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Interaction of Polar Vinyl Monomers with Lithium Picrate in Dioxane

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ABSTRACT: The interaction of some polar vinyl monomers with lithium picrate (LiPi) in dioxane at 25 °C was studied by a competition technique using cross-linked poly(ethylene oxide) (PEO) as the insoluble ligand. The original competition method was modified for the case where the ionic solute forms more than one type of complex with the soluble and/or the insoluble ligand. The Langmuir-Klotz isotherm of LiPi binding to cross-linked PEO in the presence of monomer gave the apparent binding constant of the polymer gel when in competition with monomer. The formation constants of LiPi complexes with the monomer were then calculated from the apparent binding constant as function of monomer concentration. The nature of the polar group of monomer was found to be of paramount significance. The results were discussed in view of the possibility of complex formation between monomer and active centers in the anionic polymerization of polar vinyl monomers.

Introduction

Solvation[1,2] and complex formation phenomena are known to play an important role in ionic organic reactions in low polarity media. Special interest has been shown in processes involving anionic species, and many aspects of the chemistry of carbanions with *s*-metal counterions are now extensively documented and well understood.[3-5] Yet, certain problems of fundamental significance still remain unsolved. Among these is the occurrence of complex formation between monomer and the propagating centers in the anionic polymerization of polar vinyl monomers prior to monomer addition.[6]

The possibility of specific interaction with the monomer arises when ion pairing of the growing chain ends occurs to a considerable extent, a situation often encountered in ionic polymerization processes. Thus, conductivity measurements show that the anionic active centers of polar vinyl monomers exist predominantly as ion pairs or higher associates, even in THF,[7] the extent of chain propagation on free anions being negligible. On the other hand, the polar group of the monomer or the chain substituents is often a strong electron pair donor and can compete with the solvent for coordination of the counterion. Indeed, interaction of the active centers with neighboring monomer untis, e.g., the penultimate effect, is rather well-known.[8,9] Similar interactions with monomer are difficult to study in real polymerizing systems, even if they occur, since the reaction sequence is quickly completed by monomer addition to the growing chain end. No direct experimental evidence has been presented to prove complex formation.

Specific interaction between monomer and counterion in the chain propagation step is expected to have a profound effect on the reaction mechanism, especially in copolymerization processes. In certain systems, it may prove to be more important than monomer affinity for the free anion and give rise to reordering the apparent monomer reactivities. This possibility offers an indirect approach to checking the hypothesis of monomer coordination to the active centers in the anionic polymerization of polar monomers. It is the purpose of the present work to make the first step in this direction by providing a scale of relative affinities of some polar vinyl monomers for lithium counterions.

The interactions were studied in dioxane, a solvent of comparatively low cation affinity, since most of the common polar vinyl monomers are not typical electron donor ligands and cation binding is expected to be weak and hence solvent sensitive. Lithium picrate (LiPi) was selected as the reference salt since it does not initiate the polymerization of these monomers. The salt is poorly dissociated in dioxane, and mainly tight ion pairs are formed in solution. What must be avoided is the formation of free ions because their high reactivity will cause much of the reaction to proceed via the free ions instead of the ion pairs. Complex formation is most probable for lithium and magnesium counterions.[10] Finally, a simple method for the determination of the constants of alkali cation complex formation in solution was recently reported by Smid and Sinta for alkali picrates.[11] It utilizes polymer gels of known binding capacity for the ionic solute to compete with the solube ligand. In this study, cross-linked poly(ethylene oxide) (PEO) was used as the polymer gel. Both linear and cross-linked PEO are known to coordinate alkali picrates in solvents of low polarity,[12,13] and cross-linked PEO shows a very good swelling capacity in dioxane.

Experimental Section

Dioxane was refluxed over sodium-potassium alloy and distilled before use. Methyl isopropenyl ketone was prepared by aldol

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condensation of methyl ethyl ketone with paraformaldehyde and subsequent dehydration of the resulting product.[14] The other monomers were commercially available from Fluka AG. They were dried over calcium hydride, and freshly distilled portions were used. Acrylamide was used without purification.

