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Cation and Anion Binding Properties of Poly(vinylbenzoglymes)

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ABSTRACT: Polystyrene derivatives with one or two $O(CH_2CH_2O)_nCH_3$ (n = 2, 3, or 7) substituents on the benzene ring were prepared by radical polymerization of the corresponding monomers. Extraction of alkali picrates from water into CH_2Cl_2 was used to evaluate the cation binding capabilities of these poly(vinylbenzoglymes). In some of the systems the close proximity of the glyme chains in the macromolecule considerably improves the cation binding in comparison to the monomeric benzoglyme analogues by supplying more coordination sites for the cation solvation shell. Dissolved in water the polymers exhibit inverse temperature solubility, and those with short glyme chains have tightly coiled conformations resulting in micellar or polysoap properties. Strong interactions are observed with organic solutes, poly(vinylbenzodiglyme-3) (a polymer containing two $O(CH_2CH_2O)_2CH_3$ substituents per benzene ring) being especially effective. Binding constants of picrate and methyl orange to the poly(vinylbenzoglymes) and their copolymers with vinylbenzo-18-crown-6 were determined by optical spectroscopy between 35 and 5 °C, and the binding enthalpies and entropies were obtained from the van't Hoff plots. Binding of cations to the polyglymes is very weak in water, but conversion to a polycation can be accomplished by means of crown ether-complexable cations when crown ether monomers are incorporated in the backbone. Such mixed crown glyme-containing polymers show strong hydrophobic interactions with organic solutes and cations can be used to enhance electrostatically the binding of anionic organic solutes.

Recently reported studies on the properties of aqueous solutions of polymers endowed with crown ethers as pendant groups have demonstrated that poly(vinylbenzo-18-crown-6) (P18C6) exhibits micellar characteristics and strongly interacts with a variety of organic solutes.[1,2] The tightly coiled polysoap type macromolecule binds solutes such as picrate, methyl orange, or dodecyl sulfate with an avidity exceeding that of more commonly known solute binding polymers like poly(vinylpyrrolidone) or bovine serum albumin. If the bound solute is a reactant whose reactivity depends on the polarity of its environment, catalysis may occur. For example, P18C6 accelerates the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate in water by more than a factor 10^4.[2,3] Also, the association of anionic solutes to P18C6 can be electrostatically enhanced and regulated by converting the neutral polymer into a polycation, using crown ether-complexable cations like K^+ or Cs^+.[1-4]

It may be anticipated[3] that polystyrenes with short glyme substituents anchored to the benzene ring exhibit micellar characteristics and solute binding properties similar to those of poly(vinylbenzo-18-crown-6). To verify this we synthesized styrene monomers with one or two $O(CH_2CH_2O)_nCH_3$ (n = 2, 3, or 7) substituents attached to the benzene rings (for structures the reader is referred to the Results and Discussion section). The poly(vinylbenzoglymes) derived from these monomers exhibit inverse temperature solubility in water[5] similar to that observed for P18C6,[1] and one of the polymers binds picrate anions even more strongly than does P18C6. However, addition of cations has little effect on the binding of anionic solutes, contrary to that found for P18C6. Binding of alkali ions to glymes is weak in water, and this prevents the conversion of the neutral polymer into a polycation of sufficiently high charge density. In nonaqueous media, cation binding is much stronger, and to evaluate the importance of cooperativity of closely spaced glyme moieties in their association with alkali ions, extraction experiments were employed to compare the cation binding properties of the poly(vinylbenzoglymes) with their monomeric analogues. The results of the cation and anion binding experiments, including those involving some copolymers of vinylbenzo-18-crown-6 and vinylbenzoglymes, are reported in this paper.

Experimental Section

Materials. 1-Chloro-3,6-dioxaheptane ($Cl(CH_2CH_2O)_2CH_3$) was prepared in 75% yield from the monomethyl ether of diethylene glycol and $SOCl_2$ in the presence of pyridine. The compound is a colorless liquid, bp 58–59 °C (4 mm). **1-Chloro-3,6,9-trioxadecane** ($Cl(CH_2CH_2O)_3CH_3$, bp 70–71 °C (4 mm), 70% yield) and **1-chloro-3,6,9,12,15,18,21-heptaoxatetraeicosane** ($Cl(CH_2CH_2O)_7CH_3$, bp 150–155 °C (1 mm), 68% yield) were prepared by procedures similar to the one above.

4′-Methylbenzo-2,5,8,11,14,17-hexaoxaoctadeca-9-ene or 4′-Methylbenzodi(glyme-3) (I). To a slurry of 0.1 mol of NaH and 50 mL of dimethylformamide was added a 100-mL solution of 0.05 mol of 4-methylcatechol (Aldrich); the mixture was stirred under N_2 at room temperature for 15 min. To this mixture 0.11 mol (17.7 g) of 1-chloro-3,6-dioxaheptane dissolved in 100 mL of DMF was added dropwise over a 15-min period. After the mixture was heated for 20 h at 100 °C it was filtered and the solids washed with DMF. The residue obtained after solvent removal was dissolved in 250 mL of H_2O and the aqueous mixture was extracted four times with 100 mL of CH_2Cl_2; the organic layer was washed with a 2% HCl solution, followed by washing with H_2O, and dried over $MgSO_4$. The oily residue obtained after filtration and solvent removal yielded on vacuum distillation 14.0 g of I (80% yield) as a pale yellow liquid: bp 176–178 °C (1 mm); NMR ($CDCl_3$) δ 2.25 (s, 3, CH_3), 3.35 (s, 6, OCH_3), 3.65 (m, 12, CH_2), 4.10 (m, 4, CH_2), 6.80 (m, 3, aromatic). Anal. Calcd for $C_{17}H_{28}O_6$: C, 62.17; H, 8.59. Found: C, 62.12; H, 9.06. A similar procedure was used in the preparation of **4′-methylbenzo-2,5,8,11,14,17,20,23-octaoxatetraeico-12-ene** or **4′-methylbenzodi(glyme-4) (II)** from 4′-methylcatechol and 1-chloro-3,6,9-trioxadecane and of **4′-methylbenzodi(glyme-8) (III)** from the same catechol and 1-chloro-3,6,9,12,15,18,21-heptaoxatetraeicosane. Compound II was obtained in 70% yield by vacuum distillation: bp 227–229 °C (1 mm); NMR ($CDCl_3$) δ 2.25 (s, 3, CH_3), 3.35 (s, 6, OCH_3), 3.65 (m, 20, CH_2), 4.10 (m, 4, CH_2), 6.80 (m, 3, aromatic). Anal. Calcd for $C_{21}H_{36}O_8$: C, 60.56; H, 8.71. Found: C, 59.99, H, 9.21. Product III was purified on neutral Al_2O_3 (activity I) with THF as elutant: yield 40%; NMR ($CDCl_3$) δ 2.25 (s, 3, CH_3), 3.35 (s, 6, OCH_3), 3.65 (m, 52, CH_2), 4.10 (m, 4, CH_2), 6.80 (m, 3, aromatic). Anal. Calcd for $C_{37}H_{68}O_{16}$: C, 57.79; H, 8.91. Found: C, 57.58; H, 9.05.

