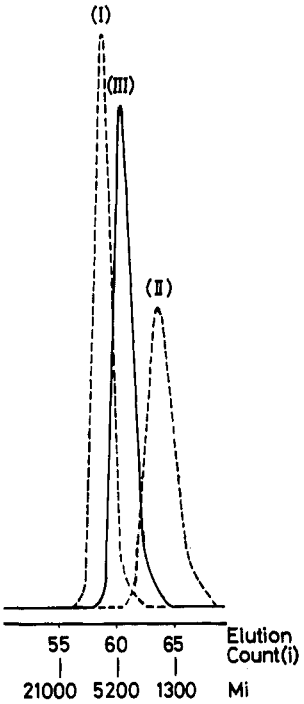

**Figure 8.** GPC curves of the polymerization product from $\beta$-butyrolactone: (I) with (TPP)AlCl (**1a**), (II) with (EtioP)AlCl (**2a**), (III) with the equimolar mixture of **1a** and **2a**. See Table II.

(EtioP)AlCl (**2a**) was also examined in order to investigate the relationship between the exchange of aluminum-carboxylate groups and the insertion reaction of $\beta$-butyrolactone to the aluminum-carboxylate bond. If no exchange reaction occurs with the axial carboxylate groups, the polymer is considered to grow on respective aluminum porphyrin, resulting in a bimodal distribution of the chain length (molecular weight). As shown by a single narrow peak in the GPC curve illustrated in Figure 8 (III), the product had a narrow and unimodal distribution of the chain length (molecular weight). It is clear that the exchange of carboxylate groups on (porphinato)aluminum occurs much faster than the insertion of $\beta$-lactone into aluminum-carboxylate bonds.

## Conclusion

Exchange of alkoxide or carboxylate groups on aluminum porphyrin was directly confirmed by $^1$H NMR spectroscopy by using combinations of two types of aluminum porphyrin with different alkoxide or carboxylate groups. A much faster rate for the exchange of alkoxide or carboxylate groups compared with the insertion of epoxide or $\beta$-lactone into aluminum-alkoxide or -carboxylate bonds was also confirmed by taking advantage of the narrow molecular weight distribution of the polymer formed as the product of successive insertions. These interesting findings will develop novel aspects in the elucidation of the mechanism of the polymerization reaction.

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# Binding to Polymer-Bound Crown Ethers and Linear Polyethers. Cooperative and Environmental Effects

**Wen-Ying Xu, Bruno Roland, and Johannes Smid***

*Polymer Research Center, Chemistry Department, College of Environmental Science and Forestry, State University of New York, Syracuse, New York 13210.*
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ABSTRACT: Binding of sodium and potassium picrate to polystyrene- and polymethacrylate-bound benzo-15-crown-5, benzo-18-crown-6, and linear polyethers was studied in toluene, dioxane, and tetrahydrofuran, and the results were compared with those obtained for the monomeric ligand analogues. The measurements were carried out spectrophotometrically by letting the soluble ligand, L, compete for the salt $A^-M^+$ with a crown ether or polyether ligand immobilized on a solvent-swollen network N according to the reaction $A^-M^+N + L \rightleftharpoons (K)\ A^-M^+L + N$. Formation constants, $K_L$, of the ion pair-ligand complexes $A^-M^+L$ in dioxane and THF were calculated from the equilibrium constant, $K$, of the competition reaction and the known binding constants, $K_N$, of the picrate salts to the network polymers. Comparison of $K_L$ or $K$ values of the polymeric ligands and their corresponding monomeric analogues clearly shows polymeric effects. Cooperative effects in ion binding can be observed when crown ether or linear polyether ligands are closely spaced along the polymer chain. The interionic ion pair distance of the poly(crown ether)-bound ion pairs depends on the crown content of the polymer. Comonomer units such as styrene, methyl methacrylate, or glycidyl methacrylate did not greatly affect the binding of picrate salt to the polymeric ligand, but incorporation of monomers with long polyethylene oxide side chains significantly enhances the binding to polymer-bound crown ether, possibly as a result of the more polar environment of the ethylene oxide unit surrounding the crown-bound ion pair.

## Introduction

Earlier reports on the binding of ionic solutes to polymers with pendant crown ether ligands indicated a dependence of the binding constants on the presence of neighboring ligands or comonomer substituents.[1-8] Cooperation of two crown ether ligands in the formation of stable 2:1 crown–cation complexes (for example, with potassium ions and benzo-15-crown-5 ligands) is well-documented.[3,6,9] Even when only 1:1 complexes are stable neighboring ligands or other chemical groups can modify the binding constants.[7,8] Many of these effects were derived from extraction data. However, extraction equilibrium constants are composite constants containing the partition coefficients of the ligands and their complexes. Hence, their interpretation in terms of the actual binding behavior of the ligands is not straightforward. Also, the presence of water in the organic phase can affect the binding constants.

When the complex formation of the ionic solute to the ligand is accompanied by a shift in the optical spectrum, binding constants in apolar solvents can be obtained spectrophotometrically. This is the case for certain picrate salt–crown ether systems. However, no spectral shifts are found with compounds such as 8-anilinonaphthalene-1-sulfonate or methyl orange. Moreover, binding constants in solvents like toluene are not easily obtained due to the insolubility of most ionic solutes, while in ethereal solvents binding constants are often too high to measure accurately.

We recently developed a technique that circumvents some of these problems.[10,12]

A competition method based on equilibrium 1 can be

$$A^-M^+N + L \overset{K}{\rightleftharpoons} A^-M^+L + N \qquad (1)$$

effectively employed in the measurement of absolute or relative affinities of soluble ligands, L, with respect to an ionic solute $A^-M^+$. A resin-immobilized crown ether or oligo(oxyethylene) (Glyme) denoted by N is used as the competing ligand. The concentration of the soluble complex $A^-M^+L$ is measured spectrophotometrically. It can be easily verified that $K = K_L/K_N$, where $K_L$ is the formation constant of the $A^-M^+L$ complex and $K_N$ the binding constant of $A^-M^+$ to the network N. We have reported several $K_N$ values for binding of alkali picrates and sulfonates to crown ether containing networks in dioxane and other ethereal solvents.[13,14] When a network is used for which $K_N$ is known, $K_L$ can be calculated when $K$ is measured. In toluene the uncompexed salts are insoluble, and $K_N$ cannot be determined. However, $K$ values can still be measured, and they provide a relative scale of ligand affinities with respect to the ionic solute used.