Lithium picrate was prepared from lithium carbonate and picric acid in ethanol.[15] The product was recrystallized from acetone–benzene, dried in vacuum, and characterized spectrophotometrically ($\lambda_{\max} = 335$ nm in dioxane). Poly(ethylene oxide) of molecular weight 3×10^6, trade name Badimol, was purchased from Chemical Works Dimitrovgrad, Bulgaria. Cross-linked PEO was prepared by ^{60}Co γ irradiation of 2% aqueous solutions of the linear polymer.[16] The resulting gels were continuously washed with distilled water and freeze dried. Samples prepared with a total irradiation dose of 5 Mrad were used.

The interaction of lithium picrate in dioxane with cross-linked PEO was characterized by the rearranged form of the Langmuir adsorption isotherm, as suggested by Klotz et al.:[17]

$$1/R = 1/n_0 + 1/(n_0 K_0^{\mathrm{N}} A) \qquad (1)$$

where $1/R$ denotes the molar ratio of total EO units to bound salt and A is the free salt concentration. The constant $1/n_0$ represents the effective number of EO units involved in the complexation per lithium cation. K_0^{N} is the intrinsic binding constant of the polymer gel, while the product $n_0 K_0^{\mathrm{N}}$ is the equilibrium constant of the interaction of a single EO unit with lithium picrate.

The interaction was studied following the experimental procedure of Smid et al.[11] Polymer samples of equal weight (30–40 mg) were immersed in picrate solutions of different volume (5–20 mL) so that the total LiPi concentration was kept constant (ca. 8×10^{-5} M), while the "concentration" of the polymer gel changed. Cross-linked PEO was added without preswelling in pure solvent. This required a longer time to reach equilibrium, and the samples were kept overnight. The volume degree of swelling in pure dioxane and in the presence of LiPi salt was kept constant.[15] After equilibrium was reached, aliquots were taken to determine the picrate concentration in the liquid phase (measured spectrophotometrically), which directly gave the free salt concentration. The concentration of polymer-bound salt was obtained as the difference to total LiPi concentration.

In the competition experiments, solutions of different monomer concentration were prepared in a given dioxane of lithium picrate and the above procedure was again applied. Four to six series of experiments were performed with each of the monomers to determine the apparent binding constant of the polymer gel as a function of the concentration of competing monomer. Dilution resulting from the addition of monomer to the LiPi solution was taken into account, but it never exceeded 15%. All experiments were carried out at room temperature. The optical spectra were taken on a SPECORD UV–vis spectrophotometer, Carl Zeiss Jena, GDR.

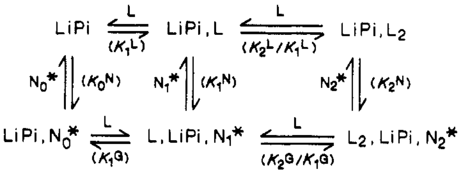
Results and Discussion

In the competition method of Smid and co-workers,[11,18,19] the constants of complex formation in solution are determined from the equilibrium distribution of the ionic solute between the polymer gel and the supernatant solution containing the soluble ligand:

$$1/F_{\mathrm{N}} - 1 = K_{\mathrm{L}}/K_{\mathrm{N}}(1/F_{\mathrm{L}} - 1) \qquad (2)$$

where F_{N} and F_{L} are the fractions of complexed ligand of the immobilized gel and complexed soluble ligand, respectively, while K_{N} and K_{L} are the respective constants of solute binding to the ligands. The experimental data are taken at fixed concentration of the salt and the polymer gel and different concentrations of the soluble ligand. Hence, the method refers to the simplest case of solute binding when only one type of interaction is preferred in both phases. Whenever the salt appears to form more than one type of complex with any of the competing ligands, the respective plots can be expected to deviate from linearity. Such systems can be studied by introducing a second variable, the concentration of the polymer gel, i.e., by combining the competition approach with the procedure of Langmuir–Klotz. Thus, the competition equilibria in the ternary system of two ligands in competition for lithium picrate can be depicted as shown on Scheme I, the starred species being polymer bound. Only complexes of the soluble ligand with a single LiPi ion pair are taken into account.

