Viscosity studies of crown ether-containing polymers in solutions of alkali salts. Intra- *versus* intermolecular crown—cation complexes

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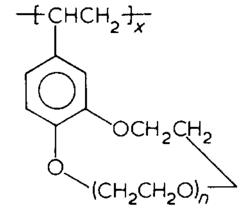
The complexation of cations to poly(vinylbenzocrown ethers) strongly affects the viscosity of the polymers. In mixtures of THF-MeOH the reduced viscosities of the polymer—salt solutions at constant polymer concentration pass through a maximum, their values depending on the cation-to-crown ratio and the binding constant of the cations to the poly(crown ethers). Crosslinking and abnormally high viscosities are found when a cation can complex simultaneously with two crown ligands, e.g. in mixtures of potassium salts with styrene copolymers containing pendent benzo-15—crown-5 moieties. In such systems competition exists between the formation of inter— and intramolecular 2:1 crown—cation complexes, and their relative importance depends on the crown content of the copolymer. Spectrophotometric measurements in THF mixtures of styrene—vinylbenzo-15—crown-5 copolymers and potassium picrate reveal that at low crown concentration, intramolecular complexes can form when crown ligands are separated, on the average, by less than four styrene units. The data, in combination with calculations on the distribution of crown ligands along a chain as a function of crown content, can be used to rationalize the viscosity behaviour of these polymer solutions.

INTRODUCTION

Polymers to which macrocyclic polyethers (crown ethers) are anchored as pendent groups change into polycations when dissolved in solutions containing crown complexible cations[1-6]. The charged poly(crown ether), with cations complexed to the crown ligands, possesses all the properties of a typical polyelectrolyte. For example, it can form polysalt complexes with polyanions[4], and its reduced viscosity rapidly increases on diluting the polymer—salt solution. Most of the alkali and alkaline earth cations form 1:1 stoichiometric complexes with the common monomeric crown ethers[7,8], but in a number of systems the cation is associated with two crown ligands. Such sandwich type complexes are frequently encountered when the cation diameter exceeds that of the crown cavity. This is the case for K^+ or Ba^{2+} and ligands with a 15-crown-5 ring or for Cs^+ and an 18-crown-6 type ligand[3,9,10]. The stability of these complexes can be considerably improved by linking the two crown moieties with a short chain to form a bis(crown ether)[11], or by attaching the crown ligands to a macromolecule[1-6].

Charging the neutral poly(crown ether) in solution with cations is likely to enhance its intrinsic viscosity due to chain expansion. When the cation complex involves two crown ligands, the complex formation may be intra— or intermolecular in nature, depending on the concentration of crown units, the distance between the ligands on the polymer chain, and the cation to crown ratio. A strong increase in viscosity should result when the cation bridges two crown ligands of different chains. This may eventually lead to gelation or precipitation.

In this paper we report on the viscosity behaviour of homopolymers and styrene copolymers of 4-vinylbenzo-15-crown-5 and 4-vinylbenzo-18-crown-6 (depicted below). The copolymers were synthesized in order to determine the formation of intra— and intermolecular cation—crown complexes as a function of copolymer composition and distance between crown ligands on the chain. Formation of such complexes was studied by viscometry, and independently from optical measurements by looking at the formation of crown separated ion pairs in mixtures of the respective copolymers with potassium picrate in tetrahydrofuran.



EXPERIMENTAL

Materials

The synthesis of 4-vinylbenzo-15-crown-5 and of 4′-vinylbenzo-18-crown-6 have been previously re-

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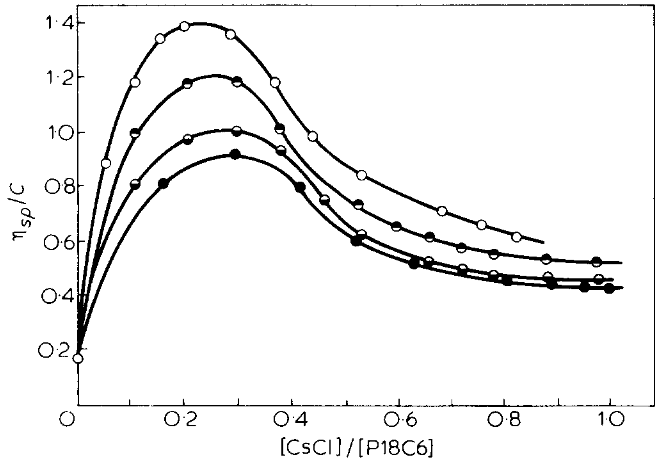


Figure 1 Dependence of reduced viscosity of P18C6 on the concentration of CsCl; solvent: THF–MeOH (v/v = 1/1), T = 25°C; concentration of polymer: (○) 0.0508 g dl^{-1}; (◓) 0.106 g dl^{-1}; (◒) 0.212 g dl^{-1}; (●) 0.318 g dl^{-1}

ported[1,12,13]. The two homopolymers and the styrene copolymers were made in a 10% monomer or comonomer solution in benzene at 70–80°C with azobisisobutyronitrile as initiator[1]. The polymers were purified by precipitation from petroleum ether or hexane[1], and dried under vacuum. The crown content of the copolymers was determined by ^{1}H n.m.r. The six styrene copolymers with 4-vinylbenzo-15-crown-5 contained 1.5, 2.3, 5.8, 11.8, 18 and 48%, respectively, of crown monomer units on a molar basis, while one copolymer with 5.5 mole % of 4-vinylbenzo-18-crown-6 was used. The homopolymers are abbreviated as P15C5 and P18C6, the copolymers as 1.5% SP15C5, etc., meaning a styrene copolymer with, on the average, 1.5 crown monomer units per 100 chain monomer units. The number average molecular weight as determined by osmometry ranged from 35 000 to 45 000 except for a 5.5% SP15C5 which had an $M_n \approx 100\,000$.

