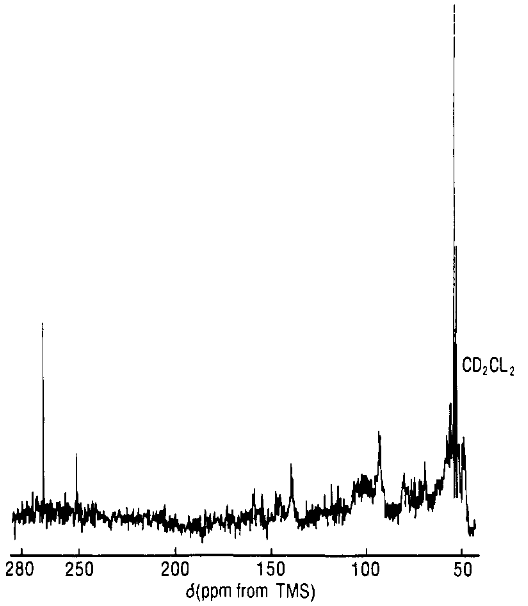
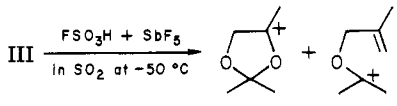


Figure 7. ^{1}H decoupled ^{13}C NMR spectrum of the 2,2,4-trimethyl-1,3-dioxolan-4-yl cation (FSO$_3$H + SbF$_5$ in liquid SO$_2$ at −50 °C).

nitrogen analysis of the corresponding hydrazone indicated it to be ~34.8 mol %. ^{13}C NMR of poly-II (Figure 6) provided further evidence for the presence of a significant amount of isomerized monomer units in the chain since the peaks observed at δ 187.5 and 27.3 may be attributed to the carbonyl and acyclic methyl groups (i.e., −OC(CH$_3$)$_2$−), respectively. These results are in agreement with those reported by Goodman and Abe[3] for the polymerization of III. Although the authors did not elaborate further on the mechanism, they suggested the intermediacy of the carbenium ion, while Kennedy[8] suggested a concerted bimolecular mechanism involving the nucleophilic attack of the olefin on the 2-position of the 1,3-dioxolane ring with simultaneous ring opening. Our own results favor the mechanism involving the rearrangement of the propagating cyclic carbenium ion to an acyclic carbenium ion. Protonation of III in the superacid medium showed in the ^{13}C NMR both the cyclic X and the rearranged XI carbenium ions at δ 269.56 and 252.03, respectively (Figure 7).



X XI

Acidic hydrolysis of poly-I and poly-II was found to cause considerable degradation, probably involving the chain end or the main-chain carbonyl functionality. The poly(hydroxymethylene) obtained from poly-I in low yield showed an IR spectrum essentially identical with that obtained from poly(vinylene carbonate), consistent with the atactic structure of the polymers.

Acknowledgment. The authors are indebted to Mr. G. E. Babbitt for obtaining the 20-MHz ^{13}C NMR spectra and Mr. R. A. Kirk for experimental assistance. The ^{1}H and ^{13}C NMR spectra on the Bruker HX 270 instrument (270 MHz) were kindly provided by Mr. P. Demou of the Department of Chemistry, Yale University, New Haven, CT 06520.

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Polycation–Polyanion Complexes in the Linear Diblock Copolymer of Poly(styrene sulfonate)/Poly(2-vinylpyridinium) Salt

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ABSTRACT: From spectrophotometric analysis in aqueous medium, the degree of ionization of poly(2-vinylpyridine) in a linear diblock copolymer of a poly(styrene sulfonate)/poly(2-vinylpyridine) salt was obtained as a function of pH. The spectrophotometric titration curve was compared with the titration curves of a diblock copolymer of poly(ethylene oxide)/poly(2-vinylpyridine) and of homopoly(2-vinylpyridine). The strong increase of basicity of pyridine groups in the polyampholyte copolymer is explained by invoking a stoichiometric interaction between oppositely charged groups. The formation of an internal polysalt is discussed in relation to conformational changes obtained from viscosity data.