4′-Formylbenzo-2,5,8,11,14,17-hexaoxaoctadeca-9-ene or 4′-Formylbenzodi(glyme-3) (IV). This material was prepared from 3,4-dihydroxybenzaldehyde and 1-chloro-3,6-dioxaheptane by the same procedure used for I. The product was obtained by vacuum distillation in 65% yield: bp 196–197 °C (1 mm); NMR ($CDCl_3$) δ 3.35 (s, 6, OCH_3), 3.65 (m, 12, CH_2), 4.10 (m, 4, CH_2), 7.00 (m, 3, aromatic), 8.40 (s, 1, CHO). **4′-Formylbenzo-2,5,8,11,14,17,20,23-octaoxatetraeico-12-ene or 4′-formyl-**

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benzodi(glyme-4) (V) was prepared in 60% yield (yellow liquid, bp 234–235 °C (1 mm)) from 3,4-dihydroxybenzaldehyde and 1-chloro-3,6,9-trioxadecane, following the method outlined for I: NMR ($CDCl_3$) δ 3.35 (s, 6, OCH_3), 3.65 (m, 20, CH_2), 4.10 (m, 4, CH_2), 7.00 (m, 3, aromatic), 8.40 (s, 1, CHO).

4′-(Hydroxyethyl)benzo-2,5,8,11,14,17-hexaoxaoctadeca-9-ene or 4′-(Hydroxyethyl)benzodi(glyme-3) (VI). To CH_3MgI prepared from 0.97 g of Mg and 4.72 g (0.04 mol) of CH_3I in 200 mL of ether was added dropwise over a period of 30 min 6.8 g (0.02 mol) of IV dissolved in 100 mL of ether. After the mixture was stirred overnight at room temperature it was treated with 150 mL of saturated NH_4Cl, and the aqueous layer after separation was extracted with 3 × 100 mL of $CHCl_3$. The combined organic layers were dried over $MgSO_4$, filtered, and evaporated. The resulting oil was placed on Al_2O_3 (activity I) and eluted with $CH_2Cl_2/CHCl_3$ to yield 5 g of a yellow oil (70%): NMR ($CDCl_3$) δ 1.45 (d, 3, CH_3), 2.74 (s, 1, OH), 3.35 (s, 6, OCH_3), 3.65 (m, 12, CH_2), 4.10 (m, 4, CH_2), 4.60 (q, 1, CH), 7.00 (m, 3, aromatic). **4′-(Hydroxyethyl)benzo-2,5,8,11,14,17,20,23-octaoxatetraeico-12-ene** or **4′-(hydroethyl)benzodi(glyme-4)** (VII) was prepared from V via the same Grignard reaction described for VI. The product was obtained as an oil in 70% yield: NMR ($CDCl_3$) δ 1.45 (d, 3, CH_3), 2.75 (s, 1, OH), 3.35 (s, 6, OCH_3), 3.65 (m, 20, CH_2), 4.10 (m, 4, CH_2), 4.60 (q, 1, CH), 7.00 (m, 3, aromatic).

4′-Vinylbenzo-2,5,8,11,14,17-hexaoxaoctadeca-9-ene or 4′-Vinylbenzodi(glyme-3) (VIII). A trace of *p*-toluenesulfonic acid was added to 6.0 g (0.02 mol) of VI dissolved in 200 mL of benzene, and the mixture was stirred and refluxed for 24 h with azeotropic removal of water. The solution was washed with a saturated Na_2CO_3 solution, followed by water, and then dried over $MgSO_4$ and filtered; the solvent was removed. The resulting oil was placed on a column of neutral Al_2O_3 (activity I) and eluted with a mixture of ether and hexane (4:1), yielding 4 g (67%) of a colorless oil: NMR ($CDCl_3$) δ 3.35 (s, 6, OCH_3), 3.65 (m, 12, CH_2), 4.10 (m, 4, CH_2), 5.40 (m, 2, $=CH_2$), 6.65 (m, 1, $=CH$), 7.00 (m, 3, aromatic). Anal. Calcd for $C_{18}H_{28}O_6$: C, 63.53; H, 8.24. Found: C, 63.09; H, 8.16. **4′-Vinylbenzo-2,5,8,11,14,17,20,23-octaoxatetraeico-12-ene** or **4′-vinylbenzodi(glyme-4)** (IX) was obtained as a colorless oil in 60% yield by the same procedure used for VIII: NMR ($CDCl_3$) δ 3.35 (s, 6, OCH_3), 3.65 (m, 20, CH_2), 4.10 (m, 4, CH_2), 5.40 (m, 2, $=CH_2$), 6.60 (m, 1, CH), 7.00 (m, 3, aromatic). Anal. Calcd for $C_{22}H_{36}O_8$: C, 61.68; H, 8.41. Found: C, 61.76; H, 8.38.