Tetrahydrofuran, methanol and methyl ethyl ketone were spectrograde solvents and used without further purification. Sodium tetraphenylboron (Fisher) was used in the preparation of the corresponding potassium and caesium salts[14]. Potassium picrate was prepared as described[11]. Metal chlorides were all reagent grade and dried in a vacuum oven before use.

Viscosity measurements

Viscosities were measured in Ubbelohde viscometers at 25° ± 0.02°C. Flow times were greater than 100 s and no kinetic corrections were applied. In one set of experiments the polymer concentration was kept constant, and the cation-to-crown ratio varied, by adding to the poly(crown ether) solution to be measured either a known quantity of solid salt or a salt solution containing the same concentration of polymer. The measurements were carried out in methyl ethyl ketone or in an equal volume mixture of THF–methanol. In a second series of experiments an 8% copolymer solution in MEK containing the appropriate amount of salt was successively diluted with solvent and the flow times were recorded. Dilution by pure solvent assured a constant crown-to-cation ratio throughout the experiment. To compare the viscosity behaviour of the respective copolymers at a given ionic strength the amount of salt used with the copolymers was the same. For 2.3% SP15C5 the crown-to-cation ratio was chosen to be 2. This means that for the same amount of polymer and salt, the crown-to-cation ratio for the 5.8% SP15C5 solution was 5, etc. Exceptions to this procedure are noted.

Spectrophotometric measurements

Spectra of potassium picrate in tetrahydrofuran in the presence of crown polymers were measured on a Cary-15 spectrophotometer. Picrate concentrations ($\sim 10^{-3}$ M) were such that free ion dissociation could be neglected[11]. The three main species present are the THF solvated and crown complexed tight ion pairs absorbing in the 357–362 nm region, and the crown separated ion pair absorbing at 380 nm and containing two crown ligands[6,11,15].

RESULTS AND DISCUSSION

Experiments at low polymer concentration

Preliminary data in an equal volume mixture of THF/MeOH (the methanol was needed to improve salt solubility) revealed a pronounced increase in the reduced viscosity of P18C6 on adding KCl or CsCl[1,2]. For example, the η_{red} of a 1% solution of P18C6 (M_n = 110 000) increases from 0.15 to about 1.0 on addition of CsCl (Cs^+/P18C6 = 0.5), and further increases by at least a factor of three when this solution is diluted to 0.02%[1]. The neutral poly(crown ether) is changed to a Cs^+ charged polycation, and the binding constant of Cs^+ to P18C6 in this solvent mixture (the binding constant is only 110 M^{-1} in water[4]) must be quite large since the viscosity curve continues to go up even below a 0.01% solution, hence, Cs^+ remains bound.

The effect of charge on η_{red} is depicted in *Figure 1* where at four different but constant P18C6 concentrations the ratio Cs^+/P18C6 is increased by adding CsCl. A maximum in the reduced viscosity is found as a function of the ratio of Cs^+-to-crown ligand. This maximum is higher at low polymer concentration, and is reached at a Cs^+-to-crown ratio of approximately 0.2, and slightly above this at higher [P18C6]. Similar types of experiments shown in *Figures 2* and *3* reveal the η_{red} dependence on the cation for both P18C6 and P15C5. For P18C6 the maximum viscosity at constant polymer concentration decreases in the order $Cs^+ > K^+ > Na^+$ and for P15C5 in the order $K^+ > Cs^+ > Na^+$.

The viscosity behaviour of the two poly(crown ethers) as a function of the number of cations bound to a chain resembles

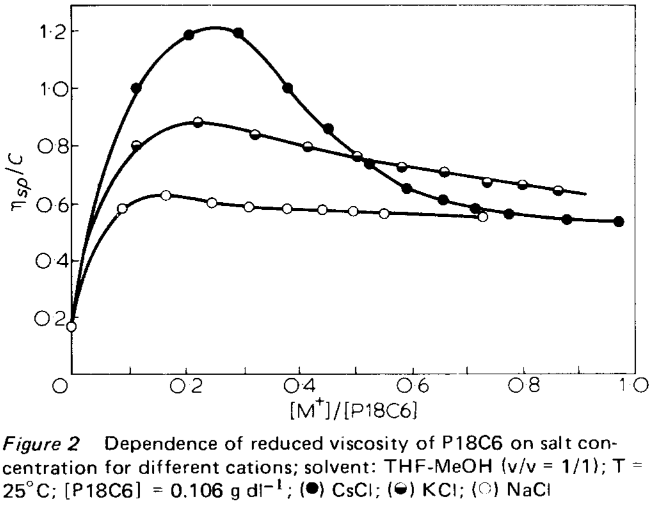


Figure 2 Dependence of reduced viscosity of P18C6 on salt concentration for different cations; solvent: THF-MeOH (v/v = 1/1); T = 25°C; [P18C6] = 0.106 g dl^{-1}; (●) CsCl; (◓) KCl; (○) NaCl

