es]=2.7×10^{-2} *M*) at 25 °C.

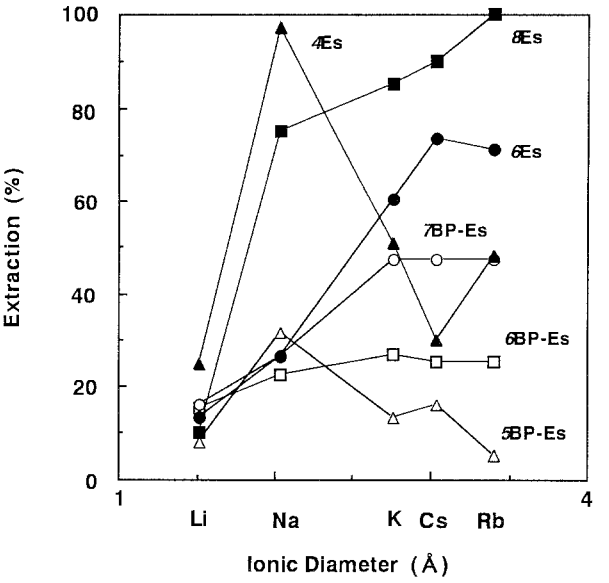
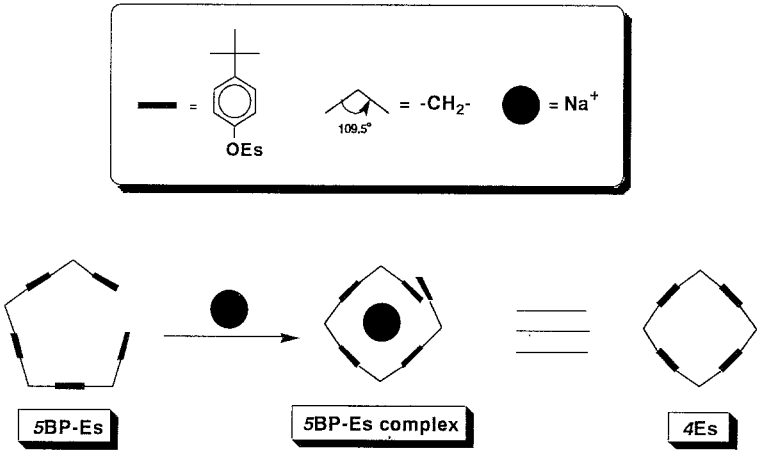


Figure 2. The extraction percentages of alkali metal picrates by *n*BP-Es and *n*Es from a neutral aqueous solution ([Pic]=2.7×10^{-5} *M*, [MCl]=1.0×10^{-2} *M*) into CH_2Cl_2 solution ([*n*Es], [*n*BP-Es]=2.7×10^{-3} *M*) at 25 °C.



Scheme 1

Complexation studies in apolar solvents were carried out by ^{1}H-NMR spectroscopy. The signals in ^{1}H-NMR spectrum of *4*Es in $CDCl_3$ at room temperature changed by adding Na^+ ion in CD_3OD to a $CDCl_3$ solution of *4*Es. And all signals became sharper and remained unchanged after the molar ratio of *4*Es to Na^+ ion has reached unity (5). This indicates 1 : 1 stoichiometry for the complex of *4*Es with Na^+. However, the ^{1}H-NMR spectrum of *5*BP-Es was almost unchanged by adding variable amount of Na^+ in the same condition. This NMR studies indicate that the complexing ability and the stability of complex of *5*BP-Es are lower than those of *4*Es, arising from the conformational flexibility in solutions.

The extraction ability of the ethyl acetate of *p-tert*-butylphenol resin with molecular weight distribution toward alkali metal cations was determined in the same manner described in *n*BP-Es experiments. The resin obtained was classified into two types based on the molecular weight : BP- I has lower molecular weight, the number-average molecular weight (Mn) = 1×10^3, and BP- II has higher, Mn = 2×10^3. The extraction results were shown in Figure 3. The affinity toward alkali metal cations depended on the molecular weight of ligand. BP- I showed the affinity toward Na^+, as the same of *5*BP-Es. On the other hand, BP- II showed the affinity toward K^+, Rb^+ and Cs^+, which is equal to that of *7*BP-Es. It is found that the ester derivative of *p-tert*-butylphenol resin has the affinity toward alkali metal cations, even though it has molecular weight distribution and the composition is heterogeneous.

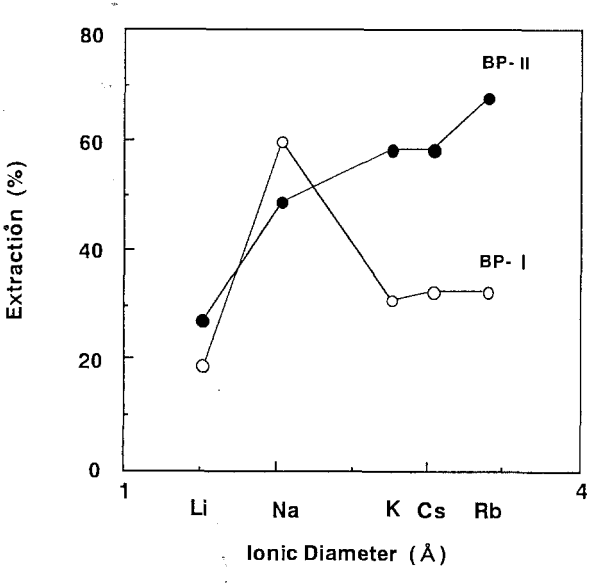


Figure 3. The extraction percentages of alkali metal picrates by BP- I and BP- II from a neutral aqueous solution ([Pic]=2.7×10^{-5} *M*, [MCl]=1.0×10^{-2} *M*) into CH_2Cl_2 solution ([BP- I], [BP- II]=2.0×10^{-2} g/mL) at 25 °C.

In conclusion, the ethyl acetate derivatives of all-*ortho* oligomers of *p-tert*-butylphenol-formaldehyde resins were prepared and some higher oligomers showed the affinity as well as the selectivity toward alkali metal cations. The same derivative of *p-tert*-butylphenol resin with molecular weight distribution also showed the affinity toward alkali cations. The phenolic resin is expected to be applied to wider fields of host-guest chemistry.

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