Polyelectrolyte complexes are the result of mixing two highly, but oppositely, charged homopolymers in aqueous media. Studies on the electrochemical behavior and the application of these complexes in various fields have been reported.[1-3] Less attention seems to have been paid thus far to the properties of charged block copolymers in dilute aqueous solutions. Stille have reported on the properties of block copolymers containing cationic sequences based on 2-vinylpyridine and anionic sequences based on methacrylic acid.[4] The copolymers were polyampholytes and their use in the formation of desalination membranes was stressed.[5]

Since charged block copolymers are models for a special kind of polyelectrolyte, it seemed desirable to undertake a more systematic investigation of their polyelectrolyte properties. In this preliminary paper we report on the

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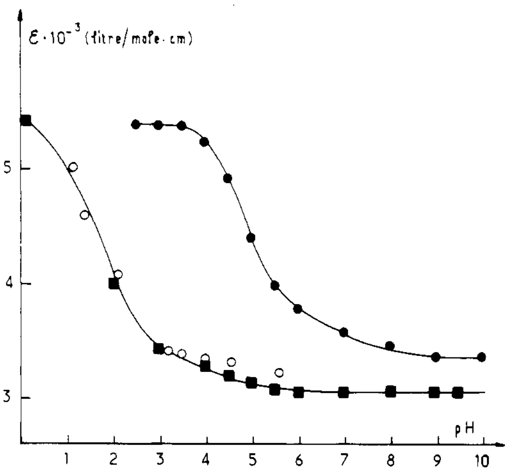

Figure 1. Spectroscopic measurements on copolymers PSS/P2VP (●) and PEO/P2VP and homopolymer P2VP (○).

properties in aqueous solution of the poly(styrene sulfonate)/poly(2-vinylpyridine) copolymer system. This copolymer contains within the same chain a long sequence of polybasic type followed by a strong polyacid sequence. Attention is focused on the special polyelectrolyte behavior of this polyampholyte. In particular the electrochemical characteristics of the basic poly(2-vinylpyridine) in the presence of the strong electrical field generated by the neighboring poly(styrene sulfonate) chain were analyzed. Polyanion–polycation interactions were investigated by spectroscopic and viscosity measurements.

Experimental Section

The diblock copolymer poly(styrene sulfonate/poly(2-vinylpyridine) (PSS/P2VP) was prepared by the classical anionic polymerization of styrene with functional end groups in tetrahydrofuran followed by the polymerization in situ of the vinylpyridine component. The average molecular weights of 21 000 and 25 000 for PSS and P2VP sequences, respectively, were determined by light scattering on tetrahydrofuran solutions. The polystyrene sequence was sulfonated according to a technique developed by Turbak,[6] who used a triethyl phosphate-sulfur trioxide complex by which parasite reactions and polymer degradation were reduced to a minimum. To about 100 mL of chloroform was added a given volume of freshly distilled $PO(OC_2H_5)_3$. After this solution had been cooled to −50 °C, a calculated amount of liquid sulfur trioxide, slightly in excess of that required for the 1:1 sulfonation of polystyrene and sufficient to form a 3:1 complex with the three ester oxygens, was then added. A 1% (w/v) solution of copolymer in chloroform was slowly introduced over a period of 2–3 min with stirring, to give an immediate white precipitate. The sulfonation yield was 96%, as was found by elementary analysis.

The preparation of the diblock copolymer of poly(ethylene oxide)/poly(2-vinylpyridine) (PEO/P2VP) has been described elsewhere.[7] The average molecular weights of PEO and P2VP were 18 000 and 15 000, respectively. The intrinsic viscosities were measured with an automatic viscosimeter.[8] Deionized water with a resistivity of 18 MΩ, filtered with a 0.45 μm microfilter, was used throughout, and solutions of polymer in water were made up by weight. The spectrophotometric determinations were made with a Carry 14 Varian spectrophotometer at room temperature.