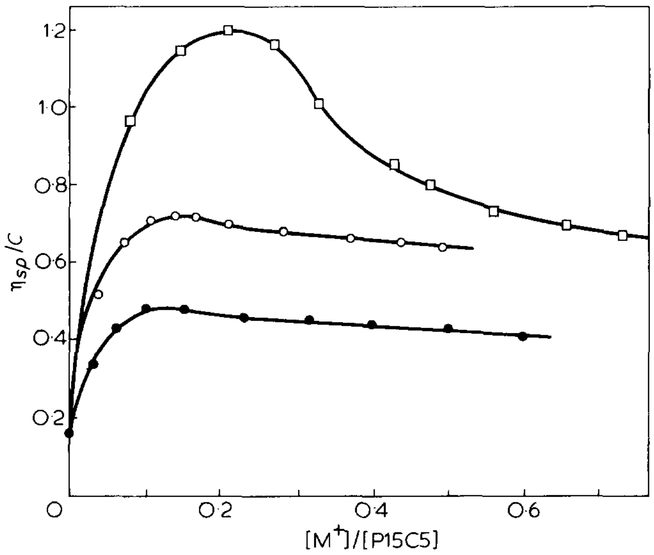


Figure 3 Dependence of the reduced viscosity of P15C5 on salt concentration; solvent: THF–MeOH (v/v = 1/1); T = 25°C; [P18C6] = 0.1025 g dl^{-1}; (□) KCl; (○) CsCl; (●) NaCl

the change in η_{red} observed for polymethacrylic acid as a function of the degree of neutralization[16,17]. The shapes of the curves may be rationalized by considering two opposing effects: greater charge repulsion resulting in chain expansion when more cations become bound at higher salt-to-crown ratios, and chain contraction due to counter ion screening of the positive charges which eventually reverses the expansion as the electric potential on the chain increases. Since Cs^+ forms a 2:1 crown cation complex with benzo–18–crown–6 ligands, the highest Cs^+-to-crown ratio on the polymer chain is 0.5. The η_{red} maximum, however, occurs between a ratio of 0.2 to 0.3. The fact that maximum chain expansion occurs when only 40 to 60% crown ligands are complexed to Cs^+ indicates that anion shielding becomes a major factor when the chain is only partially charged. The same can be said for the other systems.

The maximum η_{red} for P18C6 and P15C5 depends on the type of cation and parallels the affinity of the cations for the two polymers. The dependence is consistent with extraction equilibria and conductance data for these polymer–cation systems. For example, the equilibrium constants for extraction of alkali picrate salts from water into methylene chloride (which measures the equilibrium M^+ (aq) + Pi^- (aq) + Crown (org) $\rightleftarrows$ complex (org)) were found to be $10^{-3} K_e(M^{-2})$ = 45 (Na^+), 570 (K^+), and 150 (Cs^+) for P15C5 and 25 (Na^+), 720 (K^+) and 1650 (Cs^+) for P18C6[1]. Similar trends in the alkali complexation constants to P15C5 and P18C6 can be derived from conductance data in methyl ethyl ketone. The extent to which the conductance of a salt solution is lowered on addition of P15C5 or P18C6 depends on the cation binding constant to the polymer. In MEK the conductance data show the cation binding constant to P15C5 to decrease in the order $K^+ > Cs^+ > Na^+$ and to P18C6 in the order $Cs^+ > K^+ > Na^+$ [3]. Potentiometric measurements of cation binding to P18C6 in water also yields $Cs^+ > K^+ > Na^+$ [4,18]. Although binding constants are solvent dependent and the order may be reversed in some cases[18], the trend in the viscosity maxima is consistent with the known affinity of the two polymers for the respective cations.

The shape of the viscosity curves may also depend on other factors. Conductance[3] and potentiometric[4,18] measurements of cation binding to poly(crown ethers) show a decrease in the binding constant as the ratio bound cation to total crown increases, and for 1:1 cation–crown complexes (e.g. Na^+ and K^+ with P18C6) a rapid decrease is observed when this ratio exceeds 0.5 (ref 6), probably as a result of strong electrostatic repulsion or steric hindrance. This may be a contributing factor in obtaining the η_{red} maxima at low cation-to-crown ratios. The high maxima for K^+/P15C5 and Cs^+/P18C6, apart from the high binding constants, may also result from the 2:1 crown–cation complexes formed in these systems. The closely spaced crown ligands must be forced apart to accommodate the large cations. This is likely to enhance the chain expansion beyond that caused by charge repulsion. Whether the intramolecular 2:1 crown–cation complexes involve the linking of two more distant crown moieties of the chain is not known, but this could conceivably cause the polymer chain to contract. Certainly formation of intermolecular 2:1 crown–cation complexes cannot be important at these concentrations, since in that case the viscosity would increase at higher concentration, not decrease as is observed. Ion pairing as observed by Schoene and Vollmert[19] in the styrene–acrylate copolymers in THF could also affect the viscosity behaviour, although the dielectric constant of our solvent mixture is considerably higher and the crown interaction with the cation would tend to form a more ionizable loose ion pair.

