A further consequence of a temperature dependent ϕ is expressed by $\partial(\Delta G_m/T)/\partial T \neq 0$. As a consequence, a combinatorial contribution to ΔH_m must be recognized, as has been done already by Everett and Munn[18] for the system n-hexane + n-hexadecane. They obtain this contribution by assuming eq 16 to be the correct expression for (ΔG_m). Another possibility would be to accept eq 15, and use a revised version of (16) to obtain (ΔH_m). In our work, eq 11 corresponds to (16), whence

$$\begin{aligned}\Delta\bar{h}_1^{\infty} &= R\frac{\partial \ln a_1}{\partial(1/T)} = R\frac{\partial}{\partial(1/T)}[\ln v_1/v_2 + \chi] \\ &= RT^2(\alpha_2 - \alpha_1) + R[\partial\chi/\partial(1/T)]\end{aligned} \tag{17}$$

Here α_1 and α_2 are thermal expansion coefficients for the components of the liquid state. Typically, $\alpha_1 \sim 10^{-3}$, $\alpha_2 \sim 5 \times 10^{-4}$ deg^{-1}, $T = 300$°K, making the combinatorial contribution to $\overline{\Delta h_1}^{\infty}$ of the order of -100 cal. Values of $\overline{\Delta h_1}^{\infty}$ extrapolated from calorimetric heats of dilution to high concentrations of polymer tend to fall in the range 0–400 cal. (For example, a very large value of $\overline{\Delta h_1}^{\infty} \simeq 360$ cal has been obtained for the system polyisobutylene–benzene.[19]) The importance of the combinatorial contribution is evident. On the other hand, using segment fractions in the combinatorial entropy (*e.g.*, our eq 13) produces simply

$$\overline{\Delta h_1}^{\infty} = R[\partial\chi^*/\partial(1/T)] \tag{18}$$

Recent statistical theories[8] attempt to predict the χ parameter and its temperature dependence using only data on the pure components. The theories should be capable of deciding which of the expressions for the combinatorial entropy produces more consistent values of χ (or χ^*) and the respective temperature dependences. Since the combinatorial contribution to $\overline{\Delta h_1}^{\infty}$ is completely formal, we would expect the segment fraction route, leading to χ^*, to be superior.

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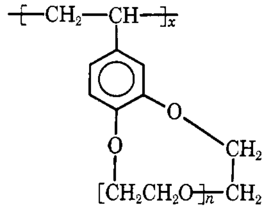
Communications to the Editor

Cation Binding Properties of Poly(vinyl macrocyclic polyethers)

Considerable interest is currently shown in the cation binding properties of macrocyclic polyethers, a class of compounds recently synthesized and studied by Pedersen.[1] The so-called crown compounds strongly increase the solubility of inorganic salts in nonpolar media[1] and form crystalline complexes with many salts.[2,3] They are found to affect greatly the ion pair structure of alkali carbanion salts[4] and the reaction rate and stereospecific course of reactions involving ion pairs.[5] The cyclic polyethers have also gained prominence as model compounds for the study of ion movement across biological membranes. Eisenman, *et al.*,[6] and others[7,8] have found that the specific effect exerted by these crown compounds on the cation transport resembles that of natural ion carriers such as monactin and valinomycin.

We would like to report some interesting results on the cation binding properties of polymers containing the macrocyclic polyether moiety as a pendant group. We were particularly interested in comparing the properties of these polymers with those of the monomeric analogs in order to determine the extent of cooperative effects in the cation complexation of the polymeric species. Two polymers were investigated, *i.e.*, poly(2,3-4′-vinylbenzo-1,4,7,10,13-pentaoxacyclopentadec-2-ene) or poly(vinylbenzo-15-crown-5) (P-15C5) and poly(2,3-4′-vinylbenzo-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene) or poly(vinylbenzo-18-crown-6) (P-18C6). They can be prepared from the corresponding vinyl monomers by a radical initiator, or anionically with sodium α-methylstyrene tetramer in THF at $-80°$. Molecular weights of 100,000 are easily obtainable. The structures of the repeating units are depicted below.



P-15C5, $n = 3$
P-18C6, $n = 4$

The actual complexation behavior was investigated by a method similar to one employed by Pedersen[9] and others.[10] Picric acid is dissolved in aqueous hydroxide containing the desired cation and the solution shaken with an equal quantity of an immiscible organic solvent (*e.g.*, methylene chloride) containing the poly(vinyl crown) compound or its monomeric analog (the latter one contains a methyl group at the 4′ position, the two compounds being denoted as 15C5 and 18C6). After equilibrium is reached, the picrate salt concentration in the organic layer is measured by optical spectroscopy.

The results, presented in Table I, are expressed as per cent of picrate salt extracted, based on the total amount of picrate present. While the picrate transfer depends on the complexing strength of both the water and cyclic polyether, as well as on the partition coefficients of the various species,[10] the extracted amount of picrate nevertheless is indicative of the cation complexing efficiency of the respective crown species.