Scheme I



The experimentally recorded concentrations of lithium picrate in the supernatant solution, $[\mathrm{LiPi}]_s$, and in the polymer gel, $[\mathrm{LiPi}]_b$, give the total concentration of all LiPi species in the respective phase:

$$[\mathrm{LiPi}]_s = [\mathrm{LiPi}] \sum_{m=0}^{m} K_m^{\mathrm{L}}[\mathrm{L}]^m \qquad (3)$$

$$[\mathrm{LiPi}]_b = [\mathrm{LiPi}] \sum_{m=0}^{m} K_m^{\mathrm{N}} K_m^{\mathrm{L}}[\mathrm{N}_m^*][\mathrm{L}]^m \qquad (4)$$

where $K_0^{\mathrm{L}} = 1$.

K_m^{L} and K_m^{N} are the formation constants of the complexes $\mathrm{LiPi,L}_m$ and $\mathrm{L}_m\mathrm{,LiPi,N}_m^*$ in the supernatant solution and in the gel, respectively, and [LiPi] is the free salt concentration. N_m^* denotes the concentration of polymer segment involved in coordination of the respective $\mathrm{LiPi,L}_m$ species. Since

$$[\mathrm{N}_m^*] = n_m[\mathrm{N}_0^*]/n_0$$

where $1/n_m$ refers to the number of EO units bound per lithium cation in the respective complex, on combining eq 3 and 4 one arrives at the following correlation between experimentally recorded values:

$$\frac{[\mathrm{N}_0^*]}{[\mathrm{LiPi}]_b} = \frac{\sum_{m=0}^{m} K_m^{\mathrm{L}}[\mathrm{L}]^m}{1/n_0 \sum_{m=0}^{m} n_m K_m^{\mathrm{N}} K_m^{\mathrm{L}}[\mathrm{L}]^m} \frac{1}{[\mathrm{LiPi}]_s} \qquad (5)$$

Following the procedure of Klotz et al.,[17] eq 5 can be presented as follows:

$$\frac{[\text{-EO-}]_{\mathrm{total}}}{[\mathrm{LiPi}]_b} = 1/n_0 + \frac{\sum_{m=0}^{m} K_m^{\mathrm{L}}[\mathrm{L}]^m}{\sum_{m=0}^{m} n_m K_m^{\mathrm{N}} K_m^{\mathrm{L}}[\mathrm{L}]^m} \frac{1}{[\mathrm{LiPi}]_s} \qquad (6)$$

The plot of $[\text{-EO-}]/[\mathrm{LiPi}]_b$ vs $1/[\mathrm{LiPi}]_s$ from eq 6 is not to be linear since the fraction of uncomplexed soluble ligand varies with the ratio between the components. However, when the soluble ligand is taken in sufficiently large excess with respect to the salt, the equilibrium concentration [L] is practically equal to the total concentration $[\mathrm{L}]_0$ which can be easily kept constant in the experiment so that the proportionality coefficient of eq 6 turns into a constant:

$$[\mathrm{L}] \approx [\mathrm{L}]_0 = \text{constant}$$

$$1/R = 1/n_0 + 1/(K'A') \qquad (7)$$

Here, A' is the overall picrate concentration in the supernatant solution, by analogy with the equation of Langmuir–Klotz. K' is the apparent binding constant of the salt to a single EO unit of the polymer gel when in competition with the soluble ligand, and as seen from eq 6 and 7, it is a function of $[L]_0$ of the common formula

$$\sum_{m=0}^{m} (n_m K_m^{N} - K')K_m^{L}[L]_0^{m} = 0 \qquad (8)$$

The type of function depends on the mode of complex formation in the supernatant solution and in the polymer gel. Thus, when only one type of complex is formed in both phases, $1/K'$ is a linear function of $[L]_0$:

$$1/K' = 1/n_0K_0^{N} + (K_1^{L}/n_0K_0^{N})[L]_0 \qquad (9)$$

In this case, the method of Smid and co-workers and the combined Klotz–Smid procedure are equivalent. The Klotz–Smid method has the advantage that it is not necessary to know in advance the binding constant of the polymer gel. The values of $1/n_0$ and $1/n_0K_0^{N}$ can be determined from the intercepts of the plots of eq 7 and 9, respectively. This may prove to be very useful in determining the absolute values of complex formation constants in solvents where the ionic solute is insoluble but can be solubilized by the studied ligands, e.g., in the case of alkali picrates in toluene.[20]