Results and Discussion

In Figure 1 is reported the spectrophotometric behavior of PSS/P2VP and PEO/P2VP copolymers and of homopolymer P2VP as a function of the pH of the aqueous solutions. ϵ [L/(mol cm)] is the molar extinction coefficient measured at the maximum absorption of the polymer solution in the UV absorption spectrum (λ 2625 Å).

The PSS/P2VP polymer solution became turbid at pH <2.5, and in the case of P2VP homopolymer phase separation occurred at and above pH 5. The PEO/P2VP solution was transparent at all pH values. As has been shown elsewhere, the change of UV adsorption as a function of pH reflects the change of the degree of ionization of the polybase P2VP.[9] From the limiting values of $\epsilon_m = 3360$ for PSS/P2VP, $\epsilon_m = 3060$ for PEO/P2VP, and $\epsilon_M = 5435$ (Figure 1), the true degree of ionization α of the pyridine groups for both polymers was calculated by assuming linearity between the absorption coefficient and α. Plots of α vs. pH, i.e., the spectrophotometric titration curves, are given in Figure 2.

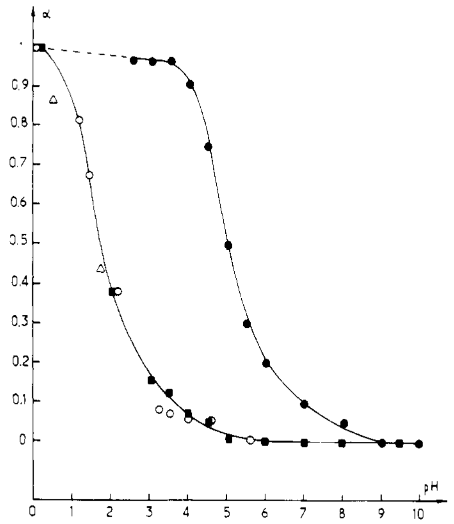

Figure 2. Dependence of the degree of ionization on pH for: (●) PSS/P2VP ($\epsilon_M = 5435$, $\epsilon_m = 3360$); PEO/P2VP ($\epsilon_M = 5435$, $\epsilon_m = 3060$); (○) P2VP ($\epsilon_M = 5435$, $\epsilon_m = 3222$); and (Δ) P2VP taken from ref 7.

Because of the hydrophilic PEO chain, the aqueous solutions of the copolymer PEO/P2VP are stable in the pH domain of unneutralized P2VP (see the plateau region above pH 6.5); ϵ_m can therefore be determined without ambiguity. On the other hand, homopolymer P2VP, because of its weak basicity, precipitates out of aqueous solutions near pH 5, and ϵ_m (or α) becomes difficult to determine since there is no limiting plateau behavior. The limiting ϵ_m depends on the nature of the accompanying sequence, as shown in Figure 1. For the homopolymer P2VP, ϵ_m was measured in ethanol and found to equal 3221; whether the same value can be used in water is of course questionable.[10] The α vs. pH curve of P2VP differs slightly from the curve relative to PEO/P2VP in the pH range 3.5–5.5, where α becomes zero.

In Figure 2, a remarkable shift of the α vs. pH curve toward higher pH values is displayed by the PSS/P2VP polymer. The protonation of pyridine groups is zero at pH 5 for both P2VP and PEO/P2VP and also at pH 8.5 for copolymer PSS/P2VP. Moreover, near the isoelectric point $\alpha = 0.86$, the α vs. pH curve for PSS/P2VP reaches a plateau, a feature which seems to be characteristic for polyampholytes and has been observed in the titration curves of some proteins.[12]