Intra– versus intermolecular complex formation. Crosslinking effects

When a poly(crown ether) solution contains cations that can interact simultaneously with two crown ligands (e.g. K^+ with benzo-15-crown-5), both intra– and intermolecular 2:1 crown–cation complexes may exist. The cation in the latter complex functions as a crosslink between two polymer chains, giving rise to an enhanced viscosity. The relative importance of the two complex formation processes should depend on the total ligand concentration and the spacing between crown ligands on a polymer chain. To demonstrate these effects, copolymers of 4-vinylbenzo-15-crown-5 (M_1) and styrene with different crown to styrene ratios were synthesized. The number average molecular weight of these copolymers were all between 35 000 and 45 000. Determination of the crown content of the various copolymers (by ^1H n.m.r.) as a function of the composition of the starting monomer mixture (the copolymers were recovered after 20–60% monomer conversion) yielded reactivity ratios r_1 = 1.1 and r_2 = 0.85. These values appear reasonable, and are comparable with those reported for the monomer pair 2,5–dimethoxystyrene (M_1) and styrene, r_1 = 1.13 and r_2 = 0.77 (ref 20). The results suggest an essentially random distribution of crown ligands in the respective copolymers.

Figure 4 depicts the reduced viscosity dependence on polymer concentration for several styrene–crown copolymers in methyl ethyl ketone (MEK). For the sake of clarity, some plots were omitted. The results reveal that in systems where only 1:1 crown–cation complexes are formed the increase of η_{red} with polymer concentration, *C*, is normal. For example, at a crown-to-cation ratio of 2, the reduced viscosity of 2.3% SP15C5/NaBPh$_4$ changes from 0.28 to 0.58 when *C* increases from 1 to 8 g dl^{-1}, and for 5.5% SP18C6/KBPh$_4$, η_{red} increases over this concentration range from 0.42 to 0.65. Under the same conditions the reduced viscosity for 2.3% SP15C5/KBPh$_4$ is enhanced from 0.28 to 1.13 (and to 1.95 at 10 g dl^{-1}) and for 5.5% SP18C6/CsBPh$_4$ from 0.42 to 1.42. The latter two systems form stable 2:1 crown–

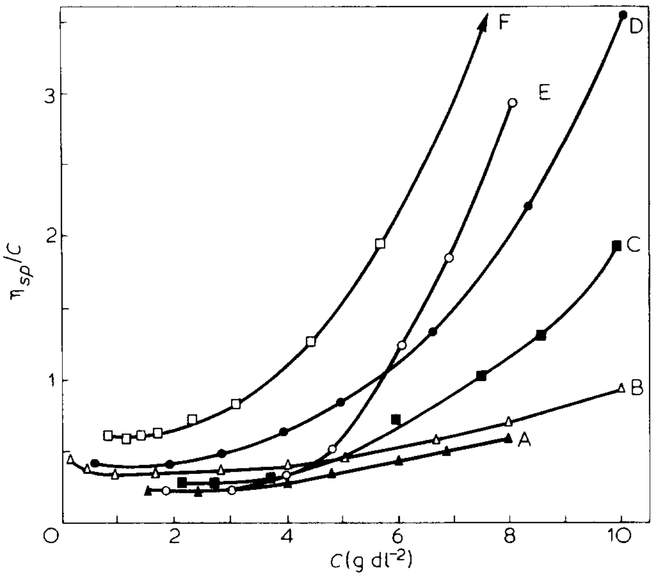


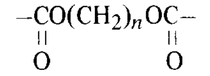
Figure 4 Dependence of reduced viscosity on polymer concentration for styrene–vinylbenzo-15-crown-5 copolymers in the presence of alkali tetraphenylboron. Solvent: methyl ethyl ketone, T = 25°C. (A) 2.3% SP15C5/NaBPh$_4$ = 2; (B) 11.8% SP15C5/KBPh$_4$ = 10; (C) 2.3% SP15C5/KBPh$_4$ = 2; (D) 5.8% SP15C5/KBPh$_4$ = 5; (E) 5.8% SP15C5/KBPh$_4$ = 2; (F) 5.8% SP15C5 (high M_n)/KBPh$_4$ = 5. Ratios refer to molar concentration of crown monomer units-to-cation in the solutions

cation complexes, and some of them are apparently of the intermolecular variety. It should be pointed out that, given the experimental conditions ([Crown] and $[M^+] > 10^{-3}$ M) the binding of cation to these crown polymers in whatever type of complex is essentially complete. This was shown from conductance data for mixtures of alkali tetraphenylboron salts and crown ethers in MEK and acetone[3,21].

Viscosity experiments on solutions of copolymers with different crown content but the same K^+ concentration show that the η_{red} *versus C* plot increases only moderately for 11.8% SP15C5, 18% SP15C5, and 48% SP15C5 (only the first plot is shown in *Figure 4*), but sharply curves upward for 2.3% SP15C5 and for 5.8% SP15C5 (notice in the latter case the difference between a low and high molecular weight sample). In the five systems the $[K^+]$ is the same at corresponding total polymer concentrations, with the crown-to-cation ratio equal to 2 for 2.3% SP15C5 and changing to 5 for 5.8% SP15C5, 10 for 11.8% SP15C5, 16 for 18% SP15C5 and 42 for 48% SP15C5. Hence, with all the cations bound, the five polymer solutions should have about an equal number of charges per polymer chain, and their behaviour from an electrostatic point of view should not differ much. The η_{red} values for the five copolymers at 10 g dl^{-1} with increasing crown content are 1.95, 3.54, 0.92, 1.03 and 0.79, respectively. Although intermolecular complexation and, therefore, crosslinking are favoured at increasing crown concentration, the concentration increase in this case is accomplished by changing the crown content of the polymer chain at constant total polymer concentration. This reduces the spacing between crown ligands and promotes the formation of intramolecular 2:1 crown complexes.