Monosubstituted Benzoglymes. Heptaethylene Glycol 4′-acetophenyl methyl ether or 4′-acetophenylglyme-8 (X) was prepared from equimolar quantities of the chloride of heptaethylene glycol monomethyl ether and *p*-hydroxyacetophenone (Aldrich), using NaH and DMF as outlined for the di(glyme) derivatives above. The product was isolated in 45% yield by vacuum distillation as a viscous oil: bp 190–194 °C (4 mm); NMR ($CDCl_3$) δ 2.50 (s, 3, CH_3), 3.35 (s, 3, OCH_3), 3.65 (m, 26, CH_2), 4.10 (m, 2, CH_2), 7.00 (d, 2, aromatic), 8.00 (d, 2, aromatic).

Heptaethylene Glycol 4′-(Hydroxyethyl)phenyl Methyl Ether or 4′-(Hydroxyethyl)phenylglyme-8 (XI). Sodium borohydride was added to a solution of X in absolute ethanol; the mixture was stirred at room temperature for 24 h and then poured into an equal volume of water and neutralized with dilute acetic acid. The aqueous solution was extracted with chloroform, and the organic layer was dried with $MgSO_4$, filtered, and evaporated. A clear oil was obtained in 85% yield: NMR ($CDCl_3$) δ 1.30 (d, 3, CH_3), 2.80 (s, 1, OH), 3.35 (s, 3, OCH_3), 3.65 (m, 26, CH_2), 4.10 (m, 2, CH_2), 4.70 (q, 1, CH), 6.85 (d, 2, aromatic), 7.25 (d, 2, aromatic).

Heptaethylene Glycol 4′-Vinylphenyl Methyl Ether or 4′-Vinylphenylglyme-8 (XII). This product was prepared by the same dehydration procedure used for the diglyme compound VIII. The styrene derivative was purified on neutral Al_2O_3 (activity I) and eluted with benzene, giving XII in 70% yield: NMR ($CDCl_3$) δ 3.35 (s, 3, CH_3), 3.80 (m, 28, CH_2), 5.40 (m, 2, $CH_2=$), 6.55 (m, 1, $-CH=$), 6.90 (d, 2, aromatic), 7.25 (d, 2, aromatic). Anal. Calcd for $C_{23}H_{38}O_8$: C, 62.42; H, 8.66. Found: C, 62.20; H, 8.81.

Picric acid was recrystallized from ethanol, while methyl orange, the metal hydroxides, and methylene chloride were reagent grade materials.

Table I
Extraction Equilibrium Constants, K_e, for Glyme Compounds and Their Polymeric Analogues in H_2O/CH_2Cl_2[a]

	$K_e \times 10^{-3}$ M^{-2}			
glyme	Na^+	K^+	Rb^+	Cs^+
I	0.40	0.45	0.10	
P-I	0.99	3.1	4.0	3.5
II	0.73	3.5	4.4	3.1
P-II	1.8	6.0	6.5	5.4
III	1.2	15	17	18
P-XII	0.62	2.4	1.9	2.3
P-I-18C6	250	895	970	2300
P-II-18C6	250	904	950	2400
P18C6	50	1160	1000	2150

[a] [Picric acid] = 0.001 M; [glyme monomer units] = 0.01–0.001 M; [MOH] = 0.01 M. In the experiments with crown ether containing copolymers all concentrations were lower by a factor of 10.

Polymerization Procedures. Deaerated benzene solutions of the glyme substituted styrenes containing the appropriate amounts of monomer and initiator (azobis(isobutyronitrile)) were polymerized at 70 °C for 24 h. The polymer precipitated as an oil on addition of a 20 times excess of hexane and was dried under vacuum. The number average molecular weights were determined by high-speed membrane osmometry and ranged from 30 000–60 000. All three glyme substituted polystyrenes were colorless, transparent materials ranging in consistency from highly viscous oils to sticky solids. Copolymers of vinylbenzo-18-crown-6[6] and the vinylbenzoglymes VIII and IX were prepared in benzene from equimolar mixtures of the respective monomers. ^1H NMR shows the copolymer composition to be nearly equimolar in the two comonomers, implying that copolymerization reactivity ratios in these systems are close to unity, similar to what is observed for copolymers of styrene and vinylbenzocrown monomers.[7]

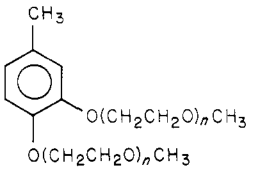
Extraction Measurements. Details of picrate extraction experiments have been reported elsewhere.[8-10] In most studies a 10 mL 10^{-3} M aqueous picric acid solution containing 0.01 M of the appropriate metal hydroxide was extracted with 10 mL of CH_2Cl_2 containing a glyme compound. For each glyme compound, extractions were carried out at glyme to picrate ratios of 1, 2, 5, and 10. With crown ether containing polymers concentrations of all reagents were reduced by a factor of 10. Concentrations of extracted picrate salts in the CH_2Cl_2 layer were determined spectrophotometrically at 378 nm, ϵ_m 18 000.[9] It was ascertained that transfer of glyme compounds to the aqueous phase was negligibly small, i.e., less than 2% for III, the most water-soluble compound.

Anion Binding Measurements. Binding constants of picrate and methyl orange anions in water to poly(vinylbenzoglymes) were determined spectrophotometrically in a Cary 15 spectrophotometer between 5 and 35 °C. The temperature in the water-jacketed optical cells was maintained to about 0.1 °C by means of a Haake FJ circulating bath. The main absorption bands of the free and polymer-bound picrate anion are λ_m 354 nm, ϵ_m 14 500 and λ_m 384 nm, ϵ_m 19 800, respectively. The ratios of the molar extinction coefficients of free to bound species are 1.18 at 354 nm and 0.585 at 384 nm. The sodium picrate concentration was kept constant at 10^{-5} M, while the polyglyme concentration was varied between 10^{-3} and 10^{-4} M. Fractions of bound and free picrate anions were calculated from the recorded optical spectra and from the known spectra of the free and bound picrate anion.