In order to discuss from a more quantitative point of view the strong increase in the basicity of pyridine in PSS/P2VP, we show in Figure 3 the dependence on α of pH + log [$\alpha/(1-\alpha)$]. This quantity is derived theoretically from the analysis of the equilibrium processes

$$P^{+(\nu+\delta\nu)} \rightarrow P^{+\nu} + \delta\nu H^{+} \qquad (1)$$

where $P^{+\nu}$ represents the PSS/P2VP chain with ν protonated pyridinium groups. Using eq 1, we shall treat the macromolecule and its environment as a two-phase system. The macromolecular phase consists of the molecule itself,

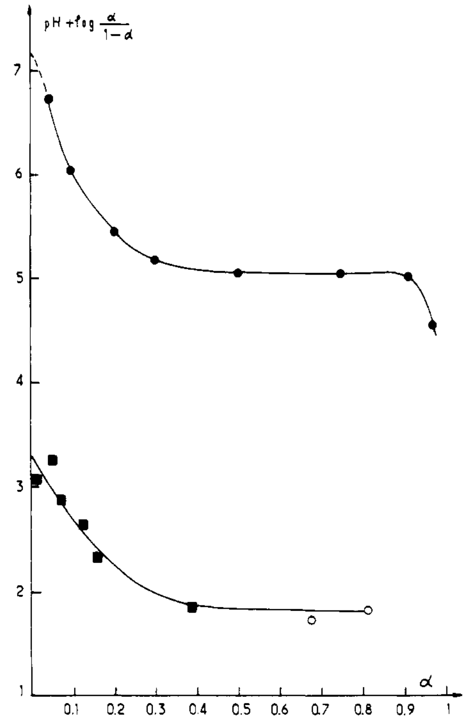

Figure 3. Dissociation constant of one pyridinium group as a function of the degree of ionization α: (●) PSS/P2VP; (■) PEO/P2VP; and (○) P2VP.

and the other phase consists of the electrically neutral volume which can be assigned to each polymeric ion. At equilibrium:

$$\mu_{\mathrm{P}^{(\nu+\delta\nu)}} = \mu_{\mathrm{P}^{(\nu)}} + \delta\nu\mu_{\mathrm{H}^+} \tag{2}$$

$$\mu_{\mathrm{H}^+} = \mu^0{}_{\mathrm{H}^+} - 2.3RT(\mathrm{pH}) \tag{3}$$

$$\mu_{\mathrm{P}^{(\nu)}} = E - TS_{\mathrm{P}} + m[\alpha\mu^0{}_{\mathrm{NH}^+} + (1-\alpha)\mu^0{}_{\mathrm{N}}] + m'\mu^0{}_{\mathrm{SO_3^-}} + 2.3RTm[\alpha \log \alpha + (1-\alpha)\log(1-\alpha)] \tag{4}$$

$$\alpha m = |\nu| \tag{5}$$

In eq 4, the free energy of one macromolecule bearing ν pyridinium groups is split into several contributions: E and S_{P} are respectively the electrostatic free energy and the configurational entropy of the total chain. The last term on the righ-hand side of eq 4 is the free energy of mixing charged and uncharged groups along the PV2P chain, m and m' being the number of monomers in the PV2P and PSS chains, respectively. PSS is a strong polyelectrolyte which should be completely ionized at all pH values investigated here.[13,14] The quantity $\mu^0{}_i$ is the free-energy part of one monomer (the subscripts NH^+, N, and $\mathrm{SO_3}^-$ represent pyridinium, pyridine, and sulfonate groups, respectively) which includes neither the electrostatic free energy of the monomer subject to electrostatic forces of neighboring monomers nor the orientational possibilities included in S_{p}. Since

$$\mathrm{d}\mu_{\mathrm{P}^{(\nu)}}/\mathrm{d}\alpha = m(\mu^0{}_{\mathrm{H}^+} - 2.3RT(\mathrm{pH})) \tag{6}$$