Another point is the different limits of sensitivity of the two methods. An important feature of the method of Smid is the requirement for comparable binding capacities of the competing ligands. Thus, in studies of weak interactions, polymer gels of low affinity for the ionic solute are employed, e.g., gels with anchored poly(ethylene glycol) chains,[20] to allow effective competition by the ligand in solution. If the affinity of the polymer gel for the salt is much higher, the large quantity of soluble ligand needed to release the gel-bound picrate may modify the physical properties of the solvent.[20] In contrast to this, the limits of sensitivity of the Klotz–Smid method are independent of the binding capacity of the polymer gel because of, as seen from eq 9, the ratio between intrinsic and apparent binding constants and concentration of the soluble ligand:

$$n_0K_0^{N}/K' = 1 + K_1^{L}[L]_0$$

In this sense, the Klotz–Smid procedure is an apt supplement to the competition approach. When it is possible to select a proper polymer gel probe of comparable binding capacity with the soluble ligand, the method of Smid and Sinta[11] should be preferred, since it is more simple. If this is not possible, the modified Klotz–Smid procedure can be applied as an alternative in determining complexation constants in the range 10^{4}–10^{-1} M^{-1}, irrespective of the binding capacity of the gel. Here, the lower limit of sensitivity is likewise related to the highest acceptable concentration of the soluble ligand. The upper limit is defined by the spectral characteristics of alkali picrates and the requirement for a sufficient excess of the soluble ligand, i.e., at least 10-fold excess with respect to the salt.

Experimental data of $1/K'$ as a function of $[L]_0$ allow the analysis of complexation equilibria as shown on Scheme I. Thus, linear relationships can be derived from eq 8 to give two individual complexation constants, provided $n_0K_0^{N}$ is known in advance:

$$(n_0K_0^{N} - K')/K'[L]_0 = K_1^{L} + K_2^{L}[L]_0 \qquad (10)$$

$$K' = n_1K_1^{N} + (1/K_1^{L})(n_0K_0^{N} - K')/[L]_0 \qquad (11)$$

Equations 10 and 11 refer to the formation of two different types of complex in the supernatant solution and in the polymer gel, respectively. Higher polynoms derived from eq 8 have to be minimized to best fit the computed curve with the experimental points. In principle, Scheme I can be further extended to analyze complex formation of higher stoichiometry. However, resolution can be expected to quickly drop down, and a reliable analysis of cascade complex formation, e.g., when long-chain multidentate ligands are involved, seems to be doubtful. Once the constants of solute binding to the soluble ligand and the polymer gel are known, the respective constants of interaction in the polymer gel K_m^{G}, as shown in Scheme I, can be easily derived; for instance, $K_1^{G} = n_1K_1^{N}K_1^{L}/n_0K_0^{N}$.

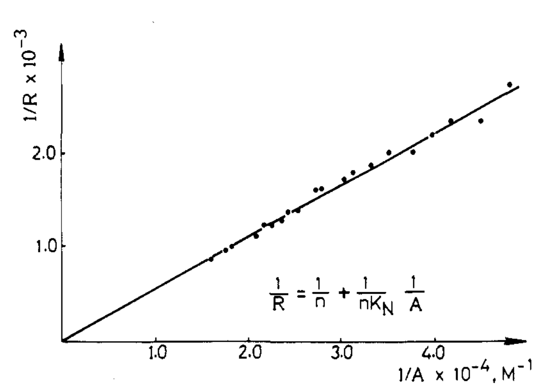


Figure 1. Langmuir–Klotz isotherm of the binding of lithium picrate to cross-linked PEO at 25 °C in dioxane: [LiPi] ~ 8 × 10^{-5} M.

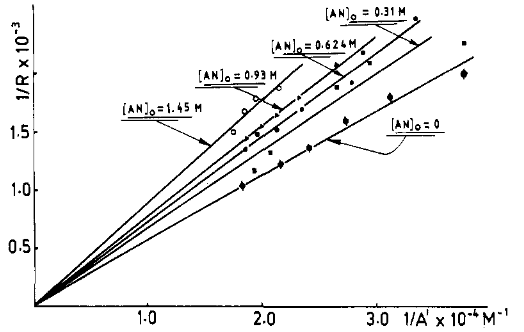


Figure 2. Klotz plots of LiPi binding to cross-linked PEO in the presence of acrylonitrile (AN). $[AN]_0$: (⧫) 0 M; (■) 0.31 M; (●) 0.624 M; (▲) 0.93 M; (○) 1.45 M.