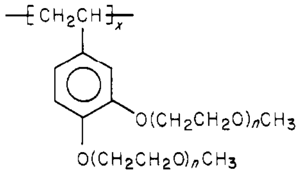
Experiments with the sodium salt of methyl orange were performed in a similar way. The absorption maxima of the free and bound dye are λ_m 465 nm, ϵ_m 2.7 × 10^4 and λ_m 435, ϵ_m 2.26 × 10^4, respectively, while the ratios of their molar extinction coefficients are 1.25 at 465 nm and 0.95 at 435 nm. The temperature dependence of the spectra of the two anions is negligibly small.

Results and Discussion

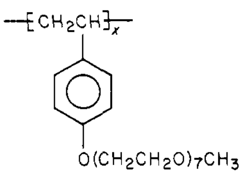
Extraction Data. The structures of the methylbenzoglymes and poly(vinylbenzoglymes) used in the extraction experiments are shown below. The 4′-methylbenzoglymes I and II are the low molecular weight analogues of the two polymers derived from the 4′-vinylbenzoglymes VIII and IX. The two polymers have been abbreviated in this paper as P-I and P-II, respectively. The polymer derived from the vinylbenzoglyme XII has been labeled P-XII, while P-I-18C6 and P-II-18C6 are abbreviations of the crown-containing random copolymers of 4′-vinylbenzo-18-crown-6 and the two vinylbenzoglymes VIII and IX, respectively.



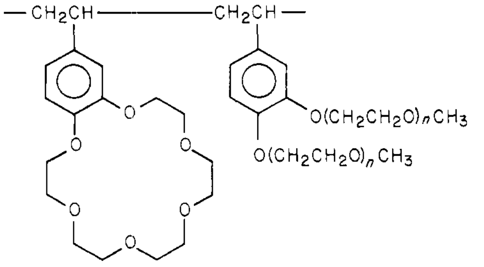
I, $n = 2$
II, $n = 3$
III, $n = 7$



P-I, $n = 2$
P-II, $n = 3$



P-XII



P-I-18C6, $n = 2$
P-II-18C6, $n = 3$

(random 1:1 copolymers)

The heterogeneous equilibrium (eq 1) describes the extraction of a picrate salt from water into an immiscible, glyme-containing organic phase. The observed 378 nm absorption maximum of the glyme–picrate complex in the CH_2Cl_2 phase suggests that the salt in this form exists as a loose ion pair.[9] At the prevailing concentrations (10^{-3}–10^{-4} M), it is most likely partially dissociated into free ions.[9] In the absence of ion pair dissociation the extraction equilibrium constant, K_e, is given by

$$\mathrm{Pi}^- \text{ (aq)} + \mathrm{M}^+ \text{ (aq)} + \text{glyme (org)} \xrightleftharpoons{K_e} \text{complex (org)} \quad (1)$$

$$K_e = \frac{[\text{complex}]}{\gamma_{\pm}^2[\mathrm{M}^+][\mathrm{Pi}^-]\{[\text{glyme}]_0 - [\text{complex}]\}} \quad (2)$$

$\gamma_{\pm}$ being the mean activity coefficient of the ions in the aqueous phase while $[\text{glyme}]_0$ refers to the initial glyme concentration (for polymers expressed in terms of concentration of glyme monomer units). More complex relationships can be derived to take ion pair dissociation into account.[8,10] However, dissociation constants of ion pairs complexed to polymers depend on the electrostatic potential on the macromolecule. Therefore, they vary as a function of the number of ion pairs bound per chain molecule. To avoid this problem, apparent K_e values were calculated by assuming no ion pair dissociation. This causes K_e to vary slightly with glyme concentration, but generally by not more than 20% between the lowest and highest glyme concentration used. The deviation was minimized by using the same picrate concentration in all extraction experiments, except where crown-containing polymers were used (high complexation in the latter systems requires lower picrate concentrations). The apparent K_e values listed in Table I, therefore, are expected to provide a reasonable comparison between the complexing abilities of different glyme compounds.

The open chain glyme type complexing agents, as expected, are much less efficient in binding alkali ions than crown ethers with an equal number of binding sites, but the differences are smaller when sufficient binding sites in the glyme compound are available to complete the solvation shell. For example, the respective K_e values for potassium picrate in H_2O/CH_2Cl_2 differ by more than a factor of 1000 between benzo-18-crown-6[9] and the six oxygen-containing benzoglyme I. On the other hand, increasing the numbers of oxygen atoms to eight increases K_e by nearly a factor of 8 (compare II with I), and, while no extraction data are available for dibenzo-24-crown-8, its binding constant to K^+ in methanol is smaller by about a factor of 30 compared to that of dibenzo-18-crown-6. The fact that II can assume conformations where all eight oxygen atoms are close enough to K^+ to function as binding sites for this cation considerably improves this complexing agent relative to the crown ether. Compared under identical conditions, the two compounds may have comparable complex formation constants to K^+ or Cs^+. In fact, some of the modified glyme compounds such as those with terminal quinoline moieties (the podand type chelating agents synthesized by Vögtle and Weber) are as effective in binding cations as some of the most powerful crown ethers.[12,13]

Alkali and alkaline earth salts of fluorenyl carbanions,[14,15] tetraphenylboron,[16] aromatic radical anions,[17,18] and other anions are known to form crystalline complexes with polyglycol dimethyl ethers with a 1:1 or 2:1 glyme to salt ratio, depending on the type of glyme and cation. While glyme 5 (the number following the glyme refers to the number of oxygen atoms, i.e., tetraethylene glycol dimethyl ether) or glyme 6 form 1:1 complexes with Na^+ in THF,[14] glyme 3 and glyme 4 can also form stable 2:1 complexes.[16,19] With potassium salts 2:1 glyme–cation complexes are found for glyme 4 and glyme 5, while glyme 6 and glyme 7 form 1:1 complexes.[14] The number of sites to which Na^+ binds to a glyme is probably not more than six, and higher K_e values for this cation with glymes of more than six oxygen atoms are basically due to a statistical factor resulting from the increased number of available binding sites.[14] However, K^+ may have as many as ten oxygen atoms in its solvation shell (e.g., dibenzo-30-crown-10 has all of its ten oxygen atoms wrapped around the K^+ ion and is a very effective complexing agent for this cation[11]). Hence, changing from benzoglyme I to II considerably increases the K_e for potassium picrate as well as for the Rb and Cs salts, and a further strong increase is found with the 16 oxygen-containing benzoglyme III. The Cs^+ cation is known to form stable sandwich type complexes with benzo-18-crown-6 moities attached close together on a polymer chain.[9] Hence, its solvation shell may accommodate as many as 12 oxygen atoms. The selectivity of the three benzoglymes is poor, at least with respect to K^+, Rb^+, and Cs^+.