This paper describes the results of studies where the ligand L is a benzo-18-crown-6 or benzo-15-crown-5 moiety anchored to a polystyrene or poly(methacrylate) backbone. Different comonomer units were inserted in order to alter the neighboring groups around the ligand and to influence the binding of picrate salts to the immobilized crown ethers. The results show that these environmental effects can be quantitatively evaluated by the equilibrium method.

## Experimental Section

**Materials.** Homopolymers and styrene copolymers of 4′-vinylbenzo-15-crown-5 (VB15C5), 4′-vinylbenzo-18-crown-6 (VB18C6), and 4′-vinylbenzodi(glyme-3) (VBG3) were available in our laboratory from earlier investigations.[2,6,7,15] The corresponding low molecular weight analogues 4′-methylbenzo-15-crown-5 (MB15C5), 4′-methylbenzo-18-crown-6 (MB18C6), and 4′-methylbenzodi(glyme-3) (MBG3) were also used previously.[10,15] The homopolymers PMG8 and PMG22 obtained by polymerization of $CH_2{=}CH(CH_3)COO(CH_2CH_2O)_nCH_3$ (Polysciences) with $n = 8$ (MG8) and $n = 22$ (MG22), respectively, were recently reported by us.[16] The monomer 2,3-[4′-(1″-methacryloylethyl)-benzo]-1,4,7,10,13-pentaoxacyclopentadec-2-ene or 4′-(1″-methacryloylethyl)benzo-15-crown-5 (MAB15C5) was synthesized by reacting methacryloyl chloride and 4′-(1″-hydroxyethyl)benzo-15-crown-5 (a precursor in the synthesis of 4′-vinylbenzo-15-crown-5[6]) in tetrahydrofuran following a procedure published for the nearly identical monomer 4′-(methacryloylmethyl)benzo-15-crown-5.[17] The MAB15C5 monomer, recrystallized from petroleum ether, gave a melting point of 47 °C. Anal. Calcd for $C_{20}H_{28}O_7$:C, 63.14; H, 7.42. Found: C, 63.40; H, 7.20. $^1H$ NMR ($CDCl_3$) 1.60 (d, 3, $CH_3$), 2.00 (s, 3 , $CH_3$), 4.0 (m, 16, $CH_2$), 5.0 (q, 1, CH), 5.85 (m, 2, $=CH_2$), 6.9 (m, 3, arom—CH).

Copolymers of MAB15C5 with styrene, methyl methacrylate, and MG22 and of VB18C6 with MG22 were synthesized in benzene with AIBN as initiator. The polymers were precipitated from hexane, and those synthesized from the monomer MG22 were further purified by ultrafiltration to remove residual MG22. All polymers were subsequently freeze-dried from benzene. Their composition was determined by $^1H$ NMR. Those containing the MG22 monomer were analyzed by UV using the 280 nm ($\epsilon_m$ 2850) peak of the benzocrown ether ligand. Copolymer compositions were found to be close to those of the original monomer mixtures at around 50%–70% monomer conversion. Toluene was distilled from $CaH_2$, and dioxane and tetrhydrofuran from $LiAlH_4$.

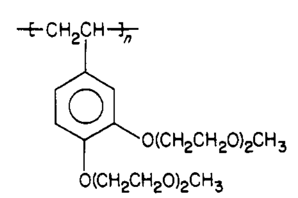
Three networks with immobilized ligands were employed in this work. RN18C6 is a microporous 2% cross-linked polystyrene resin with benzo-18-crown-6 (B18C6) ligands bound to the phenyl rings of the polystyrene backbone via a $-CH_2N(CH_3)CH_2-$ chain (9% ring substitution). Its synthesis was recently described.[14] It is nearly identical with the network R18C6 used in our earlier studies[10] where the B18C6 ligands are bound to the phenyl rings via a $-CH_2OCH_2-$ spacer. RG7-I was used in the determination of affinities of acylic ligands[11] and is a microporous 2% cross-linked polystyrene resin with $-CH_2(OCH_2CH_2)_6OCH_3$ ligands attached to the polystyrene phenyl rings (6.2% ring substitution). Finally, FMG8 is a flexible, transparent membrane consisting of a 4:1 molar ratio of methyl methacrylate and the monomer $CH_2{=}C(CH_3)COO(CH_2CH_2O)_8CH_3$ (Polysciences), radiation-polymerized with 5% ethylene dimethacrylate as cross-linker[11,12] (in these references FMG9 is identical with FMG8).

**Measurements.** In toluene as solvent a minimal amount of ligand L is initially used to dissolve the picrate salt. Sufficient network N (1–10 mg) is then added to bind 60–90% of the salt. After measuring the concentration of the remaining $Pi^-M^+L$ complex (see eq 1) by means of a Beckman Acta M VI spectrophotometer, small aliquots of a solution of the ligand L are added. This releases the resin-bound picrate salt. Each time after reaching equilibrium (30–60 min) the concentration of $Pi^-M^+L$ is measured. Details of the experimental procedure have been published elsewhere.[10] For experiments in dioxane or THF the picrate salt ($10^{-4}$ M) can be dissolved without the aid of a ligand. The network is added to bind as much salt as possible. In these solvents corrections must be made to account for any noncomplexed $Pi^-M^+$ left in the solution.[10]