The interaction of the monomers with lithium picrate was studied at LiPi concentrations of ca. 10^{-4}–10^{-5} M. Complex formation between cross-linked PEO and LiPi in this concentration range is illustrated on Figure 1, the binding constant $n_0K_0^{N}$ being 18 M^{-1}. As seen, the polymer gel shows relatively low affinity for lithium picrate and is a suitable probe for studies of weak interactions. It can be employed in the competition method as an alternative of glyme-containing resins[20] for determinating complex formation constants as low as ca. 1 M^{-1} in solution. Even so, some of the studied monomers fell beyond this lower limit of sensitivity. For this reason, the modified Klotz–Smid procedure was applied.

Results of the competition experiments calculated according to eq 7 are shown in Figure 2 for the case of acrylonitrile as the soluble ligand. It is clearly seen that at higher monomer concentrations, the straights grow steeper, which corresponds to reduced LiPi binding to the polymer gel. The apparent binding constant $1/K'$ was found to depend linearly on monomer concentration for six of the studied monomers, viz., methyl methacrylate (MMA), acrylonitrile, methacrylonitrile, methyl isopropenyl ketone, and 2-vinyl- and 4-vinylpyridines, as shown on Figure 3. This is an indication that 1:1 complexes are formed in solution between the monomers and lithium picrate and their formation constants were calculated from eq 9.

In the case of acrylamide, the plot of $1/K'$ vs $[L]_0$ is not linear, showing a well-pronounced tendency to level off at

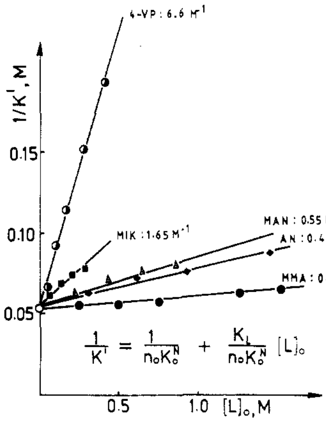


Figure 3. Linear plots of $1/K'$ vs monomer concentration $[L]_0$ according to eq 9 (see text) for methyl methacrylate (MMA), acrylonitrile (AN), methacrylonitrile (MAN), methyl isopropenyl ketone (MIK), and 4-vinylpyridine (4-VP). The calculated values of complex formation constants are shown.

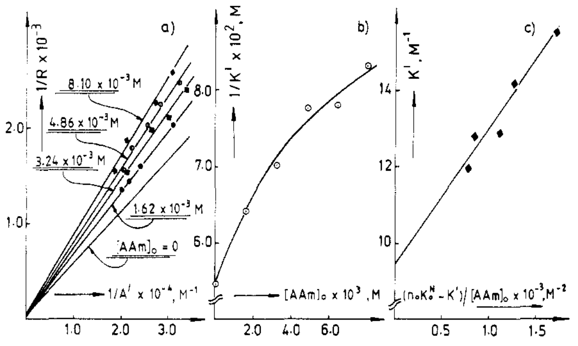


Figure 4. Interaction of acrylamide (AAm) with lithium picrate characterized by the Klotz–Smid procedure: (a) Klotz plots of LiPi binding to cross-linked PEO in the presence of AAm, eq 7; (b) dependence of $1/K'$ on AAm concentration, (⊙) experimental points, (—) computed curve; (c) plot of the linear relationship of eq 11.

the higher monomer concentrations (Figure 4b). The experimental data are best described by eq 11, which is indicative of the formation of a second complex in the polymer gel, $L,LiPi,N_1*$ as depicted on Scheme I. The plot of K' vs $(n_0K_0^N - K')/[L]_0$ is shown on Figure 4c. The constant of 1:1 complex formation of acrylamide with LiPi was found to be 280 ± 20 M^{-1}. The binding constant $n_1K_1^N$ of a single EO unit for this complex was estimated from the intercept of the plot at ca. 9.4 M^{-1}, i.e., a value twice smaller than the binding constant for the free salt. The computed curve for these constants is compared with the experimental points in Figure 4b.