The behavior of compounds I, II, and III is consistent with recently published data of Chaput et al., who determined potentiometrically and conductometrically the complex formation constants of a series of poly(ethylene glycol) derivatives to alkali ions in methanol.[20] Three of their compounds had the same structure as our benzoglymes but without the 4′-methyl group, *n* being 2, 3, or 4. The ratios of the complex formation constants for the six, eight, and ten oxygen-containing benzoglymes were found by Chaput et al. to be 1:4.5:16 for K^+ and 1:4.5:10 for Cs^+. The ratios of our K_e values (Table I) for the six, eight, and sixteen oxygen-containing methylbenzoglymes for K^+ and Cs^+ are 1:4.3:11 and 1:4.3:15, respectively. For Na^+ the ratio of the formation constants in methanol is 1:1.5:2, and that for the K_e values in our system is 1:1.8:3.0. The rather close similarity in the complexation behavior of the respective benzoglymes as a function of the number of oxygen atoms in the chain for our system and that of Chaput et al. demonstrates that in the heterogeneous extraction system the composite K_e values[8,10] do reflect the complexing abilities of these glyme ligands to alkali ions. The ratios in the two systems are of course not identical since in our series of benzoglymes one of the compounds has 16 instead of 10 oxygen atoms. Moreover, the solvent is different, and this parameter can drastically affect ligand selectivities for cations.[21]

The data of Table I further demonstrate that in a number of instances incorporation of a benzoglyme structure into a polymer chain can significantly improve picrate extraction. This polymer effect is larger when the monomeric benzoglyme does not have sufficient oxygen binding sites per molecule to supply the maximum possible number of sites for the cation solvation shell. In the polymer, the lack of binding sites on a single chain can be compensated for by using oxygen atoms of neighboring chains. Hence, when I is replaced by P-I, the increase in K_e is small for Na^+ but much larger for K^+, Rb^+, and Cs^+, cations which can accommodate at least ten oxygen atoms as long as they are placed in the proper position. The latter requirement is more easily met for linear glyme molecules than for the glyme-containing homopolymers, especially when the glyme chains are long. In the latter systems, steric restraints due to close packing may hinder the glyme chains in assuming conformations which can serve as effective solvation shells. This may be the reason why not much improvement is obtained when II is replaced by P-II, although K^+ and certainly Cs^+ can accommodate more than eight oxygen atoms. Comparison of III and P-XII also shows that it is not sufficient to have many sites in close proximity. P-XII has a chain with eight oxygen atoms on each benzene ring, while compound III has two eight-oxygen chains on the same ring which is comparable to a glyme chain with 16 oxygen atoms. Restraints on the mobility of the glyme chains in P-XII may in part account for its lower cation complexing power in comparison to III or even P-II and P-I. Another uncertain factor is hydration of the transferred cation. It is not unlikely that especially for the polymers the cations, upon extraction, may retain a few molecules of hydration water, since such species could be stabilized by hydrogen bonding of the water molecules with other glyme oxygen atoms. The presence of water in the cation solvation shell would of course reduce the number of sites to be supplied by the glyme chain.

The K_e values of the benzo-18-crown-6 containing copolymers P-I-18C6 and P-II-18C6 are nearly identical with that of the homopolymer poly(vinylbenzo-18-crown-6), with the exception of the value for Na^+, which is about five times higher for the copolymers. Apparently, no additional binding sites from glyme chains are used once the cation is sequestered by the benzo-18-crown-6 moiety. It is known that a sandwich type 2:1 benzo-18-crown-6–Cs^+ complex is formed on binding Cs^+ to P18C6.[1,9] The fact that the copolymers give identical K_e values for Cs^+ shows that the presence of glyme chains does not interfere with the formation of the Cs^+ crown complexes. The higher Na^+ extraction constants for the copolymers may not be surprising. The binding constant of Na^+ to P18C6 in water is more than 20 times lower than that to its monomeric analogue B18C6,[4] probably because Na^+ must be more extensively dehydrated to permit its binding to P18C6 where there is little room for a partially hydrated cation. When benzo-18-crown-6 units are separated on a polymer chain by more flexible glyme chains as in the two copolymers, a partially hydrated Na^+ ion may be able to bind to the crown ether, and hydrogen bonds between water and glyme oxygen atoms may even promote this binding as suggested earlier.

Picrate and Methyl Orange Binding. Although poly(crown ethers) are best known for their capacity to bind cations, polymers such as poly(vinylbenzo-18-crown-6) when dissolved in water also interact with organic solutes.[1,4] The neutral P18C6 polymer binds a variety of organic molecules and exhibits typical micellar or polysoap properties. A P18C6 macromolecule of number average molecular weight M_n = 106 000 has in water an intrinsic viscosity of only 0.107 dL/g at 25 °C, suggesting a tightly coiled conformation for this polymer. This picture also emerges from viscosity data obtained for the poly(vinylbenzoglymes). For example, $[\eta]_0$ at 25 °C for polymer P-I of M_n = 60 000 was found to be 0.202 dL/g in CH_2Cl_2 but only 0.03 in water. The latter value equals the theoretical $[\eta]_0 = 0.02$ computed from the Einstein relationship $[\eta]_0 = 2.5\bar{V}$ for a spherical, solvent-impenetrable particle of density 0.83 g/mL ($\bar{V}$ = 0.012 dL/g). The $[\eta]_0$ for P-I is even slightly below the range of values 0.035–0.05 dL/g reported for the intrinsic viscosities of globular proteins[22] and nonionic micelles.[23]

Another similarity between poly(vinylbenzo-18-crown-6) and the poly(vinylbenzoglymes) is their inverse temperature solubility in water, a property not uncommon for polymers with ethylene oxide units.[5] The cloud point for both P18C6 and P-I is 37 °C, but at 25 °C P-I is considerably less soluble in water than P18C6. Poly(vinylbenzoglymes) with longer glyme chains are more soluble in water, e.g., the cloud point of P-II is 66 °C, while P-XII is very soluble.

