Previously we have found that the polyethylene segments of ethylene-vinyl ester copolymers undergo intramolecular conformational transitions in solution.[1,7] More specifically, we have identified the doubled alkanelike methylene proton peaks in the aromatic solution spectra of E-VF and E-VA copolymers as the two types of intramolecular structures, "monomeric" and "polymeric" species of the ethylene sequences. The polymeric species probably arises from intramolecular chain folding of the polyethylene segments containing 8 or more ethylene units. In addition, the existence of the polymeric structure in these copolymers appears to depend on their compositions and, to a lesser extent, on the monomer sequence distributions. It is seen that in Figure 2 the resonance peak due to the alkane-like methylene proton groups (at 1.2 ppm) is further split into two lines in the 1-chloronaphthalene solution spectrum. The spectral feature of the doubled alkanelike methylene proton resonances, which consists of a sharp line at lower field and a broad peak at higher field, is remarkably similar to those observed for E-VA and E-VF copolymers. The sharp methylene peak was then assigned to the equivalent internal methylene groups in the polymeric polyethylene sequences and the broad upfield resonances to the disordered monomeric methylene groups in accordance with our previous work.

In order to examine the effects of copolymer composition on the intramolecular structure formation we have obtained the 1-chloronaphthalene solution spectra of several E-VCl polymers. (see Figure 4). As in the cases of ethylene-vinyl ester copolymers,[1,7] the spectra of the doubled alkane-like methylene protons are indeed dependent on the comonomer (VCl) contents in the polymers. Particularly noteworthy is the fact that in the spectrum of an E-VCl polymer containing 43.3 mol % of VCl the feature of the alkane-like methylene proton resonances is significantly altered. This is consistent with the previous observation that the fraction of ethylene in blocks of 8 or more ethylene units of a statistically random copolymer containing more than 37.5 mol % of comonomer becomes negligibly small and the formation of polymeric structure by intramolecular chain folding is precluded.[7] As implied by our earlier work the results of the present study lead to an important conclusion that the intramolecular conformational transitions observed in the nmr spectra of ethylene copolymers arise from the polyethylene segments and are not affected by the nature of the comonomer units.

Acknowledgment. Part of this work was completed while the author was a visiting associate professor at National Taiwan University under the auspices of National Science Council of Republic of China. It is a pleasure to acknowledge Professor W.-C. Lin, Chairman of the Chemistry Department, for his hospitality. The author is also grateful to Dr. C. F. Hammer and P. W. Feltz for the synthesis of ethylene-vinyl chloride copolymers.

Dilute Solution Behavior of Polyelectrolytes. Potentiometric Titration Studies on Chain Conformation

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ABSTRACT: Potentiometric and viscometric studies of copoly(ethyl acrylate-acrylic acid) were made in a mixed isopropyl alcohol-water (4:1) medium as a function of ionic strength. Potentiometric titrations resulted in distinct conformational transition curves similar to those observed for poly(methacrylic acid) and poly(glutamic acid). The transition is most pronounced in the absence of salt. It is believed that our copolymer goes through a transition from a compact globular coil at a low degree of ionization to a more extended coil at a high degree of ionization. The free-energy change for the conformational transition of the un-ionized molecule estimated from the empirical Henderson-Hasselbalch extrapolations is approximately in the range of 60-90 cal/mol. In addition, the titration behavior of three copolymers of the same chain length but different acid contents was compared. The data suggest that the start of the transition region occurs at a lower degree of ionization for chains with higher acid content. However, the fraction of charge per residue at the onset of the transition is about 0.10 for the three copolymers studied.

Light-scattering and intrinsic-viscosity studies of several fractions of copoly(ethyl acrylate-acrylic acid) (mole ratio 3:1) in organic solvents and in aqueous NaCl solutions as a function of ionic strength, C_s, have been reported previously.[1] Data on radius of gyration, second virial coefficient, and intrinsic viscosity as a function of ionic strength (see Figure 1a-c for data on one fraction, F4) suggest that the polymer goes through a conformational transition from an extended coil at low C_s to a compact globular coil at high C_s. In the low C_s region below 0.1 N NaCl, the coil becomes more compact possibly attributed charged groups. In the presence of a moderate concentration of NaCl, the screening effect of the counterions tends to diminish the repulsive forces and the size of the coil becomes smaller. At high ionic strength above 0.5 N NaCl, the coil becomes more compact possibly attributed to both the further reduction in repulsive forces and the increasing intramolecular hydrophobic attraction of the ester groups along the chain.