A still more complicated picture was observed with vinylpyrrolidone. The plot of $1/K'$ vs $[L_0]$ exhibits a maximum slightly dropping down at the higher monomer concentrations as shown on Figure 5. Following the idea of stepwise complex formation according to Scheme I, this could be attributed to the formation of two complexes in the supernatant solution and three complexes in the polymer gel. The following relation then holds:

$$1/K' = (1 + K_1^L[L]_0 + K_2^L[L]_0^2)/(n_0K_0^N + n_1K_1^NK_1^L[L]_0 + n_2K_2^NK_2^L[L]_0^2)$$

Here, K_1^L and K_2^L are the formation constants of the complexes of vinylpyrrolidone with LiPi with stoichiometries of 1:1 and 2:1, respectively, while $n_0K_0^N$, $n_1K_1^N$, and $n_2K_2^N$ are the binding constants of a single EO unit of the polymer gel for the free salt, the 1:1 complex, and the 2:1 complex. With the aid of a standard minimizing procedure, the following values of the respective binding constants were computed: $K_1^L = 250 \pm 25$ M^{-1}, $K_2^L \sim 8 \times 10^3$ M^{-2}, $n_1K_1^N \sim 9.2$ M^{-1}, and $n_2K_2^N \sim 13.0$ M^{-1}. The curve corresponding to the calculated values is compared with the experimental points in Figure 5.

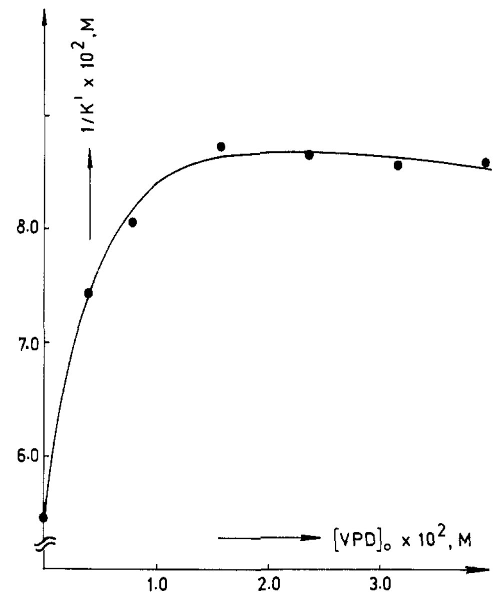


Figure 5. $1/K'$ as a function of the concentration of 1-vinyl-2-pyrrolidone (VPD): (●) experimental points, (—) computed curve.

Table I
Constants of 1:1 Complex Formation (K_1^L) with Lithium Picrate in Dioxane at 25 °C, Dielectric Constants (ε (20 °C)) and Dipole Moments (μ) of Some Polar Vinyl Monomers, and Donor Numbers (DN) of Related Saturated Compounds

monomer	K_1^L, M^{-1}	ε (20 °C)	μ, D	saturated compd	DN
acrylamide	280		3.44[a]	acetamide	
N-vinylpyrrolidone	250		4.09[a]	N-methylpyrrolidone	27.3
4-vinylpyridine	6.6	10.5	2.0	pyridine	33.1
2-vinylpyridine	1.1				
methyl isopropenyl ketone	1.65		2.8	acetone	17.0
methylacrylonitrile	0.55		3.69		
acrylonitrile	0.43	38	3.88	acetonitrile	14.1
methyl methacrylate	0.16	2.9	1.79	ethyl acetate	17.1

[a] For corresponding saturated compound.

The results of 1:1 complex formation between lithium picrate and the studied polar vinyl monomers are summarized in Table I. As seen, there is no direct relationship between the values of K_1^L and the dielectric susceptibilities or the dipole moments of the monomers. Besides, a small bathochromic shift of the UV band of lithium picrate is observed in the presence of monomer, from 335 nm to ca. 340–345 nm, depending on the type and concentration of the monomer, which gives direct evidence of increased interionic distance in the LiPi ion pairs resulting from cation coordination.[21] All this suggests that the observed effects of monomer competition with the polymer gel are most probably due to specific interaction with lithium picrate.