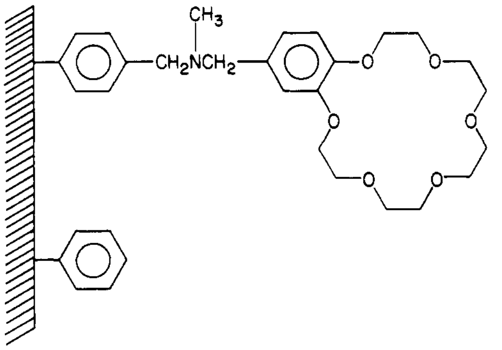
## Results

The structure of RN18C6 and that of two of the polymeric ligands are given below. An abbreviated notation has been adopted to distinguish between the various ligands. PVB15C5 and PVB18C6 refer to the homopolymers of vinylbenzo-15-crown-5 and vinylbenzo-18-crown-6, respectively. The abbreviation 12%SPVB15C5 (and similar ones) denotes a copolymer of styrene and VB15C5 with 12 mol % crown monomer units. Polymers of the two crown monomers VB18C6 or MAB15C5 with methyl methacrylate (MMA) or MG22 as comonomer have been denoted by P(%$M_1$/$M_2$), where %$M_1$ refers to the molar percentage of VB18C6 or MAB15C5 in the copolymer with the monomer $M_2$ (MMA or MG22). Abbreviated names of the monomers and of some other compounds are given in the Experimental Section. It has been assumed that the copolymers are essentially random. Hence, in a polymer such as P(8%MAB15C5/MG22) most of the MAB15C5 crown monomer units are assumed to have as their neighbors methoxypolyethylene glycol methacrylate (MG22) units.

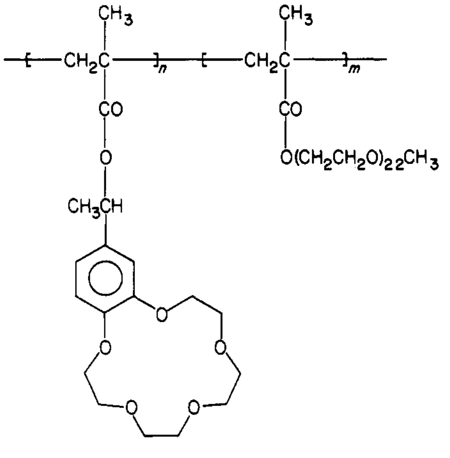
Following the procedure used for monomeric ligands,[10] the constant $K$ for the competition equilibrium 1 can be



PVBG$_3$



RN18C6



P($\frac{n}{n+m}$%MAB15C5/MG22)

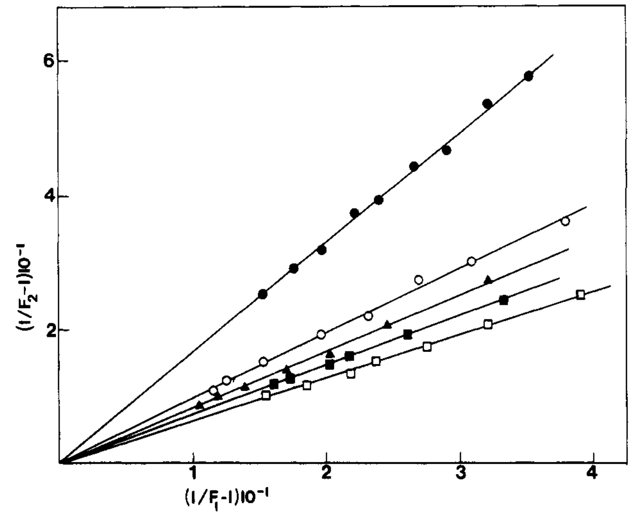


**Figure 1.** Plots of eq 2 for release of RN18C6-bound potassium picrate in dioxane on addition of PVB18C6 (●), 48%SPVB18C6 (○), MB18C6 (▲), 1.6%SPVB18C6 (■), and 19%SPVB18C6 (□); $T$ = 25 °C.

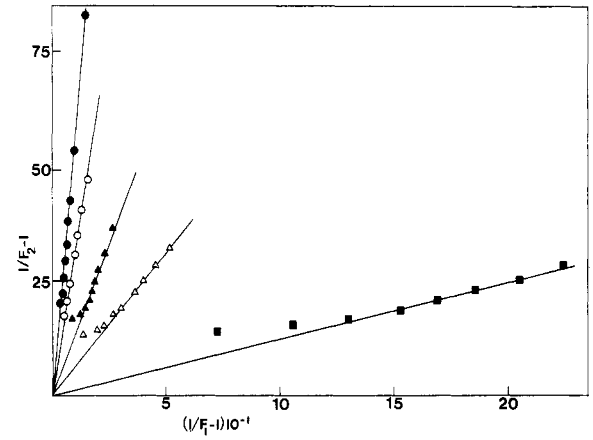


**Figure 2.** Plots of eq 2 for release of RN18C6-bound potassium picrate in tetrahydrofuran on addition of PVB15C5 (●), 48%-SPVB15C5 (○), 18%SPVB15C5 (▲), 12%SPVB15C5 (△), and MB15C5 (■); $T$ = 25 °C.

calculated from plots of the relationship

$$(1/F_2 - 1) = K(1/F_1 - 1) \qquad (2)$$

where $F_1$ is the fraction of soluble ligand L bound to picrate salt $Pi^-M^+$ ($F_1 = [Pi^-M^+L]/[L]_0$) and $F_2$ denotes the fraction of resin-bound ligand N complexed to $Pi^-M^+$ ($F_2 = [Pi^-M^+N]/[N]_0$, where the bound picrate $[Pi^-M^+N]$ is calculated by subtractng $[Pi^-M^+L]$ from the total amount of added picrate salt). In calculating $F_1$ for the copolymers, the total ligand concentration $[L]_0$ is taken as that of the crown ligand in the copolymer. Hence, it is assumed that in a copolymer such as P(8% VB18C6/MG22) the picrate salt complexes only with the crown unit. This certainly is the case when the comonomer is styrene, but it could be argued that with MG22 as comonomer the alkali ion of the salt also interacts with the glyme chain. However, binding to the latter ligand is much weaker than to a benzo-18-crown-6 ligand. We will return to this point under Discussion.