the titration isotherm can be given the more conventional form

$$\mathrm{pH} + \log\left(\frac{\alpha}{1-\alpha}\right) = \frac{1}{2.3RTm}\frac{\mathrm{d}}{\mathrm{d}\alpha}(TS_{\mathrm{P}} - E) + \frac{(\mu^0{}_{\mathrm{N}} + \mu^0{}_{\mathrm{H}^+} - \mu^0{}_{\mathrm{NH}^+})}{2.3RT} - \frac{1}{2.3RT}\left[\alpha\frac{\mathrm{d}\mu^0{}_{\mathrm{NH}^+}}{\mathrm{d}\alpha} + (1-\alpha)\frac{\mathrm{d}\mu^0{}_{\mathrm{N}}}{\mathrm{d}\alpha} + \frac{m'}{m}\frac{\mathrm{d}\mu^0{}_{\mathrm{SO_3^-}}}{\mathrm{d}\alpha}\right] \tag{7}$$

The main contribution to the excess free energy should originate from the term $TS_{\mathrm{P}} - E$ (S_{P} and E are both functions of α) and we assume, as for the treatments of monolithic polyelectrolytes, that $\mu^0{}_i$ is independent of α. The difference Δy in the ordinates of the curves of Figure 3 is then simply expressed as:

$$\Delta y = y(\mathrm{PSS/P2VP}) - y(\mathrm{PEO/P2VP}) = \frac{1}{2.3RT}\frac{\mathrm{d}}{\mathrm{d}\alpha}(T\Delta\bar{S}_{\mathrm{P}} - \Delta\bar{E}) + \Delta\mathrm{p}K_{\mathrm{B}} \tag{8}$$

$$\mathrm{p}K_{\mathrm{B}} = (\mu^0{}_{\mathrm{N}} + \mu^0{}_{\mathrm{H}^+} - \mu^0{}_{\mathrm{NH}^+})/2.3RT \tag{9}$$

The symbol Δ on the right-hand side of eq 8 stands for the difference in $\bar{S}_{\mathrm{P}}$ and $\bar{E}$ between PSS/P2VP and PEO/P2VP polymers, and barred symbols refer to the entropy and electrostatic free energy per monomer unit. In order to discuss the limiting value $\Delta y_{\alpha=0}$, let us express the electrostatic free energy in terms of the electrical potential:

$$\bar{E} = \frac{1}{2m}\int_L \phi\rho \, \mathrm{d}l \tag{10}$$

where ϕ is the electrostatic potential on the polyion surface, ρ is the polyion charge per unit length at location l, and the integral is taken over the polyion contour length. Expanding ρ and ϕ as limiting power series in α gives:

$$\bar{E} = \frac{1}{2m}\int_L \left[\phi_0 + \left(\frac{\mathrm{d}\phi}{\mathrm{d}\alpha}\right)_{\alpha=0}\alpha + \ldots\right]\left[\rho_0 + \left(\frac{\mathrm{d}\rho}{\mathrm{d}\alpha}\right)_{\alpha=0}\alpha + \ldots\right]\mathrm{d}l \tag{11}$$

$$\left(\frac{\mathrm{d}\bar{E}}{\mathrm{d}\alpha}\right)_{\alpha=0} = \frac{1}{2m}\int_L\left[\rho_0\left(\frac{\mathrm{d}\phi}{\mathrm{d}\alpha}\right)_{\alpha=0} + \phi_0\left(\frac{\mathrm{d}\rho}{\mathrm{d}\alpha}\right)_{\alpha=0}\right]\mathrm{d}l \tag{12}$$

ϕ_0 and ρ_0 are respectively the value of ϕ and ρ at location 1 for $\alpha = 0$. For copolymer PEO/P2VP, both ρ_0 and ϕ_0 are zero and the integral vanishes. In the case of copolymer PSS/P2VP, however, these terms are not zero, and ρ_0 and ϕ_0 therefore correspond to the charge and potential provided by the highly negatively charged PSS chain. Thus $\phi_0\,(\mathrm{d}\rho/\mathrm{d}\alpha)_{\alpha=0}$ is the electrostatic free energy of one positively charged pyridinium group in the electrical molecular field of the PSS chain, all other pyridine groups bearing zero charge. On the other hand, $\rho_0\,(\mathrm{d}\phi/\mathrm{d}\alpha)_{\alpha=0}$ is essentially the electrostatic free energy change of the PSS chain in the presence of one pyridinium group. This latter contribution, as explained below, originates from the configurational changes in the PSS chain.