The viscosity and solubility behavior of the poly(vinylbenzoglymes) suggest that the polysoap character of these neutral polymers and their ability to bind solutes will decrease in the order P-I > P-II > P-XII. This can be illustrated from binding studies with picrate or methyl orange anions both of which undergo optical absorption shifts when transferred from water to an apolar polymer domain (see the Experimental Section).

A comparison of picrate adsorption to vinylbenzoglyme polymers and their copolymers with vinylbenzo-18-crown-6 in aqueous solutions is given in Table II. These measurements were carried out at the same solute (10^{-5} M) and polymer concentration (5×10^{-4} M of monomer base units), except for P-XII where poor binding required a 10^{-3} M polymer concentration to register a measurable picrate adsorption. Among the polymers listed in Table II, polymer P-I, the one least penetrable to water, appears to be the most effective binder of picrate anions, at least at 25 °C. The copolymer P-I-18C6 falls just in between the two homopolymers P-I and P18C6. The more water swollen polymers with longer glyme chains, i.e., P-II and especially P-XII, are considerably less effective, although P-II still compares well with P18C6.

The polymer P-XII can be made more hydrophobic by incorporating styrene into its backbone. For example, 20

Table II
Comparison of Picrate Binding to Poly(crown ethers) and Poly(vinylbenzoglymes) in Water at 20 °C[a]

polymer	fraction of picrate bound
P18C6	0.50
P-I	0.70
P-II	0.27
P-I-18C6	0.60
P-II-18C6	0.52
P-XII	0.044
P-XII-S[c]	0.25

[a] Experimental conditions: [picrate] = 1×10^{-5} M; ratio of [monomer units] to [picrate] = 50, except for P-XII and P-XII-S where the ratio was 100. [c] Copolymer of XII with 20 mol % styrene.

mol % styrene increases the fraction of bound picrate from 0.004 for P-XII to 0.25 for the styrene-containing copolymer (Table II). For P-II, an increase from 0.45 to 0.60 at a polymer to picrate ratio of 125 was found by incorporating only 10 mol % styrene into the P-II backbone. Hence, solute binding can be maximized by addition of styrene or other apolar monomers, although a 1:1 copolymer of styrene and XII was already insoluble in water.

More detailed studies were carried out with the polymers P-I, P-II, P-I-18C6, and P-II-18C6. Solute adsorption to these macromolecules can be described by a modified form of the Langmuir adsorption isotherm[1,24]

$$\frac{1}{R} = \frac{1}{n} + \frac{1}{nKA} \tag{3}$$

where $1/R$ is the ratio of total monomer units to bound solute, A denotes the free solute concentration, K is the intrinsic binding constant, and $1/n$ represents the minimum number of monomer units per bound solute molecule, i.e., $n \times \mathrm{DP_n}$ equals the total number of solute molecules that can be bound to the polymer chain under saturation conditions. Plots of $1/R$ vs. $1/A$ for picrate and methyl orange binding to P-I are depicted in Figures 1 and 2. The linear relationships imply that in these systems the binding of the two solutes is not interfered with by already bound solute molecules. Polymers P-II, P-I-18C6, and P-II-18C6 give similar plots. The respective intrinsic binding constants were calculated from the slopes of the least-squares plots and the intercepts $1/n$. The K and $1/n$ values for picrate are collected in Table III and those for methyl orange in Table IV and are compared with our previously reported data for poly(vinylbenzo-18-crown-6). Plots of ln K vs. $1/T$ are shown in Figure 3, and the respective binding enthalpies and entropies computed from these plots can be found in Table V.

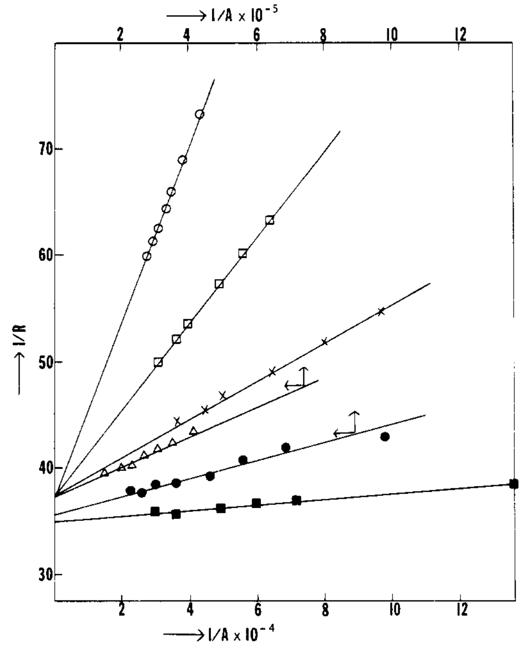


Figure 1. Plots of $1/R$ vs. $1/A$ for binding of sodium picrate to poly(vinylbenzodiglyme-3) (P-I) in water at (○) 35 °C, (□) 30 °C, (×) 25 °C, (■) 15 °C, (△) 10 °C, and (●) 5 °C. The line at 20 °C was omitted. The abscissa for the 10 and 5 °C line is on the top of the figure.