The possibility of creating and stabilizing a compact form of the molecule by interaction of polymer side-chain groups has prompted further study of the conformational transition of this copolymer. Potentiometric titration of the polyacid was selected as the tool to investigate this molecular behavior. This type of study has proved to be very helpful in identifying helix-coil transitions in polypeptides such as poly(glutamic acid) (PGA)[2-5] and poly-

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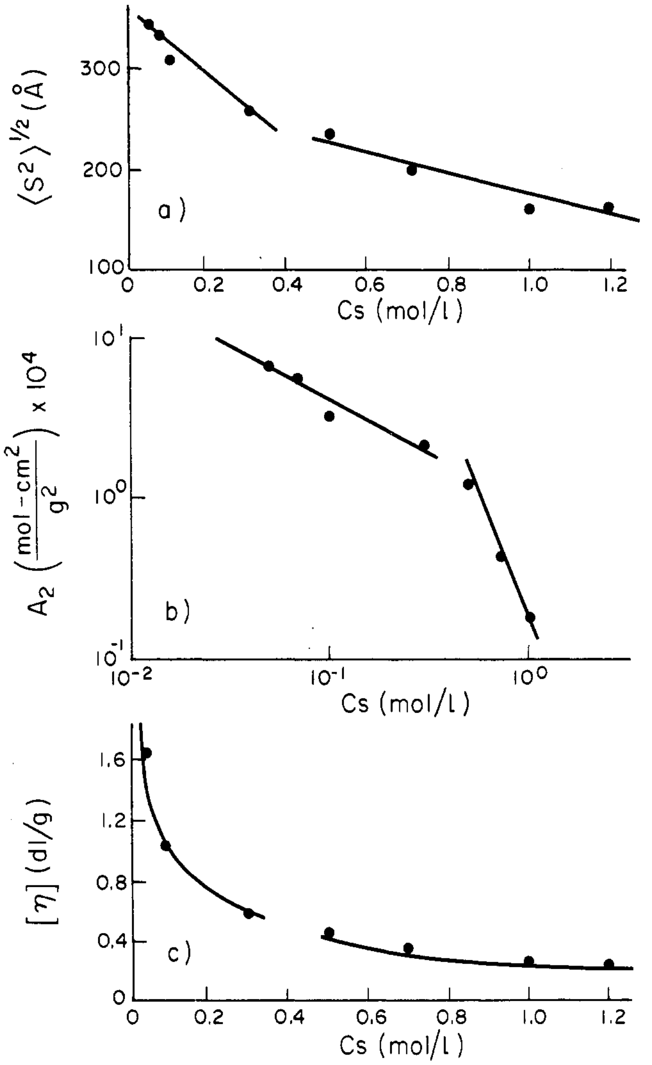

Figure 1. (a) Radius of gyration *vs.* ionic strength for sodium-copoly(ethyl acrylate-acrylic acid) F4; (b) double logarithmic plots of second virial coefficient *vs.* ionic strength for F4; (c) intrinsic viscosity *vs.* ionic strength for F4.

(lysine).[6] In addition, the method has been successfully applied to the study of synthetic polyelectrolytes such as poly(methacrylic acid) (PMAA),[2,7-9] copolymers of maleic acid and alkyl vinyl ethers,[10,11] and copolymer of maleic acid and styrene,[12] for which conformational changes of the polyions in solution have been reported. Such studies provide not only qualitative evidence of a transformation, but also can provide quantitative estimates of the free energy required for the transition.

I. Experimental Section

A. Titration. Preparation and fractionation of copoly(ethyl acrylate-acrylic acid) and characterization of the fractions have been described in detail previously.[1] A fraction of M_w = 560,000 (un-ionized) was selected for the potentiometric studies. Since other investigations of polyelectrolytes had shown that titration behavior was independent of molecular weight over a wide molecular weight range[2,9,11] and also was independent of polymer concentration,[3,9] only one fraction of the copolymer was studied at one selected polymer concentration.