At the origin, $RT\Delta y$ amounts to 2.3 kcal; this large value, which comes to within 10% of equaling the electrostatic free energy of a charged monomer in a completely ionized poly(vinyl homopolyelectrolyte),[15] suggests that ionization and configurational features for PSS/P2VP copolymer may be related as depicted in Figure 4.

Figure 4a refers to the state of the noncharged P2VP chain. The molecule in that case probably takes a "segregated" conformation with chain P2VP in a compact state and chain PSS loosely coiled around P2VP.[16] When ionization of the pyridine groups becomes effective, then opposite charges are attracted and come into contact because of the huge potential trough provided by the PSS chain. This mechanism is suggested by the value of Δy at $\alpha = 0$. Such ion pairing leads at the beginning to a kind of cross-linked structure, Figure 4b, and finally to an internal polysalt complex of extremely compact structure Figure 4c. In this frame of reference, the dominant negative contribution to the excess free energy is believed to come from the term $\mathrm{d}\bar{E}/\mathrm{d}\alpha$ regarded through ϕ_0 ($\mathrm{d}\rho/$

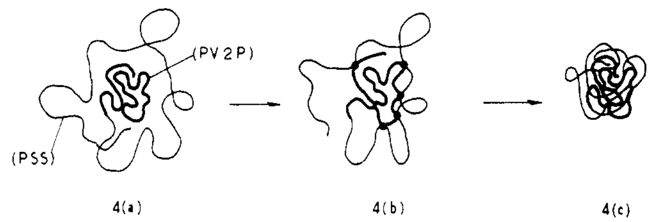

Figure 4. Conformational state of copolymer PSS/P2VP with increasing degree of ionization α: a, state of uncharged P2VP chain; b, ion-pair (SO_3^-, NH^+) formation at low α values; and c, internal polysalt complex at the stoichiometric $\alpha = 0.86$ value.

$d\alpha)_{\alpha=0}$. (Note that a negative contribution of $d\bar{E}/d\alpha$ gives a positive increase in y according to eq 8.) Actually, ρ_0 $(d\phi/d\alpha)_{\alpha=0}$ must be positive, since a reduction of the PSS dimensions owing to ion pairing results in an increasing electrostatic free energy for the PSS chain. Whether $(d\Delta\bar{S}_P/d\alpha)_{\alpha=0}$ is positive or negative is more difficult to assess. Interchain electrostatic attractions are more important in terms of energy than configuration perturbations, and the term $T\Delta S_P$ should be dominated by the electrostatic term.

In attributing all deviations from ideality to charge effects, one assumes $\Delta pK_B = 0$. Yet it is questionable whether the intrinsic dissociation constant of a pyridinium group remains the same in the presence of the PSS chain and the PEO chain. The hydration state and local dielectric constant can be different in the vicinity of a pyridinium group when the group is in the state of an (SO_3^- NH^+) ion-pair complex and in the state of a PEO environment. It is difficult to attempt a more detailed interpretation of this effect, since the usable approaches are necessarily qualitative.

So far we have discussed the significance of the shift of the ionization energies for the two polymers at the origin. One other interesting feature seen in Figure 3 is the plateau region for copolymer PSS/P2VP in the domain $0.3 < \alpha < 0.9$. In that region, the excess free energy levels off to a constant value for both polymers. For copolymer PEO/P2VP and polymer P2VP, this behavior is a characteristic of homopolyelectrolytes and has been discussed previously.[17] However, explanation of this phenomenon for copolymer PSS/P2VP requires further consideration. As a matter of fact, if the ion pairing is stoichiometric, then the net charge of the copolymer decreases with α as $(m' - m\alpha)e$, e being the elementary negative charge. Thus, from eq 10, one expects a concomitant decrease of ψ, and one would therefore expect a continuous increase in $d\bar{E}/d\alpha$, i.e., a decrease of y in Figure 3 up to the equivalent point $\alpha = 0.86$. In any explanation of the plateau behavior, the change in the conformation of the PSS/P2VP molecule during the protonation process should be taken into account. This is discussed in relation to viscosity data in the next paragraph.