Spectrophotometric detection of intramolecular complexes

To gain some insight into the relationship between the formation of intramolecular 2:1 crown K^+ complexes and the spacing between crown ligands on a styrene–vinylbenzo-15-crown-5 copolymer chain we analysed the optical absorption spectrum of a 10^{-3} M potassium picrate (K^+, Pi^-) solution in tetrahydrofuran (THF) on addition of increasing quantities of 1.5%, 5.8% and 11.8% SP15C5. The K^+, Pi^- salt in THF is a tight ion pair with a very low dissociation constant ($K_d \approx 10^{-7}$ M) and an absorption maximum at λ_m = 357 nm[11,15]. On addition of benzo-15-crown-5 a 1:1 crown complexed tight ion pair, C, K^+, Pi^- is formed first (λ_m = 361 nm, $K \approx 10^4$ M^{-1}), followed by the formation of a 2:1 crown separated ion pair, C, K^+, C, Pi^- (λ_m = 380 nm) on addition of excess crown, K being 2 x 10^2 M^{-1}. However, when the two benzo-15–crown-5 ligands are linked together at their 4′ position by a



$$-\underset{\displaystyle O}{\overset{}{C}}O(CH_2)_nO\underset{\displaystyle O}{C}-$$

chain, the interaction with K^+, Pi^- in THF leads immediately to a crown separated ion pair, $\underline{C, K^+, C}, Pi^-$ (λ_m = 380 nm). The complex formation constants of K^+, Pi^- with these macrobicyclic polyethers are in the order of $10^4 - 4 \times 10^4$ M^{-1}, depending on n (n = 2, 5, or 8), and about 300 times higher when the ligands are complexed with the free THF solvated K^+ ion[11].

When complexing K^+ to crown copolymers, a certain fraction of crown ligands on the chain, depending on crown content, will be sufficiently close to another ligand to form a macrobicyclic polyether or 'bis(crown ether)' unit, which on binding the cation produces a 2:1 intramolecular crown–cation complex. It should be possible to obtain some information on the fraction of such bis(crown ether) units as a function of crown content from a calculation of the sequence length distribution of crown ligands. By measuring the fraction of crown separated ion pairs in a K^+, Pi^-–crown copolymer solution and comparing this with the calculated fraction of crown ligands that form bis(crown ether) units, it should also be possible to determine the maximum distance between ligands (in terms of styrene units) capable of forming such a unit. Unfortunately, when the optical measurements are carried out in MEK (to compare the results with the viscosity data), the spectra of the bound and free potassium picrates are nearly identical since potassium picrate itself is a partially dissociated loose ion pair in MEK with λ_m 380 nm, the same λ_m as the crown separated ion pair. The spectral measurements, therefore, were carried out in THF as solvent.

In the actual experiments the crown polymer was added to K^+, Pi^- in THF, keeping the picrate concentration constant at 10^{-3} M. As long as $[\text{crown}] > [K^+, Pi^-]$ all K^+ Pi is bound, either as a 1:1 or 2:1 crown–K^+Pi^- complex, absorbing at 361 and 380 nm, respectively. The fractions of the two kinds of complexes can be determined from the known spectra of these two species[11]. The 2:1 crown–picrate complexes are of the intramolecular kind due to the low polycrown concentration. This was ascertained by comparing a viscosity plot of 1.5% SP15C5 in THF containing 10^{-3} M K^+Pi^- with that of a similar solution in which sodium picrate is present instead of the potassium salt. The two viscosity plots (data up to 6 g dl^{-1} of polymer) are identical, implying that the fraction of intermolecular 2:1 crown–K^+ complexes is negligibly small.

In *Table 1* the fraction f of 2:1 crown separated potassium picrate ion pairs is listed as a function of the concentration of crown ligands (in terms of crown monomer base units) for three different copolymers. The fraction, $L_{(exp)}$, of crown ligands complexed to K^+Pi^- in the form of a 2:1 intramolecular complex is given by $L_{(exp)} = 2f[KPi]_0/[\text{crown}]_0$,

Table 1 Experimental and calculated fractions of crown ligands engaged in the formation of intramolecular 2:1 Crown–K$^+$ complexes. System: potassium picrate (1 x 10^{-3} M) in tetrahydrofuran at 25°C with different copolymers of vinylbenzo-15-crown-5 and styrene

[Crown][a] x 10^3 M	f[b]	$L_{(exp)}$[c]		$L_{(calc)}$[d]		
				$n < 3$[c]	$n < 4$	$n < 5$
1.5% SP15C5						
3.78	.18	.095	.089	.083	.110	.135
6.38	.30	.095				
10.0	.39	.078				
5.8% SP15C5						
1.07	.148	.276	.33	.29	.37	.44
2.15	.434	.400				
3.29	.631	.383				
4.54	.732	.322				
5.64	.824	.292				
11.8% SP15C5						
2.5	.656	.525		.49	.59	.68

[a] Total concentration of crown ligands in the copolymer solution

[b] Fraction of crown separated potassium picrate ion pairs (λ_m = 380 nm)