Under the conditions of our experiments (concentration of picrate salt less than $10^{-4}$ M) the only ionic species in toluene is the complex $A^-M^+L$, but in *dioxane* some free $A^-M^+$ may be present in the initial stage of the reaction with L. Since $A^-M^+$ and $A^-M^+L$ have nearly identical spectra, the optical measurements yield the sum of both species. The concentration of $A^-M^+$ can be computed from the expression $1/[A^-M^+] = K_N[(1/F_2 - 1)]$,[10] where $K_N$ is the binding constant of $A^-M^+$ to the network N. For RN18C6, $K_N$ equals $1.9 \times 10^5$ M$^{-1}$ for potassium picrate in dioxane. Its value in THF was not measured but can be quite accurately estimated from that obtained for the very similar network R18C6 ($K_N = 5.4 \times 10^4$ M$^{-1}$ in THF), which also contains the benzo-18-crown-6 ligand.[13] We consistently found the $K_N$ values for RN18C6 to be about 10% above those of R18C6 for the same salt/solvent combination.[14] This would give $K_N = 6.0 \times 10^4$ M$^{-1}$ for potassium picrate/RN18C6/THF. Generally the corrections for the presence of $A^-M^+$ are minor, but at low values of $L_0$, not negligible.

Plots of eq 2 for the system RN18C6/$Pi^-K^+$ in *dioxane* as solvent for a series of styrene copolymers of *VB18C6* (as ligand L) are depicted in Figure 1. Similar plots for the same network/salt combination with a number of styrene copolymers of *VB15C5* in *tetrahydrofuran* are reproduced in Figure 2. For the sake of clarity, not all ligands are shown. Most systems exhibit reasonable linearity with the exception of some ligands in THF as solvent where deviation occurs at low values of $1/F_1 - 1$ (low concentrations of free picrate). This point will be discussed later. $K$ values for the styrene–vinylbenzocrown ether copolymers were derived from the respective plots, and their values are listed in Table I, together with the complex formation constants $K_L$. The latter were calculated from the relationship $K_L = KK_N$, using $K_N = 1.9 \times 10^5$ M$^{-1}$ for

**Table I**
**Equilibrium Constants $K$ of the Reaction $A^-M^+ - RN18C6 + L \rightleftarrows A^-M^+L + RN18C6$ and Formation Constants of $A^-M^+L$ for Potassium Picrate in Dioxane and THF at 25 °C**[a]

| dioxane | | | THF | | |
|---|---|---|---|---|---|
| ligand[b] | $K$ | $K_L \times 10^{-4}$ $M^{-1}$ | ligand | $K$ | $K_L \times 10^{-4}$ $M^{-1}$ |
| MB18C6 | 0.83 | 15.8 | MB15C5 | 0.12 | 0.72 |
| 1.6%SPVB18C6 | 0.72 | 13.7 | 12%SPVB15C5 | 0.65 | 3.90 |
| 9.1%SPVB18C6 | 0.67 | 12.7 | 18%SPVB15C5 | 1.35 | 8.70 |
| 19%SPVB18C6 | 0.64 | 12.2 | 48%SPVB15C5 | 3.20 | 19.2 |
| 48%SPVB18C6 | 0.98 | 18.6 | PVB15C5 | 5.33 | 32.0 |
| PVB18C6 | 1.65 | 31.4 | | | |
| 10%SPVB15C5[c] | 0.41 | 7.8 | | | |
| 50%SPVB15C5[c] | 0.70 | 13.2 | | | |
| PVB15C5[c] | 0.95 | 18.0 | | | |

[a] $K_L$ values were calculated from the expression $K_L = KK_N$, where $K_N = 1.9 \times 10^5$ $M^{-1}$ for potassium picrate/RN18C6 in dioxane and $6.0 \times 10^4$ $M^{-1}$ for the same system in THF. [b] The percentage preceding the styrene–vinylbenzo crown ether copolymers refers to the molar content of crown monomer units. [c] Taken from ref 10. The $K$ values were recalculated for the network RN18C6; see text.

**Table II**
**Equilibrium Constants $K$ of the Reaction $A^-M^+N + L \rightleftarrows A^-M^+L + N$ for Sodium Picrate in Toluene at 25 °C**[a]

| ligand[a] | $K$ | ligand | $K$ |
|---|---|---|---|
| MB18C6 | 0.67 | MB15C5 | 0.64 |
| 9.1%SPVB18C6 | 0.48 | MAB15C5 | 0.40 |
| PVB18C6 | 1.5 | 12%SPVB15C5 | 0.54 |
| P(10%VB18C6/ MG22) | 2.3 | P(9%MAB15C5/ MMA) | 0.62 |
| MG8 | 0.010 | P(8%MAB15C5/ MG22) | 2.2 |
| PMG8 | 0.030 | P(56%MAB15C5/ MG22) | 1.0 |
| MG22 | 0.048 (1.4) | MBG3 | 0.0026 (0.75) |
| PMG22 | 0.077 (2.4) | PVBG3 | 0.013 (3.8) |

[a] All $K$ values were determined with the resin RN18C6 except those of MBG3 and PVBG3 where RG7-I was used (values in parentheses). Those for MG22 and PMG22 were also determined with the film FMG8 (values in parentheses).

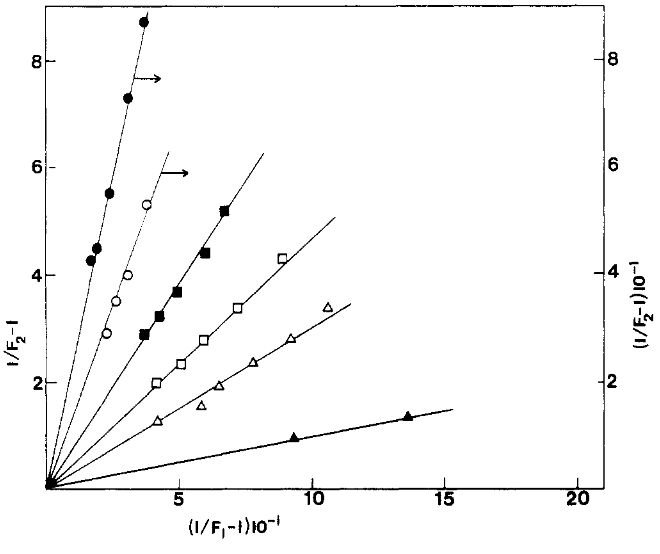


**Figure 3.** Plots of eq 2 for release of RN18C6-bound sodium picrate on addition of PMG22 (■), MG22 (□), PMG8 (△) and MG8 (▲) and for the release of sodium picrate bound to the film FMG8 on addition of PMG22 (●) and MG22 (○). Solvent toluene; $T$ = 25 °C.