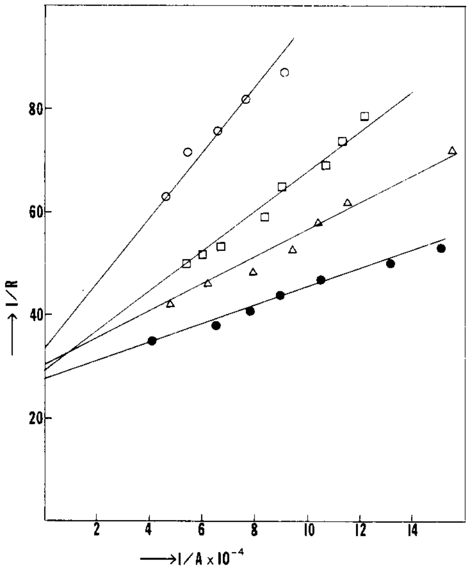


Figure 2. Plots of $1/R$ vs. $1/A$ for binding of sodium methyl orange to poly(vinylbenzodiglyme-3) (P-I) in water at (○) 35 °C, (□) 25 °C, (△) 15 °C, and (●) 5 °C. The line at 20 °C is not shown on the figure.

Of the five polymers listed in Table III, poly(vinylbenzodiglyme-3) appears to be the most effective macromolecule in binding picrate anions. It exceeds the binding power of P18C6, especially below room temperature. For example, the intrinsic binding constant of picrate to P-I

Table III
Intrinsic Binding Constants of Sodium Picrate to Poly(vinylbenzoglymes) in Water

	P-I		P-I-18C6		P-II		P-II-18C6		P-18C6[a]	
T, °C	$K \times 10^{-5}$ M^{-1}	$1/n$	$K \times 10^{-5}$ M^{-1}	$1/n$	$K \times 10^{-5}$ M^{-1}	$1/n$	$K \times 10^{-5}$ M^{-1}	$1/n$	$K \times 10^{-5}$ M^{-1}	$1/n$
5	48.5	36							6.7 (0 °C)	32
10	27.2	37	11.3	41	1.7 (6.4 °C)	64	4.8	50		
15	10.7	35							1.7 (17.5 °C)	35
20	4.4	36	4.6	42	1.0 (12 °C)	60	3.0	52		
25	2.3	38							1.34	42
30	1.0	38	1.3	48	0.55	50	1.3	54		
35	0.45	37							0.51	44

[a] Data taken from ref 1.

Table IV
Binding Constants of Methyl Orange to Poly(vinylbenzodiglyme-3) (P-I) in Water; Comparison with P18C6

	P-I		P18C6[a]	
T, °C	$K \times 10^{-5}$ M^{-1}	$1/n$	$K \times 10^{-5}$ M^{-1}	$1/n$
5			1.52	89
10	1.7	28		
15	1.3	31	1.18	92
20	0.91	31.5		
25	0.69	29	0.96	85
35	0.57	34		

[a] Taken from ref 1.

Table V
Enthalpies and Entropies of Sodium Picrate and Methyl Orange Binding to Poly(vinylbenzoglymes) and Poly(crown ethers)

polymer	ΔH, kcal/mol	ΔS, eu
	Picrate	
P-I	−26.3	−64.0
P-I-18C6	−18.1	−36
P18C6[a]	−11.9	−17
P-II	−12.6	−18
P-II-18C6	−9.7	−11
	Methyl Orange	
P-I	−7.8	−3.8
P18C6[a]	−3.9	9.7

[a] Taken from ref 1.

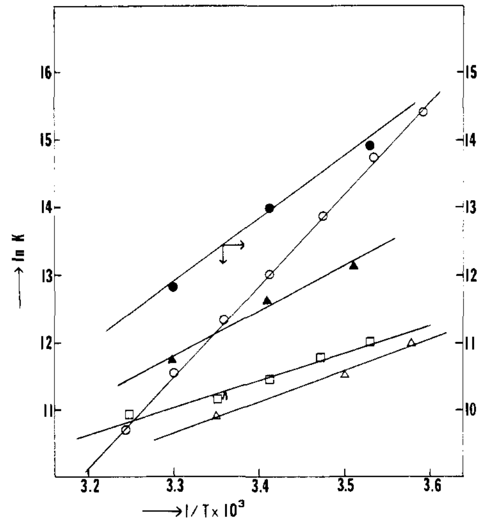


Figure 3. Temperature dependence of the binding constants of sodium picrate to P-I (○), P-II (△), P-I-18C6 (●), and P-II-18C6 (▲) and of methyl orange to P-I (□).

at 5 °C is 12 times that found for P18C6, but they are nearly the same at 35 °C. The average number of monomer units per bound picrate anion ($1/n$) is 37 for P-I, close to that found for P18C6, but $1/n$ for the latter polymer appears to be slightly temperature dependent.[1] A $1/n$ = 37 means that under saturation conditions a P-I macromolecule with an average of 180 monomer units ($M_n \approx$ 60 000) cannot bind more than five picrate anions. In this respect the polymers P-II and P-II-18C6 are even less effective as implied by their larger $1/n$ values (Table III). For methyl orange (Table IV) the intrinsic binding constant to P-I slightly exceeds the value found for P18C6, at least at the lower temperatures, but $1/n$ for P18C6 is three times higher than that for P-I. It is not clear what actually determines the $1/n$ values in these systems, and more work is needed to elucidate this point. A better comparison of binding strength can be obtained from the first binding constants $K^* = nK$. Their values (expressed in 10^5 g of polymer, a unit commonly used in this work) are given in Table VI together with those reported for poly(vinylpyrrolidone), bovine serum albumin, and a polymer with carbohydrate units. P-I and P18C6 compare very favorably with the other polymers, P-I being superior at the lower temperatures.

Table VI
Comparison of Binding Constants,[a] K^*, of Methyl Orange to Macromolecules

polymer	$K^* \times 10^{-4}$ M^{-1} (25 °C)	ref
poly(vinylpyrrolidone)	2.7	25
poly(3-*o*-vinylbenzyl-D-glucopyranose)	3.0	26
bovine serum albumin	6.1	25
poly(vinylbenzo-18-crown-6)	33.4	1
poly(vinylbenzodiglyme-3)	70	this work

[a] Binding constants, K^*, refer to the first binding constants expressed in 10^5 g of polymer.