It is clearly seen from the data of Table I that the interaction effectivity is governed mainly by the nature of the monomer polar group. Acrylamide and vinylpyrrolidone show a much higher affinity for LiPi than the other monomers studied. Amides are known to be powerful electron donors.[22] Probably this can result in a further complexation step with a second monomer molecule. The affinities of the rest of the monomers for LiPi can be expected to follow the order of donor numbers of related saturated compounds also included in Table I. From Gutmann's data,[23] the following order of decreasing binding constants is to be expected: vinylpyridines > MMA > vinyl ketones > vinylnitriles. Indeed, this order is strictly followed with the exception of the results with MMA. It is fairly possible that the interaction of MMA with lithium picrate is sterically hindered since the oxygen of the ester carbonyl is less accessible than the heteroatom of the keto and the cyano group. Steric considerations are clearly manifested in the substantial difference between the binding constants of 2- and 4-vinylpyridine and, possibly, in the different binding constants of acrylamide and vinylpyrrolidone.

It is interesting to note that the monomers exhibit the same order of descending affinity for lithium picrate as registered for the polar groups of monomer units next to the anionic active centers for lithium counterions, viz., C=O > C≡N > COOR.[24] Hence, it is tempting to relate the results of LiPi coordination to the mechanism of the anionic polymerization of polar vinyl monomers. For chain propagation to take place a solvent molecule form the immediate surrounding of the active center has to be replaced by a monomer molecule[25]. In polar solvents, solvation may be so strong that cation–monomer coordination is disfavored and the exchange is random. The situation can be thoroughly changed, however, in a medium of low solvating capacity when the monomer is capable of "expelling" solvent molecules from the solvation shell of the counterion to form a stable complex.

Intermediate complex formation in anionic polymerization was first postulated,[26] and later disproved,[27,28] for nonpolar monomers, but it can be expected to be more probably in the case of the polar counterparts.[6,10] Polar vinyl monomers are known to form complexes with a number of inorganic salts in nonaqueous solvents.[29] Interaction is also shown for the cyano[30,31] and the keto group[32] of monomer and the anionic active centers of methacrylonitrile and methyl isopropenyl ketone, which results in characteristic bands in the IR spectrum. Moreover, preliminary results suggest it is possible to follow separately complex formation and chain propagation at low temperatures.[31] The temperature dependence of the reactivity ratios r_1 and r_2 in the copolymerization of methyl acrylate and acrylonitrile (AN) with butyllithium initiator in toluene[33] was found, AN being preferentially incorporated at low temperatures. The authors assigned it to a complex formation with the monomers assuming a higher enthalpy of formation of the complex with acrylonitrile. Some polymerization kinetics data can also be interpreted in terms of specific interaction with the monomer.[6,34] All these results are indicative of complex formation between the monomer and the active centers as the first step of the chain propagation reaction in low polarity solvents. Evidence in support of this hypothesis could be provided by the monomer selectivities in copolymerizations with lithium initiators. Though the reactivity of a living polymer toward a given monomer depends on a variety of factors (monomer reactivity, ionic equilibria, intra- and intermolecular solvation of the living ends, coordination with the monomer, etc.), it would be interesting to correlate our results with copolymerization studies to show whether the preferential complexation can alter the reactivity ratios. Studies of properly selected comonomer pairs could possibly contribute to a better understanding of the mechanisms in the anionic polymerization of polar vinyl monomers. The constants of LiPi binding (K_1^L) can be used as a measure of the tendency of the polar vinyl monomers to coordinate lithium counterions. Lithium picrate as a reference salt resembles the anionic active centers of the monomers in view of the ambident character of the anion. No doubt, the absolute values of the complex formation constants will vary depending on the anion and the nature of the cation solvation shell. It may be claimed, however, that the order of monomer affinities found for LiPi will be the same for the anionic active centers of the monomers. It has to be stressed that in copolymerization studies the formation of free ions must be avoided.

Conclusions

The competition approach for determining the constants of complex formation in solution is combined with the Langmuir–Klotz procedure for studies of solute binding to polymer ligands. Thus, analysis of systems when the competing ligands form more than one complex with the solute is made possible.