[c] $L_{(exp)} = 2f\,[\text{Picrate}]/[\text{Crown}]$; fraction of crown ligands bound to K$^+$ in an intramolecular 2:1 crown–K$^+$ complex

[d] $L_{(calc)}$ is the calculated fraction of crown ligands separated by less than 3, 4, and 5 styrene units, respectively

where the subscripts denote total concentrations of picrate and crown ligand. This experimentally determined fraction is now compared with the calculated fraction, $L_{(calc)}$, of crown ligands that potentially can form an intramolecular 2:1 complex. We assume that such ligands must belong to bis(crown ether) units, B, in which two crown ligands are separated by less than a maximum number, n, of styrene units. This number, n, can be found by a comparison of $L_{(calc)}$ and $L_{(exp)}$ for experiments where $f < 1$. It is assumed that the conditions are such that every B unit binds a K$^+$ ion. We also assume that a pair, C, of adjacent crown ligands forms an intramolecular complex with K$^+$ (see, however, below). The fraction of sequences of crown monomer units longer than two is small when the crown content of the polymer chain is low and this has been neglected. A correction must be made when a crown ligand is part of two B units or a B and a C unit, i.e. when two B units or a B and C unit are adjacent to each other sharing a common crown ligand. Since a K$^+$ cation complexes with two crown ligands, only two of the three crown ligands present in a B,B unit or in a B,C unit can be involved in the formation of an intramolecular 2:1 complex.

The probability of finding a B unit with two crown monomer (M_1) units separated by up to n styrene (M_2) units is given by

$$P(B) = \sum_{1}^{n} W_{2(n)} = \sum_{1}^{n} W_{22}^{n-1}\,W_{21} = A \qquad (1)$$

and the probability of finding a B,B unit will be $P(B,B) = W_{12}P^2(B) = W_{12}A^2$. The probability for the existence of a C unit will be

$$P(C) = W_{1(2)} = W_{11}W_{12}\sum_{1}^{n} W_{2(n)} = W_{1(2)}A$$

In these experiments W_{11}, W_{12}, W_{21} and W_{22} have the same meaning as used by Vollmert[22], i.e. W_{11} is the probability that a chain radical $\sim M_2M_1\cdot$ adds a monomer molecule M_1, etc. It can be shown that $W_{12} = 1/l_1$, $W_{11} = (l_1 - 1)/l_1$, and $W_{1(2)} = (l_1 - 1)/l_1^2$, where $l_1 = r_1 M_1/M_2 + 1$ (ref 22) denotes the average sequence length of vinyl (crown ether) units and M_1 and M_2 are the molar ratios of the monomers in the feed.

From the above probabilities we can now calculate the maximum fraction of crown ligands that are involved in the formation of intramolecular complexes, i.e.

$$L_{(calc)} = \frac{2}{l_1}\left[P(B) - \frac{1}{2}P(B,B)\right] + \frac{2}{l_1}\left[P(C) - P(B,C)\right] \qquad (2)$$

which, after substituting for the various terms, W_{11}, etc., and rearrangement, gives

$$L_{(calc)} = \frac{A}{l_1}\left(2 - \frac{A}{l_1}\right) + \frac{2(l_1 - 1)}{l_1^3}(1 - A) \qquad (3)$$

It can be shown that

$$A = \sum_{1}^{n} W_{2(n)} = \sum_{1}^{n} (l_2 - 1)^{n-1}/l_2^n$$

where $l_2 = r_2M_2/M_1 + 1$ (ref 22) is the average sequence length of the styrene units. For any copolymer, l_1 and l_2 can be calculated from the known values r_1, r_2, M_1 and M_2. The first term in equation (3) represents the fraction of crown ligands belonging to bis(crown ether) units with 1 to n styrene units in between crown ligands, while the second term represents ligands belonging to pairs of adjacent crown monomer units. The latter term approaches zero at low crown content of the copolymer since then $l_1 \to 1$.

Inspection of *Table 1* shows that the best agreement between $L_{(exp)}$ and $L_{(calc)}$ is obtained when n is 2 or at the most 3. In other words, crown ligands separated from another crown ligand on the same chain by less than 3 or possibly less than 4 styrene monomer units (7 to 9 chain carbon atoms separating the benzo crown ether ligands) will preferentially form a cooperative 2:1 intramolecular crown–K$^+$ complex rather than a 1:1 crown complexed tight ion pair. It is interesting to note that the complex formation constants of K$^+$ or K$^+$Pi$^-$ in THF to two benzo-15-crown-5 ligands connected by a

$$-\underset{\displaystyle \text{O}}{\underset{\|}{\text{C}}}\text{O(CH}_2)_n\text{O}\underset{\displaystyle \text{O}}{\underset{\|}{\text{C}}}-$$

chain[11] were found to pass through a maximum for $n = 5$ (i.e. 9 chain atoms in between the two ligands). Of course, a comparison between the two systems is difficult because in the crown copolymer the ligands are part of a longer polymer chain and separated by styrene units rather than CH$_2$ groups. Certainly, too many benzene rings will interfere with a proper alignment of the two crown ligands for an effective complexation with K$^+$, and the result that not more than three styrene units are permitted between such ligands appears reasonable. (The decrease in $L_{(exp)}$ found for 15.8% SP15C5 indicates that the assumption that each B or C unit complexes a K$^+$ ion may not be entirely correct. More experiments are needed to determine whether the approximations should be further refined.)