The reduced viscosity η_{sp}/c for PSS/P2VP at $c = 0.52$ g dL^{-1} was determined experimentally in pure water and at 3×10^{-2} M NaCl and is plotted against α in Figure 5. For α from 0.20 to 0.86, the viscosity drops steadily. The decrease of molecular dimensions is caused by increasing ion pairing. Yet a decrease in dimensions causes an increase in $\bar{E}$ at a given net charge, and therefore in the plateau region the effect of a decrease in net charge on $\bar{E}$ seems to be exactly balanced by the opposite effect on $\bar{E}$ of conformational changes.

An examination of the viscosity curve shows the cause of the isoelectric jump in the spectrophotometric titration curve. The minimum in the viscosity plot occurs at the isoelectric point ($\alpha = 0.86$), and the polyampholyte has a very compact configuration near that point, as shown by the 0.25 value of η_{sp}/c in the presence of salt. One should note the more than tenfold drop in the reduced viscosity in going from the nonprotonated state of P2VP to the isoelectric point. At the maximum compactness, i.e., at the minimum in η_{sp}/c, it becomes difficult to add more ions to the polymer because of the high free-energy expense needed. Therefore, for $\alpha > 0.86$, little change in the net charge with pH is observed (Figure 2). As the net charge reverses to a positive value, the polymer expands, η_{sp}/c increases as seen in Figure 5, and the free energy increases steeply as seen in Figure 3.

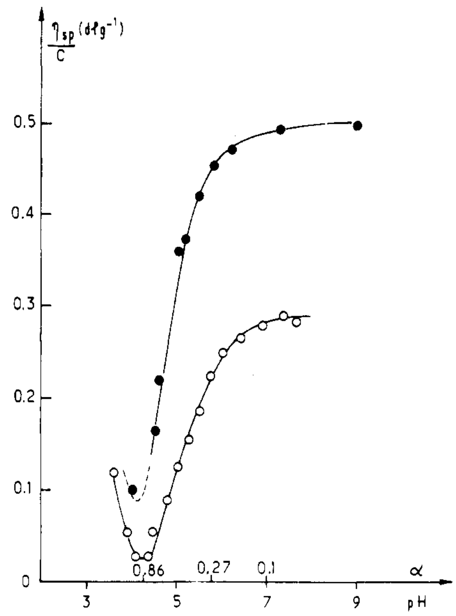

Figure 5. Reduced viscosity as a function of α for PSS/P2VP: (●) in pure water; and (○) in the presence of 3×10^{-2} M NaCl.

Conclusion

Systems of oppositely charged polyions in aqueous solutions have been studied in the past (for a review see, for example, ref 18), and much experimental work on phase separation and complex coacervation in these systems has been reported. Water-insoluble hydrous precipitates have always been obtained, and the stoichiometry of ion pairing in polysalt formation has been investigated. The reaction products have been most often found to be of stoichiometric composition (some authors have also reported a deviation from stoichiometry[1]). In the present paper, interactions between covalently attached polyions were investigated. Surprisingly, no phase separation was observed up to the isoelectric point. The mechanism of polyion interactions and the probable structure of the complexes were described in the light of viscosity data. At the present stage, more experimental data are necessary before definite conclusions about structural rearrangements and the mechanism of internal ionic bond transfer can be reached.