Cross-linked poly(ethylene oxide) has a relatively low binding capacity for lithium picrate as calculated by the Langmuir–Klotz isotherm for dioxane at 25 °C. This shows that PEO networks are a suitable probe for studies of weak interactions of the salt with the aid of the competition method.

The modified competition technique was employed to characterize the interaction of some polar vinyl monomers with lithium picrate in dioxane with cross-linked PEO as the insoluble ligand. The interaction effectivity depends mainly on the nature of the monomer polar group. The lack of correlation with dielectric constants and dipole moments of the monomers is in favor of specific complex formation. The following order of complex formation constants was found: amides > vinylpyridines > vinyl ketones > nitriles > esters. The reported values provide a scale of relative affinities of polar vinyl monomers for lithium counterions.

The complex formation constants differ considerably within a range of 3 orders of magnitude. This suggests that selective monomer coordination might play a significant role in the mechanism of anionic polymerization of polar vinyl monomers where complexation between monomer and the growing ends has often been speculated to rationalize experimental results.

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Dielectric Relaxation Studies of Ion Motions in Electrolyte-Containing Perfluorosulfonate Ionomers. 2. CH_3COONa, KCl, and KI Systems

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ABSTRACT: The dielectric response of hydrated $CH_3COO^-Na^+$-containing Nafion perfluorosulfonate membranes was determined over the frequency range 5 Hz to 13 MHz at various fixed temperatures as a function of the concentration of the external solution in which they were equilibrated. More limited results are also presented for aqueous KCl- and KI-containing films. As in our earlier studies of aqueous NaOH- and NaCl-imbibed membranes, the observed relaxation behavior is rationalized in terms of intra- and inter-cluster ion displacements. Specifically, a relaxation of interfacial polarization due to the accumulation and dissipation of mobile ionic charge at the cluster boundaries and a longer ranged cluster-to-cluster hopping are manifest. The dependence of dielectric response on ion concentration has been largely interpreted within the framework of a dynamic equilibrium between ionic associations within a hydrophilic/hydrophobic phase-separated morphology.

Introduction

Mauritz and Fu have recently reported a dielectric relaxation study of Nafion 117 perfluorosulfonate membranes[1] that were equilibrated in concentrated aqueous NaOH and NaCl solutions.[2] In that study, hereafter referred to as "part 1", the storage and loss components of the complex dielectric constants, ϵ' and ϵ'' respectively, were determined with an impedance analyzer over the frequency (f) range 5 Hz to 13 MHz as a function of external solution concentration and temperature in the range 22–55 °C.

While the dielectric responses of these electrolyte-imbibed systems were clearly dominated by long-range ion motions, an appropriate subtraction of the low-frequency dc component from the ϵ'' vs f curves uncovered a process which was suggested to consist of the relaxation of an interfacial polarization that arises from the accumulation and dissipation of mobile ionic charges at the boundaries of ca. 40-Å-diameter clusters, as depicted in Figure 1. This mechanistic assignment was motivated largely by the observance of very high values of ϵ' at the lowest frequencies; the inapplicability of the Onsager equation (which is based on the conventional molecular dipole orientation mechanism) to the experimental data and the prior knowledge of polymer microphase separation.[3] The shift of the relaxational time scale with temperature was seen to be Arrhenius-like with a well-defined activation energy at each fixed electrolyte concentration.

The overall depression of ϵ' and ϵ'' with increasing electrolyte concentration (at a given f and temperature T) was viewed as being reflective of an increasingly suppressed ionic mobility brought about by the progression of a greater relative population of electrically neutral ion pairs as well as sluggish higher order multipole structures that conceivably evolve with internal dehydration.

In short, the results of part 1 can be at least qualitatively understood in terms of the motions of hydrated mobile ions within the phase-separated morphology. More specifically, it appears that intra-cluster ion displacements might be distinguished from inter-cluster ion hopping events.

The investigation in part 1 was initially driven by our desire to better understand the characteristic motions of Na^+, OH^-, and Cl^- ions as well as H_2O molecules in these membranes in electrochemical cells designed for the important economical production of chlorine and caustic. Within a broader scientific context, however, we are now also interested in studying the physics of very concentrated electrolytes, finely dispersed as "microsolutions" that would

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