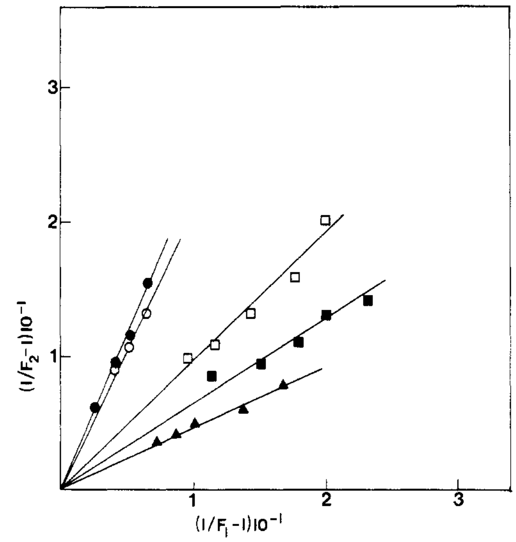


**Figure 4.** Plots of eq 2 for release of RN18C6-bound sodium picrate in toluene on addition of P(10%VB18C6/MG22) (●), P8%MAB15C5/MG22) (○), P(56%MAB15C5/MG22) (□), P-(9%MAB15C5/MMA) (■), and 9.1%SPVB18C6 (▲); $T$ = 25 °C.

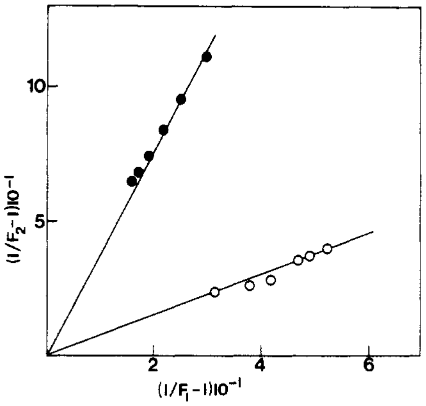


**Figure 5.** Plots of eq 2 for release of RG7-bound sodium picrate in toluene on addition of PVBG3 (●) and VBG3 (○); $T$ = 25 °C.

RN18C6/$Pi^-K^+$ in dioxane and $K_N = 6.0 \times 10^4$ $M^{-1}$ for the same system in THF.

Figure 3–5 contain plots of eq 2 for *sodium* picrate in toluene, with RN18C6 (Figures 3 and 4), RG7-I (Figure 5), or the membrane FMG8 (Figure 3) as the immobilized ligand. In all systems the plots show good linearity, and $K$ values can readily be obtained. They are listed in Table II. For comparative purposes $K$ values must all be based on the same network. Hence, those determined with RG7-I (PVBG3 and MBG3) can be converted to values based on RN18C6 by means of the relationship $K(\text{RN18C6}) = K(\text{RG7-I}) \times K_N(\text{RG7-I})/K_N(\text{RN18C6})$ were $K_N(\text{RN18C6})/K_N(\text{RG7-I}) = 292$ (this value is 10% above that for $K_N(\text{R18C6})/K_N(\text{RG7-I})$, which was reported to be 265; see ref 11). For example, for PVBG3, $K$(RN18C6) will be 3.8/292 = 0.013, and for MBG3, the $K$ based on RN18C6 will be 0.75/292 = 0.0026 (Table II). The linearity of the plots is justification of the assumption made in deriving 2, namely, that the $A^-M^+L$ complex is the only ionic species present in toluene and that it is, under our experimental conditions, not aggregated to a significant degree.

## Discussion

Prior to discussing the data it is pertinent to consider the reliability of the competition method. This can best be demonstrated by comparing $K$ values for different network polymers. If $K(\mathrm{N_1,L})$ and $K(\mathrm{N_2,L})$ are the respective $K$ values for a solute $\mathrm{A^-M^+}$ and ligand L obtained with networks $\mathrm{N_1}$ and $\mathrm{N_2}$, then $K(\mathrm{N_1,L})/K(\mathrm{N_2,L}) = K_\mathrm{N}(\mathrm{N_2})/K_\mathrm{N}(\mathrm{N_1})$, where $K_\mathrm{N}(\mathrm{N_1})$ and $K_\mathrm{N}(\mathrm{N_2})$ are the binding constants of $\mathrm{A^-M^+}$ with $\mathrm{N_1}$ and $\mathrm{N_2}$, respectively. The ratio of the two $K_\mathrm{N}$ values should, of course, be independent of the nature of the ligand L. Calculated from data given in Table II, the ratio $K_\mathrm{N}(\mathrm{RN18C6})/K_\mathrm{N}(\mathrm{FMG8})$ for sodium picrate in toluene and obtained with MG22 as ligand equals $1.4/0.048 = 29.2$, while with PMG22 as ligand this ratio comes to $2.4/0.077 = 31.1$. The difference is less than 7%. Earlier studies with the ligands dimethyldibenzo-18-crown-6 and some of the linear polyglycol dimethyl ethers using the networks R18C6, RG7-I, and FMG8 yielded values of $K_\mathrm{N}(\mathrm{R18C6})/K_\mathrm{n}(\mathrm{RG7\text{-}I}) = 265$ and $K_\mathrm{N}(\mathrm{FMG8})/K_\mathrm{N}(\mathrm{RG7\text{-}I}) = 9.75$, or $K_\mathrm{N}(\mathrm{R18C6})/K_\mathrm{N}(\mathrm{FMG8}) = 265/9./5 = 27.2$ (see ref 11, where the cross-linked film FMG9 is identical with FMG8 used in this work). Since, as stated earlier, $K$ values in toluene or dioxane for identical ligands are on the average 10% higher for R18C6 than for the nearly identical network RN18C6,[14] we find from our earlier data a value 29.9 for the ratio $K_\mathrm{N}(\mathrm{RN18C6})/K_\mathrm{N}(\mathrm{FMG8})$. Hence, using vastly different ligands L, nearly identical ratios for the binding constants of sodium picrate in toluene to the network polymers RN18C6 and FMG8 are obtained. The internal consistency of the data is gratifying and underscores the reliability of the competition method in arriving at $K$ and $K_\mathrm{L}$ values.