Focusing only on the different behavior of polymer and "monomer," one observes a strong increase in the complexing efficiency of P-15C5 as compared to 15C5, especially for the

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TABLE I
COMPLEXATION OF CATIONS TO POLY(VINYLBENZO-15-CROWN-5) AND POLY(VINYLBENZO-18-CROWN-6) AS COMPARED TO THEIR MONOMERIC ANALOGS[a]

Cation	% alkali ion extracted[b]			
	15C5	P-15C5[c]	18C6	P-18C6[c]
Li^+	<1	10.0	1.01	6.3
Na^+	10.6	24.7	13.1	20.7
K^+	22.3	85.2	85.6	90.2
Rb^+	13.0	83.7	74.0	84.2
Cs^+	3.5	68.8	71.0	87.9

[a] Concentration of picric acid, 7.0×10^{-5} *M;* macrocyclic polyether, 35×10^{-5} *M;* metal hydroxide, 0.1 *M.* [b] Based on total amount of picric acid. [c] Concentrations of the polymers are expressed as concentrations of crown units.

larger alkali ions, but also for the Na^+ and Li^+. It is interesting to notice that we have recently found spectroscopic evidence for the stable 2:1 complexes of 15C5 with fluorenylpotassium in solutions of these compounds in tetrahydrofuran.[11] Also, the crystalline complex of 15C5 and KCNS was found to be a 2:1 complex.[2] Apparently, a considerable amount of energy is gained on complexing two 15C5 molecules with alkali ions that have diameters larger than the 15C5 polyether ring. This is most likely the reason for the strong increase in the complexing efficiency of P-15C5, as two neighboring 15C5 moieties can cooperate in the complexation. CPK models of this polymer make it likely that alternating rather than adjacent crown units are cooperating. Another possible structure is that of a threefold helix with the cation sandwiched in between two crown units situated on adjacent helix turns.

The 18C6 crown ether appears to be considerably more effective in binding cations than 15C5, especially where it concerns the larger cations. This is due to the increased diameter of the polyether ring.[2] In comparing P-18C6 and 18C6, one again finds an improvement in the cation complexation of the polymer, but by no means as pronounced as with P-15C5. It is interesting that the 18C6 forms a crystalline 1:1 complex with KCNS[2] and in a THF solution with fluorenylpotassium 1:1 complexes are also observed, even with excess 18C6, contrary to the results obtained with 15C5.[11] If only one 18C6 is complexed to a cation, one does not expect a great improvement by changing to P-18C6, as cooperative effects in the cation complexation are not as important as with P-15C5. It should be pointed out, however, that 18C6 complexes of K^+ ions higher than 1:1 may exist in other media or under different conditions. It is interesting that McLaughlin, *et al.*,[12] have inferred the existence of 3:1 complexes of di-*tert*-butyldicyclohexyl-18-crown-6 for all of the alkali metal cations in the interior of phospholipid bilayer membranes.

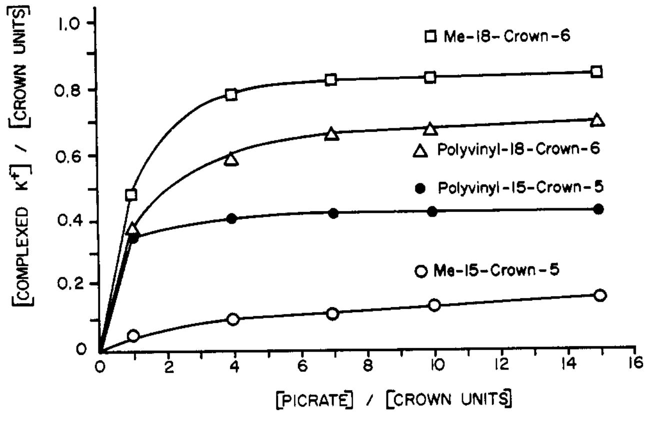

Figure 1. Complexation of potassium ions to P-15C5, P-18C6, and their monomeric analogs. Determination of number of cations complexed per crown unit; [crown] = 7×10^{-5} *M*, [base] = 0.1 *N*.

If in P-15C5 two crown units cooperate in the complexation of a cation, one may expect a maximum cation/crown ratio of 0.5. To observe the saturation point of cation complexation of P-15C5 and P-18C6, a number of experiments were carried out with increasing ratio of picrate to crown units. The results for K^+ ions are shown in Figure 1. One notices again the much greater complexation ability of P-15C5 as compared to 15C5. More important, the cation/crown ratio for P-15C5 never exceeds 0.5, while that for P-18C6 reaches about 0.7. Cooperation of two adjacent 15C5 moieties is apparently important for the complexation of at least the larger cations (*e.g.*, K^+), while this appears not to be essential for K^+ with P-18C6. However, a ratio of one K^+ per crown unit in P-18C6 may never be reached because of electrostatic repulsion between the bound cations. Experiments are in progress to determine more exactly the importance of this repulsion effect, as well as the cation binding in other types of solvents. Also, the mechanism of anionic polymerization of the vinyl monomers itself should be interesting, as the propagating carbanion pairs are probably of the separated kind due to intramolecular complexation of the cation by the crown unit. This reaction is therefore being investigated in more detail.

The preparation of the vinyl macrocyclic ethers and the polymerization procedures will be described in a future publication.

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Organometallic Polymers. IX. Polyesters of 1,1′-Bis(chlorocarbonyl)cobalticinium Hexafluorophosphate

Cobalticinium salts, in contrast to their isoelectronic ferrocene derivatives, are resistant to strong oxidizing agents such as fuming nitric acid and ozone.[1,2] However, unlike their ferrocene analogs, cobalticinium salts have not been incorporated into condensation polymers. The only metallocinium polymers previously reported have been a series of polymethylenecobalticinium salts prepared by Ito and Kenjo[3] and a series of polyferricinium salts prepared in our laboratories by oxidation of vinylferrocene and ferrocene acrylate

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