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An Analysis of the Complex Participation Model for Free-Radical Copolymerization

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ABSTRACT: The probability theory has been used to derive equations for the complex participation model for free-radical copolymerization, showing how the composition, the triad fractions, and the number fractions of sequences in a copolymer are related to the reactivity ratios, the equilibrium constant, and the monomer composition. We show how a patterned search method can be used to yield "best" estimates of the reactivity ratios and the equilibrium constant, using the experimentally determined copolymer composition, triad fractions, or number fractions of sequences provided sufficient data are available. Experimental data for the 1,1-diphenylethylene–methyl acrylate system available in the literature have been used to demonstrate this method of analysis.

Deviations in the composition of a copolymer from the predictions made on the basis of the simple terminal model for polymerization can be accounted for by amending this model in one of a number of ways. The deviations may be ascribed to effects associated with the penultimate and/or other preceding residues in the chain or to the formation of a comonomer complex which competes with monomer in the polymerization process. This latter modification was the subject of a series of papers by Litt and Seiner,[3-6] wherein they presented a quantitative theory relating the composition of a copolymer to the concentrations of the reacting monomers, the various reactivity ratios, and the equilibrium constant for formation of the complex. Herein we present an alternative to their treatment of the complex participation model. We have derived, for the first time, equations expressing the number fractions of sequences in terms of the transition probabilities and indicate how expressions for the triad fractions and the copolymer composition can be obtained.

For systems which can be represented by the complex participation model, we show how "best estimates" of the reactivity ratios and the equilibrium constant can be calculated either from the experimentally determined copolymer composition, or the triad fractions, or the number fractions of sequences using these relationships, provided that information is available for a sufficient number of initial polymers prepared from monomer mixtures which cover the complete composition range.

To demonstrate these methods, the data available in the literature[7] for the 1,1-diphenylethylene–methyl acrylate system have been used.

Theory

The complex participation model can be described on a kinetic–probabilistic basis. The eight kinetic equations required to represent the polymerization process are:

$$\sim 0 + 0 \xrightarrow{k_{00}} \sim 0 \tag{1}$$

$$\sim 0 + 1 \xrightarrow{k_{01}} \sim 1 \tag{2}$$

$$\sim 0 + \overline{10} \xrightarrow{k_{0\overline{10}}} \sim 0 \tag{3}$$

$$\sim 0 + \overline{01} \xrightarrow{k_{0\overline{01}}} \sim 1 \tag{4}$$

$$\sim 1 + 0 \xrightarrow{k_{10}} \sim 0 \tag{5}$$

$$\sim 1 + 1 \xrightarrow{k_{11}} \sim 1 \tag{6}$$

$$\sim 1 + \overline{10} \xrightarrow{k_{1\overline{10}}} \sim 0 \tag{7}$$

$$\sim 1 + \overline{01} \xrightarrow{k_{1\overline{01}}} \sim 1 \tag{8}$$

where the symbols $\overline{10}$ and $\overline{01}$ are used to represent the complex, which may add from either side in the polymerization process. In this form then, the model is completely general. Polymerization reactivity ratios can be defined in the following way:[8]

$$\begin{gathered} r_0 = k_{00}/k_{01},\ r_1 = k_{11}/k_{10} \\ p_0 = k_{0\overline{01}}/k_{0\overline{10}},\ p_1 = k_{1\overline{10}}/k_{1\overline{01}} \\ s_0 = k_{0\overline{10}}/k_{01},\ s_1 = k_{1\overline{01}}/k_{10} \end{gathered} \tag{9}$$

and the transition probabilities for the state space of events given by the eq 1–8 can be represented by the symbols P_{00}, P_{01}, $P_{0\overline{10}}$, $P_{0\overline{01}}$, P_{10}, P_{11}, $P_{1\overline{10}}$, and $P_{1\overline{01}}$, respectively. Defined on this basis

$$P_{00} + P_{01} + P_{0\overline{10}} + P_{0\overline{01}} = 1 \tag{10}$$

$$P_{11} + P_{10} + P_{1\overline{10}} + P_{1\overline{01}} = 1 \tag{11}$$

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