**Vinylbenzo(crown ether)–Styrene Copolymers. Cooperative Effects.** As pointed out, some of the plots of eq 2 derived from experiments in tetrahydrofuran deviate from linearity at low $1/F_1 - 1$ values, that is, at low concentrations of the soluble complex $\mathrm{Pi^-K^+L}$. Partial dissociation of the ion pair complex into $\mathrm{Pi^-}$ and the ligand-complexed free $\mathrm{K^+}$ ion is the most likely cause of this behavior. At 25 °C, potassium picrate in THF is a tight ion pair with an absorption maximum at 357 nm (350 nm in dioxane) and a dissociation constant $K_\mathrm{d} = 9.2 \times 10^{-8}$ M.[18] Crown-complexed separated $\mathrm{Pi^-K^+}$ ion pairs such as those with bis(crown ethers) of B15C5 have a $\lambda_\mathrm{m} = 378$–$380$ nm and a $K_\mathrm{d}$ of $2 \times 10^{-5}$–$4 \times 10^{-5}$ M.[18] Since the concentrations of $\mathrm{Pi^-M^+L}$ in our experiments are on the order of $10^{-5}$–$10^{-4}$ M, a considerable fraction of $\mathrm{Pi^-M^+L}$ is dissociated when the complex is a separated ion pair, especially at low $\mathrm{Pi^-M^+L}$ concentration. $\mathrm{Pi^-}$ and $\mathrm{Pi^-M^+L}$ have nearly the same absorption maximum, and the spectrophotometric measurements yield the sum $\mathrm{Pi^-} + \mathrm{Pi^-M^+L}$. If $[\mathrm{Pi^-}]$ is substantial, then the ratio $[\mathrm{L}]_0/[\mathrm{Pi^-M^+L}] = 1/F_1$ will be too low if no correction is made for the presence of $\mathrm{Pi^-}$. This is what is indeed observed in some of the plots (Figure 2). The error is small for MB15C5 since it forms a tight ion pair complex ($\lambda_\mathrm{m} = 365$ nm), and $K_\mathrm{d} \ll 10^{-5}$ M. Strong deviations were observed with some bis(crown ethers). These plots are not shown. For PVB15C5 and the SPVB15C5 copolymers the $\mathrm{Pi^-K^+}$ complex in THF absorbs at 380 nm, but especially for polymers with high crown content the deviation at low $1/F_1 - 1$ values does not appear to be significant (Figure 2) although the ion pairs are crown separated. This may be rationalized by noting that at the same crown concentration the polymer-bound picrate ion pairs on a SPVB15C5 chain with *high* crown content are in closer proximity, and dissociation into free ions would produce a chain of high charge density. This is energetically unfavorable, especially in a low polarity solvent such as THF.

The linearity of the plots for the systems RN18C6/$\mathrm{Pi^-K^+}$/SPVB18C6 in dioxane is not surprising. The benzo-18-crown-6 ligand forms only a 1:1 complex with $\mathrm{Pi^-K^+}$. This is the assumption used in the derivation of eq 2 in addition to the Langmuir adsorption behavior of the network polymer. Also, no dissociation into free ions is expected in dioxane. The absorption maxima of the $\mathrm{Pi^-K^+}$ complexes with MB18C6 and the SPVB18C6 polymers vary between 360 and 365 nm, suggesting that the ion pair complexes are still rather tight. There appears to be a small increase in the $\lambda_\mathrm{m}$ of the complex for copolymers with higher crown content. A similar observation was made in studies where the SPVB18C6 polymers were used as catalysts in the decarboxylation of potassium 6-nitrobenzisoxazole-3-carboxylate.[19] The polymers with high crown content were found to be more effective catalysts due to an increased interionic ion pair distance of the complexed $\mathrm{RCOO^-K^+}$ ion pair.

The data of Table I demonstrate that incorporation of MB18C6 into a polystyrene chain does not greatly affect its complex-formation constant with $\mathrm{Pi^-K^+}$ in dioxane as long as the crown ligands are spaced sufficiently far apart. However, $K_\mathrm{L}$ for the 48%SPVB18C6 is increased, and its value is nearly doubled for the homopolymer PVB18C6. This confirms earlier findings obtained in extraction experiments with $\mathrm{Pi^-Na^+}$ and $\mathrm{Pi^-K^+}$ in $\mathrm{CHCl_3/H_2O}$.[3] Extraction equilibrium constants for PVB18C6 were about 3 times those for 20%SPVB18C6. Since the partition coefficients of the two polymers are very different, interpretation of the extraction data in terms of differences in complex-formation constants was at that time speculative. The higher $K_\mathrm{L}$ value for PVB18C6 may indicate that even in systems where the ligand forms a 1:1 complex, one or more oxygen atoms from an adjacent ligand may furnish some additional interaction energy.

$K_\mathrm{L}$ for the complex of $\mathrm{Pi^-K^+}$ with MB15C5 equals $7.2 \times 10^3\ \mathrm{M^{-1}}$, close to the value $6 \times 10^3\ \mathrm{M^{-1}}$ previously estimated from spectrophotometric data.[18] In both studies the $\lambda_\mathrm{m}$ of the complex was recorded at 362 nm, although at high MB15C5 concentration a 2:1 complex is formed with $\lambda_\mathrm{m} = 378$ nm. For bis(crown ethers) with terminal B15C5 ligands the 2:1 complex with $\mathrm{Pi^-K^+}$ is readily formed, and $K_\mathrm{L}$ varies between $10^4$ and $17 \times 10^4\ \mathrm{M^{-1}}$, depending on the length and structure of the connecting chain.[18] This situation also exists in the SPVB15C5 polymers. In fact, the $\mathrm{Pi^-K^+}$ complexes with PVB15C5 and with the copolymers 12%-, 18%-, and 48%SPVB15C5 all are crown-separated ion pairs in THF with $\lambda_\mathrm{m} = 380$ nm. The observed increase in $K_\mathrm{L}$ as a function of the crown content of SPVB15C5 (Table I) reflects the increased probability for two B15C5 ligands to cooperate in the formation of an intramolecular 2:1 crown-separated ion pair complex. The $K_\mathrm{L}$ of PVB15C5 is higher than that found with any of the bis(crown ethers). One plausible explanation for this observation is that for polymers with a high molar percentage of crown monomer units a specific crown ligand can probably find more than one partner in its vicinity to form a 2:1 crown cation complex.