Poly(vinylbenzo-18-crown-6) was found to possess the capability to regulate the binding of anionic solutes like methyl orange in the presence of crown ether complexable cations. The neutral polymer is converted to a polycation, and the charge density which controls the solute interaction electrostatically is a function of the cation concentration and the binding constant of the cation to the poly(crown ether).[1,4] For example, the binding of picrate or methyl orange to P18C6 is drastically enhanced on addition of small amounts of Cs^+ cations. This effect is especially advantageous when the solute interaction with the neutral polymer is weak as is the case with 6-nitrobenzisoxazole-3-carboxylate[3] or with the dye 2-(4′-hydroxybenzeneazo)benzoate.[4] However, this cation promoted solute binding cannot be realized for the poly(vinylbenzoglymes). Cation binding to the latter polymer is so weak in water that even in the presence of 1 M KCl the neutral polyglyme does not convert into a K^+ charged polymer of sufficiently high charge density to improve the binding of picrate or methyl orange. But the capability of cation control can be built into the polyglyme polymer by using copolymers of vinylbenzoglymes and vinylbenzocrown ethers. Polymers such as P-I-18C6 and P-II-18C6 bind picrate or methyl orange more effectively when K^+ or Cs^+ are present. For example, 60% picrate ([sodium picrate] = 8.8×10^{-6} M) is bound to P-I-18C6 at a ratio of monomer units to picrate of 65, while under the same conditions 74% picrate is bound with 0.01 M KCl present and 97% picrate is adsorbed with 0.01 M CsCl (94% with 0.003 M CsCl). Hence, incorporation of crown monomer units into the backbone (in addition to hydrophobic monomers) is another way of improving the solute binding capability of poly(vinylbenzoglymes) without affecting their micellar character.

The data of Table V suggest that the solute binding to P-I is largely enthalpic in nature, the entropy being strongly negative. The high exothermicity is unusual, although the association of *p*-nitrophenolate to α-cyclodextrin has a ΔH = −7.2 kcal/mol[27] while binding of 6-nitrobenzisoxazole-3-carboxylate to P18C6 also is strongly exothermic, ΔH being −11.8 kcal/mol and ΔS = −28 eu.[3] The enthalpy values for P-I-18C6, P-II, and P-II-18C6 were derived from only three binding constants in a narrow temperature range, and their accuracy is probably not better than 2 kcal/mol. Nevertheless, the observed pattern in the enthalpy values as a function of polymer structure appears to be consistent, i.e., $-\Delta H$ for P-I > P-I-18C6 > P18C6 for both picrate and methyl orange.

It is not easy to rationalize the strong exothermicity of picrate binding to P-I. Hydrophobic interactions of organic solutes with macromolecules generally have low ΔH and frequently positive ΔS values, as in the binding of methyl orange to P18C6[1] or other polymers. As implied by the optical shift, picrate anions, on binding to P-I, release hydration water, and this is expected to increase the entropy of binding, but other factors may be more important. For example, cation binding to a cryptand ligand also releases hydration water, but the process for Rb^+ or Cs^+ in water is accompanied by a decrease in entropy of as much as −20 eu.[28] It may be that on binding picrate to the tightly coiled P-I molecule the expansion of the chain needed to accommodate the large anion may permit some water to penetrate into the polymer domain and to hydrogen bond to the glyme oxygen atoms. This at least could be one possible cause for the large negative ΔH and ΔS values, but more work is required to verify this.

In conclusion, it was shown that in aqueous solution some of the poly(vinylbenzoglymes) assume tightly coiled conformations and exhibit micellar character with strong binding of organic solutes such as picrate anions or methyl orange. Binding of alkali ions to these neutral polymers is very weak in water, but incorporation of crown ether monomers into these polymers provides a means to convert the poly(vinylbenzoglymes) into positively charged species using crown ether complexable cations. This further promotes and regulates the binding of organic anions. Extraction data show that in a solvent such as methylene chloride cation binding to the poly(vinylbenzoglymes) can be considerably more effective than to the corresponding monomeric analogues due to cooperative interactions with oxygen atoms of neighboring glyme chains which provides a more complete solvation shell for the cations.

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Dimensional and Hydrodynamic Properties of Poly(hexyl isocyanate) in Hexane

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ABSTRACT: Narrow-distribution fractions of poly(hexyl isocyanate) (PHIC) ranging in weight-average molecular weight $\bar{M}_w$ from 7×10^4 to 7×10^6 were studied by light scattering, viscosity, and sedimentation velocity measurements with hexane of 25 °C as a solvent. The molecular-weight dependence of the z-average mean-square radius of gyration $\langle S^2 \rangle_z$ was analyzed in terms of the Benoit–Doty theory for the Kratky–Porod wormlike chain, with the result that the persistence length q is 42 ± 1 nm and the molar mass per unit contour length M_L is $715 \pm 15\ \mathrm{nm}^{-1}$. With these parameter values, the measured values of $\langle S^2 \rangle_z$ as well as the angular dependence of the particle scattering function can be accurately fitted to the known theories for the wormlike chain model. When the data for the intrinsic viscosity $[\eta]$ and the sedimentation coefficient s_0 were compared with those of Yamakawa–Fujii's theories for the wormlike cylinder, with q and M_L fixed to 42 nm and 715 nm^{-1}, respectively, it was found that the best agreement between theory and experiment can be obtained only if inconsistent values, 1.6 nm for $[\eta]$ and 2.5 nm for s_0, are used for the diameter of the cylinder.

The recent calculations by Yamakawa and Fujii[1,2] of the intrinsic viscosity $[\eta]$ and sedimentation coefficient s_0 of a wormlike cylinder have afforded methods for estimating the parameters q, M_L, and d from viscosity and sedimentation velocity measurements. Here q, M_L, and d represent, respectively, the persistence length, the molar mass per unit contour length, and the diameter of the cylinder. However, the validity of these methods was suspected

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