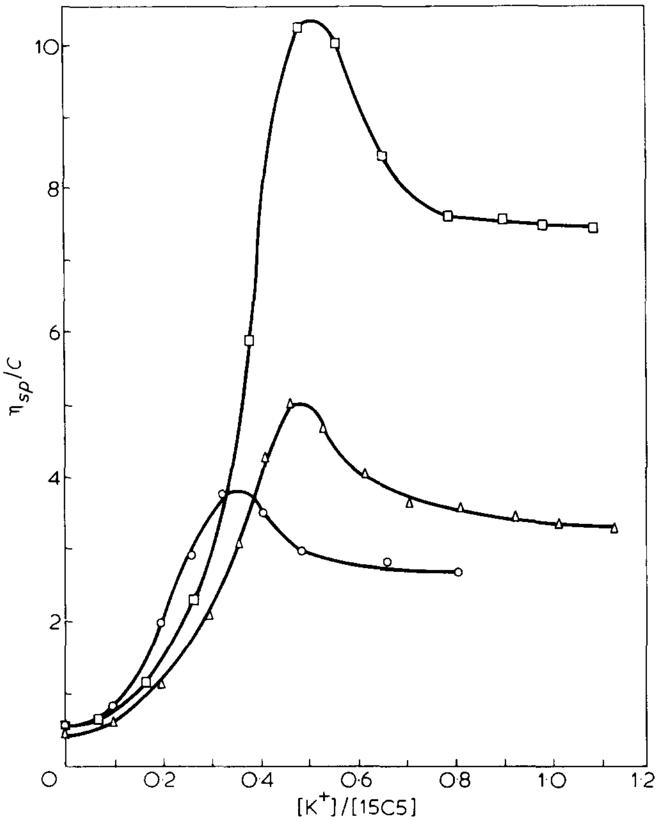


Figure 5 Dependence of reduced viscosity of styrene–vinylbenzo-15-crown-5 copolymers on the salt concentration expressed as $K^+/15C5$ (molar ratio of $KBPh_4$ and crown monomer units). Solvent: methyl ethyl ketone; T = 25°C; [polymer] = 8 g dl^{-1}; (○) 5.8% SP15C5; (△) 11.8% SP15C5; (□) 18% SP15C5

Complex formation of K^+ with two adjacent crown ligands, i.e. a *C*-type unit (see above), may be more difficult than when the two crown ligands are separated by one or a few styrene units due to steric hindrance in accommodating the large K^+ cation and to the difficulty in properly aligning the two ligands for complexation with the cation. In this respect it is pertinent to mention that the extraction equilibrium constant for the reaction $K^+(H_2O) + Pi(H_2O) + crown(CHCl_3) \rightleftarrows K^+, Pi^-, crown(CHCl_3)$ is ten times greater for 20% SP15C5 than for the homopolymer P15C5 (ref 6), suggesting that it is indeed more difficult to insert a K^+ ion in between two adjacent crown ligands, at least when they are part of a large block of crown ligands. For 1.5% SP15C5 the fraction of crown ligands belonging to such *C*-type units is only 0.026, but this increases to 0.17 for 11.8% SP15C5. If we exclude these pairs of adjacent ligands from forming an intramolecular complex, then agreement between $L_{(calc)}$ and $L_{(exp)}$ for the copolymers is best for $n < 5$ instead of $n < 4$.

Let us now attempt to apply these results to the viscosity data in MEK, assuming that the $KBPh_4$/MEK system will not behave too differently in its binding to the crown polymers than the KPi/THF system. For 11.8% SP15C5, $L_{(calc)}$ for $n < 3$ is equal to 0.49 (see *Table 1*). At a crown-to-cation ratio of 10 (used in the viscosity measurement for this polymer) a fraction 0.2 of the available crown ligands would be sufficient to complex all K^+ ions as a 2:1 intra– or intermolecular complex. Since a fraction 0.49 is available for intramolecular complexation, crosslinking need not occur if the intramolecular complexation is preferred. This is also true for the 18% and 48% SP15C5 polymers at the crown-to-cation ratios of 16 and 42 used in the viscosity experiments. No abnormal increase in viscosity is observed experimentally in any of these systems. On the other hand, at the experimental crown-to-cation ratio of 5 for 5.8% SP15C5 a fraction 0.4 of available crown ligands is needed if all complexes are of the 2:1 intramolecular type, but $L_{(calc)}$ for $n < 3$ is only 0.29 for this polymer. Hence, in this system intermolecular 2:1 complexes can form and this is the case as shown in *Figure 4*. The same holds for 2.3% SP15C5, where $L_{(calc)}$ for $n < 3$ is 0.13 while at a crown-to-cation ratio of 2 all crown ligands would be needed if 2:1 intramolecular complexes were formed exclusively. In the latter polymers many crown–cation complexes are of the 1:1 type. The observed viscosity behaviour of the respective polymers, therefore, is consistent with the calculated fraction of crown ligands that can participate in intramolecular complex formation.