Cooperative effects in poly(crown ethers) were previously reported from extraction data[3,6] and spectral and viscosity data.[9,20] They also were reported by other researchers.[4,5,21,22] The changes in $K_\mathrm{L}$ with crown content of the polymer are more dramatic in THF than in dioxane (Table I). At least two opposing factors must be considered when the solvent is changed. A low dielectric constant makes ion pair separation more difficult in dioxane, while stripping away $K^+$-bound solvent molecules to accommodate the crown ligand requires more energy in THF (for example, $K_N$ for $Pi^-K^+$ with RN18C6 is 3 times higher in dioxane than in THF; see footnote *a* of Table I). Therefore, it is not surprising that with 10%- or 12%SPVB15C5, $Pi^-K^+$ forms a 1:1 complex with $\lambda_m$ = 362 nm in dioxane but a 2:1 complex ($\lambda_m$ = 380 nm) in THF. For the 48%-SPVB15C5 and for the homopolymer, 2:1 complexes are formed with $Pi^-K^+$ in both dioxane and THF. At higher concentrations of 10%SPVB15C5 the 1:1 complex in dioxane changes to a 2:1 complex, since the concentration of pairs of crown ligands that are close enough to form an intramolecular 2:1 complex also increases. Note that for this copolymer $K_L = 7.8 \times 10^4$ $M^{-1}$ in dioxane while for MB15C5 in THF $K_L$ is only $7.2 \times 10^3$ $M^{-1}$, both numbers referring to 1:1 complexes. This is an example of the stronger interaction of THF with $K^+$.

The variation in the interionic distance of the crown-complexed ion pair as a function of solvent, composition of the crown copolymer, and the concentration of crown ligands is an important factor in the application of such polymers for anion-activated catalysis. The rate and course of such reactions can be very sensitive to small changes in the distance between the reactant anion and its countercation.[1]

**Environmental Effects in Ion Binding to Crown-Containing Polymers.** Table II contains *K* values for a number of polymeric ligands and their monomeric analogues with sodium picrate in toluene. In this solvent no free picrate salt ($Pi^-M^+$) is present, and dissociation into free ions does not occur. $K_L$ values cannot be calculated since binding constants of $Pi^-Na^+$ to the network cannot easily be measured in toluene. However, *K* values for a series of ligands accurately reflect the relative affinities of these ligands for an ionic solute as long as they are measured with the same network.

Let us first compare the linear polyether type ligands MBG3, MG8, and MG22. Their ion-chelating properties are expected to resemble the polyglycol dimethyl ethers $CH_3O(CH_2CH_2O)_nCH_3$ with $n = 5$ (glyme 6), $n = 7$ (glyme 8), and $n = 21$ (glyme 22; the number following the glyme refers to the number of available oxygen binding sites). For the system RG7-I/$Pi^-Na^+$ in toluene we reported *K* values of 1.51, 2.74, and 13.0 for glymes 6, 8, and 22, respectively.[11] When converted to values based on RN18C6 (dividing by 292) we find $K = 0.0052$ (glyme 6), 0.0094 (glyme 8), and 0.045 (glyme 22). This compares very favorably with the data of Table II: $K = 0.0026$ for MBG3, 0.010 for MG8, and 0.048 for MG22. The lower value for MBG3 compared to glyme 6 is reasonable because of the lower basicity of the two phenoxy-type oxygen atoms, although this should in part be compensated for by their favorably fixed conformation relative to each other. The increase in *K* with chain length results form a statistical factor. The $Na^+$ ion in the $Pi^-Na^+$ ion pair cannot accommodate more than five adjacent oxygen atoms of a glyme ligand,[11] and for polyethers with longer chains *K* chiefly increases as a result of the larger number of available binding sites.[11]

The polymeric ligands PVBG3, PMG8, and PMG22 all complex more effectively with sodium picrate in toluene than do their corresponding low molecular weight analogues MBG3, MG8, and MG22: PVBG3 by a factor of 5, PMG8 by a factor of 3, and PMG22 by a factor 1.7. The result for PVBG3 confirms our earlier findings, namely, that the extraction equilibrium constant for $Pi^-Na^+$ in $H_2O/CH_2Cl_2$ increases by more than a factor of 2, for $Pi^-K^+$ by 7, and for $Pi^-Rb^+$ by 40 when PVBG3 is substituted for MBG3 as the extracting agent.[15] The dependence on cations results from the fact that the larger $K^+$ and $Rb^+$ ion can accommodate more than five oxygen binding sites, especially when the ligand-complexed ion pairs are separated as in $CH_2Cl_2$. The additional binding sites can be furnished in the polymeric ligands by oxygen atoms belonging to neighboring ligands. In addition to these cooperative effects the increased polarity of the environment surrounding the ligand-bound ion pair may contribute to stabilize the complex. Bound to PMG8 and PMG22 the $Pi^-Na^+$ may well be largely embedded in an ether-type medium rather than in toluene. With PMG22 some of the increase may be offset if oxygen atoms close to the polymer backbond would be less accessible for binding. Such considerations make it difficult to pinpoint the exact cause for the enhanced binding of these ion pairs to the polymeric ligands, and the term environmental effect only focuses on one possible cause.

Comparison of MB18C6 with 9.1% SPVB18C6 and of MB15C5 with 12%SPVB15C5 reinforces the conclusion derived from the dioxane systems, namely, that for 1:1 complexes a polymeric ligand and its monomeric analogue are very similar in their binding behavior as long as cooperative effects stemming from other chain-bound ligands or comonomer substituents are absent. The slight difference between MB15C5 and MAB15C5 probably results from a substituent effect that is quite dramatic for 4′-substituted benzo-15-crown-5 ligands complexing with sodium ions.[23] As in dioxane, the homopolymer PVB18C6 is more effective than the SPVB18C6 copolymer.

To gain better insight into the role of comonomer units on the binding efficiency of polymeric ligands, styrene was replaced by methyl methacrylate (MMA) or by MG22. Comparison of P(9%MAB15C5/MMA) with 12%-SPVB15C5 or MAB15C5 shows that MMA as comonomer unit, like styrene, does not greatly affect the binding of $Pi^-Na^+$ to the crown ligand. We also made recently a copolymer of 10%VB18C6 and 90% glycidyl methacrylate, anticipating that the cation-binding ethylene oxide unit in the latter monomer may assist in the binding of $Pi^-Na^+$. However, equilibrium studies in chlorobenzene (the polymer is not soluble in toluene) yielded *K* values of 0.99 for MB18C6 and 0.95 for the 10%VB18C6–glycidyl methacrylate copolymer.[24]

When surrounded by long polyethylene oxide chains the crown ligands appear to be more effective in binding $Pi^-Na^+$ (Table II). Replacing styrene by MG22 increases *K* by a factor of 5 for P(10%VB18C6/MG22) as compared to 9.1%SPVB18C6, and changing MMA into MG22 increases *K* for P(8%MAB15C5/MG22) by nearly a factor of 4 compared to P(9%MAB15C5/MMA). For all these polymers *K* was calculated by assuming that only the crown ligand binds $Pi^-Na^+$. However, binding of sodium picrate to PMG22 is not negligible, especially when one takes into account that in these polymers the MG22 content is about 10 times that of the crown monomer unit. It is possible to include the contributions of the two ligands by assuming two independent competition equilibria involving ligands $L_1$ (the crown ether) and $L_2$ (MG22) with equilibrium constants $K_1$ and $K_2$, respectively. As pointed out, the *K* values of Table II for all polymers were calculated by assuming that only the crown ligand $L_1$ binds the picrate salt. Since the spectrum measures the sum of $Pi^-M^+L_1$ and $Pi^-M^+L_2$, *K* is defined by the expression (see eq 1)

$$K = \frac{[N][[Pi^-M^+L_1] + [Pi^-M^+L_2]]}{[Pi^-M^+N]L_1} \tag{3}$$

It can easily be shown that $K = K_1 + aK_2$, where $a = L_2/L_1$.

For the copolymer P(10%VB18C6/MG22), $L_2 = 9L_1$; hence, $K = K_1 + 9K_2$. Taking $K_1 = 0.48$ (9.1%SPVB18C6) and $K_2 = 0.077$ (PMG22) (Table II), we calculate $K_{\text{calcd}} = 1.17$. The experimental $K$ value is 2.3 $M^{-1}$. A similar calculation for P(8%MAB15C5/MG22) with $K_1 = 0.40$ (MAB15C5) and $K_2 = 0.077$ yields $K_{\text{calcd}} = 1.27$, or $K_{\text{exptl}}/K_{\text{calcd}} = 1.75$. The calcultion for P(56%-MAB15C5/MG22) is less reliable since crown ligands anchored to the polymer backbone will be surrounded by both MG22 and MAB15C5 units.

The substantial increase in $K$ may result from a combination of cooperative and pure environmental effects. Conceivably, an oxygen atom from a poly(ethylene oxide) chain adjacent to a crown-complexed picrate ion pair may function as an additional binding site for the sodium ion, especially if the ion protrudes from the crown cavity. This is not too likely, especially with the 15-crown-5 ligands, since the spectra show the ion pairs to be crown-complexed tight ion pairs, with the ligand externally complexed to the cation. As noted earlier, no binding enhancement was found with glycidyl methacrylate as comonomer, although the ethylene oxide unit is a good cation-solvating ligand. A more conclusive experiment to separate cooperative from pure environmental effects (suggested by a referee) would be the use of potassium picrate with a polymer MG22 and a 15-crown-5 monomer. In such a system $K^+$ is likely to form a 2:1 crown–cation complex, and the totally sequestered cation would be inaccessible to binding sites on the MG22 chains. Hence, any increase in $K$ values can then be attributed to pure environmental effects. For example, the more polar glyme environment may facilitate ion pair separation in forming the 2:1 crown–cation complex. Unfortunately, in solvents like toluene, addition of potassium salts to benzo-15-crown-5 containing polymers [or to similar bis(crown ethers)] usually produces an insoluble complex.[16] This probably results from the formation of some intermolecular 2:1 crown–cation complexes or from the strong dipole–dipole interactions between the crown-complexed loose ion pairs.[25]

We realize that our calculations are only approximate. For example, a more careful study is needed to determine the monomer sequence distribution of the copolymers. It has been assumed that MG22 resembles methyl methacrylate in its copolymerization behavior, but macromers may well give different reactivity ratios. Nevertheless, we have established that the competition method employing immobilized crown ethers or linear polyethers can provide reliable information on polymeric effects resulting from the incorporation of ligands into a macromolecule. More significant effects may emerge with comonomers of higher polarity or with substituents that can interact with the counteranion of the polymer-bound ion pair.

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**Registry No.** MB18C6, 32702-28-6; SPVB18C6, 54052-38-9; PVB18C6, 31943-71-2; SPVB15C5, 53896-75-6; PVB15C5, 31943-70-1; MB15C5, 32702-27-5; P(VB18C6/MG22), 98104-95-1; MG8, 98104-88-2; PMG8, 98104-89-3; MG22, 26915-72-0; PMG22, 87105-87-1; MAB15C5, 98104-90-6; P(MAB15C5/MMA), 98104-91-7; P(MAB15C5/MG22), 98104-92-8; MBG3, 73033-18-8; P(VBG3), 73016-21-4; (VB18C6)·(glycidyl methacrylate) copolymer, 98104-94-0; 4′-(1″-hydroxyethyl)benzo-15-crown-5, 41757-96-4; sodium picrate, 3324-58-1; potassium picrate, 573-83-1; methacryloyl chloride, 920-46-7.

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