Crosslinking in polymers such as 11.8% SP15C5 must occur eventually when at constant polymer and, therefore, crown concentration, the concentration of cations is increased, since not enough crown ligands are available to form exclusively intramolecular complexes. To check this the respective viscosities of 8 g dl^{-1} solutions of 5.8%, 11.8% and 18% SP15C5 in MEK were measured as a function of the ratio $KBPh_4$/crown (constant crown concentration). The results are presented in *Figure 5* and reveal a strong enhancement in the reduced viscosities of all three polymers with a maximum of η_{red} at a cation-to-crown ratio close to 0.5 (about 0.4 for 5.8% SP15C5). The observed decrease in viscosity beyond the ratio 0.5 is not due to an increase in ionic strength of the solution. Addition of the non-complexible $N(propyl)_4BPh_4$ to 18% SP15C5 at a K^+ to crown ratio 0.5 (i.e. when η_{red} is maximal) did not lower the viscosity, while addition of $KBPh_4$ decreased the viscosity. Most likely, intermolecular 2:1 complexes are broken up under formation of 1:1 complexes when the K^+ to crown ratio exceeds 0.5. The lower crown concentration in the 5.8% SP15C5 solution may be the reason that the maximum viscosity occurs at a cation-to-crown ratio less than 0.5 as formation of 1:1 complexes competes more effectively with that of intermolecular complexes.

The viscosity maximum for the three copolymers increases in the order 5.8% < 11.8% < 18% SP15C5 (*Figure 5*), a sequence that is not immediately obvious. Calculations show that if only 2:1 complexes exist at a cation-to-crown ratio of 0.5, the concentration of intermolecular 2:1 complexes (crosslinks) increases in the order 5.8% < 18% < 11.8% SP15C5 when the fraction, $L_{(calc)}$, of crown ligands for $n < 4$ is exclusively used to form intramolecular complexes. In that case the 11.8% copolymer should exhibit the highest viscosity. Taking $n < 3$ for $L_{(calc)}$ we find the order to be 5.8% < 11.8% ≈ 18%. The higher than expected viscosity of 18% SP15C5 indicates that the approximations in $L_{(calc)}$ may be too crude at higher crown content of the chain. Furthermore, we assumed that all ligands belonging to the fraction $L_{(calc)}$ will participate in intramolecular complexes; hence, the calculated concentration of crosslinks represents a minimum. Since intermolecular complex formation depends on the square of the total crown concentration, crown ligands normally forming intramolecular complexes may, at high crown content, compete effectively for intermolecular complex formation, leading to the higher than expected viscosity for the 18% SP15C5.

In conclusion, we have demonstrated that the viscosities of styrene–vinyl-crown ether copolymer solutions in the presence of cations that form 2:1 crown–cation complexes depend on the crown content of the polymer chain and tha.

calculations and spectrum measurements leading to a relationship between the spacing of crown ligands on a chain and the fraction of intramolecular 2:1 crown–cation complexes are helpful in rationalizing the viscosity data.

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REFERENCES

1 Kopolow, S., Hogen Esch, T. E. and Smid, J. *Macromolecules* 1973, **6**, 133
2 Kopolow, S., Machacek, Z., Takaki, U. and Smid, J. *J. Macromol. Sci., Chem.* 1973, **7**, 1015
3 Shah, S. C., Kopolow, S. and Smid, J. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 2023
4 Varma, A. J. and Smid, J. *J. Polym. Sci., Polym. Chem. Edn.* 1977, **15**, 1189
5 Smid, J. *Pure Appl. Chem.* 1976, **48**, 343
6 Wong, K. H., Yagi, K. and Smid, J. *J. Membr. Biol.* 1974, **18**, 379
7 Pedersen, C. J. and Frensdorff, H. K. *Angew. Chem.* 1972, **11**, 16
8 Christensen, J. J., Hill, J. O. and Izatt, R. M. *Science* 1971, **174**, 459
9 Takaki, U., Hogen Esch, T. E. and Smid, J. *J. Am. Chem. Soc.* 1971, **93**, 6760
10 Takaki, U. and Smid, J. *J. Am. Chem. Soc.* 1974, **96**, 2588
11 Bourgoin, M., Wong, K. H., Hui, J. Y. and Smid, J. *J. Am. Chem. Soc.* 1975, **97**, 3462
12 Smid, J., El Haj, B., Majewicz, T., Nonni, A. and Sinta, R. *Org. Prep. Proc. Int.* 1976, **8**, 193
13 Kikukawa, K., Nagira, K. and Matsuda, T. *Bull. Chem. Soc. Jpn.* 1977, **50**, 2270
14 Carvajal, C., Tölle, K. J., Smid, J. and Szwarc, M. *J. Phys. Chem.* 1965, **87**, 5548
15 Wong, K. H., Bourgoin, M. and Smid, J. *Chem. Commun.* 1974, 715
16 Gregor, H. L., Gold, D. H. and Fredrick, M. *J. Polym. Sci.* 1957, **23**, 467
17 Katchalsky, A. and Eisenberg, H. *J. Polym. Sci.* 1951, **6**, 145
18 Wong, L. and Smid, J. *J. Am. Chem. Soc.* 1977, **99**, 5637
19 Schoene, W. and Vollmert, B. *Ang. Makromol. Chem.* 1970, **13**, 23
20 Kamogawa, H. and Cassidy, H. G. *J. Polym. Sci. A* 1964, **2**, 2409
21 Ungaro, R., El Haj, B. and Smid. J. *J. Am. Chem. Soc.* 1976, **98**, 5198
22 Vollmert, B. 'Polymer Chemistry', Springer–Verlag, New York, 1973, p 117