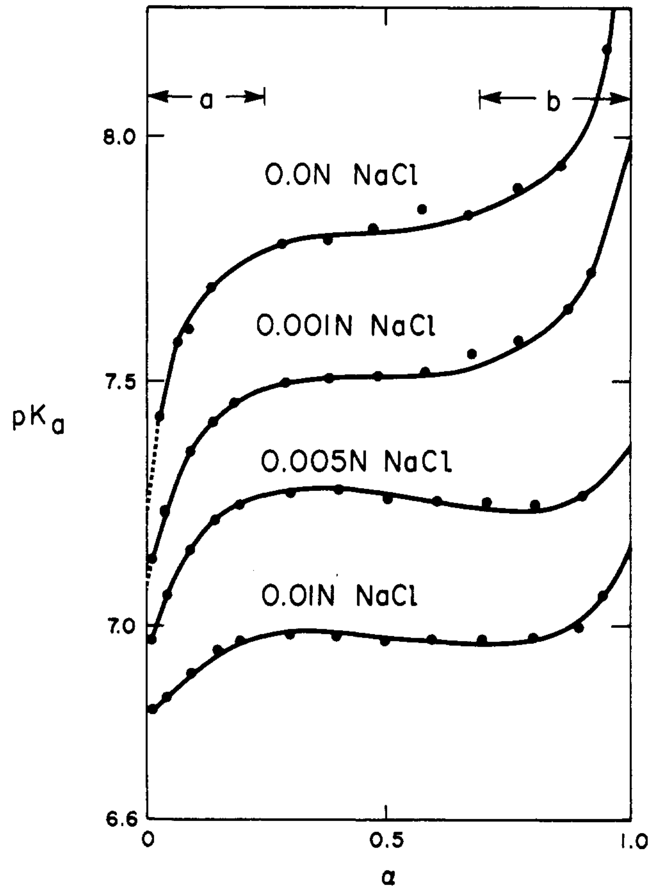

Figure 2. Potentiometric titration curves for F4 in isopropyl alcohol-water (4:1) at the indicated NaCl concentrations.

Although the behavior of the copolymer in an aqueous medium was of interest in this study, it was impossible to perform potentiometric titrations in water, since the un-ionized copolymer was insoluble. Therefore, it was necessary to find a titration solvent in which the polymer would be soluble in both the un-ionized and ionized forms. An isopropyl alcohol-water (4:1) mixture was selected. Solutions for titration were prepared by dissolving the copolymer in isopropyl alcohol and adding water and NaCl to give the desired composition and ionic strength. An initial polymer concentration of 0.01 equiv/l. in the acid moiety (*i.e.*, 0.4 g/dl of the copolymer) was used in each titration.

A Corning Model 12 research pH meter sensitive to 0.002 pH unit was used in conjunction with a Sargent combination pH electrode. Although standard buffers can be prepared for *methanol* and *ethanol*-water mixtures,[13] no standard buffer is available for isopropyl alcohol-water (4:1). Therefore, the electrodes were standardized against aqueous Fisher Scientific Certified buffers of pH 4.0, 7.0, and 10.0 prior to each titration. The pH values as measured refer to a 1 *m* standard state in pure water. Corrections of these values to a standard state in an isopropyl alcohol-water (4:1) mixture would only shift the titration curves vertically, rather than alter the shape of the curves. Therefore, no correction has been applied; all values reported are apparent pH. A similar situation was also encountered by Olander and Holtzer[5] in the case of a dioxane-water mixture.

Titrations were performed at 25 ± 0.1° by the addition of carbonate-free 0.01 *N* NaOH in isopropyl alcohol-water (4:1) at an ionic strength identical with that of the polymer solution, in order to maintain a constant chemical composition of the solvent. The ionic strengths of the solutions were from 0, 0.001, 0.005, and 0.01 *N* NaCl. The degree of ionization α, defined as the fraction of carboxylic acid dissociated, was determined for each addition of titrant in the following manner. The pH was measured after each

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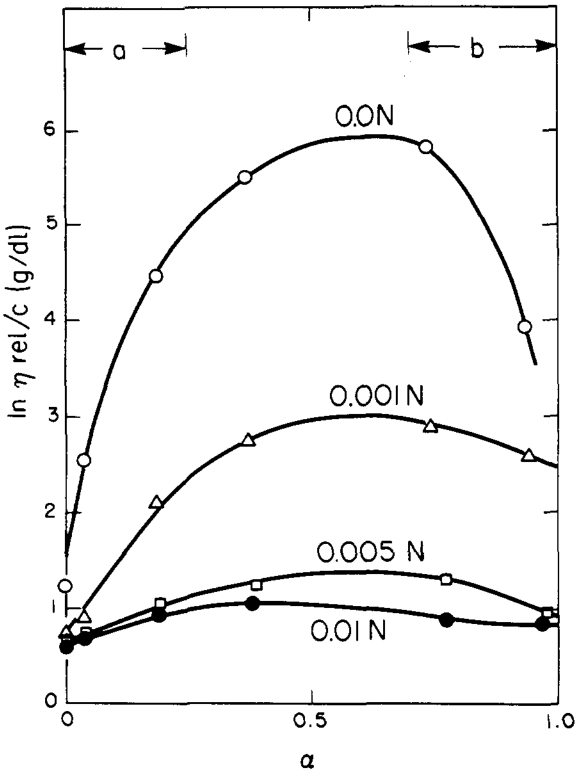

Figure 3. Inherent viscosity *vs.* degree of ionization for F4 in isopropyl alcohol-water (4:1) at the indicated NaCl concentrations.

addition of titrant. If the pH value was in the range of 5-9, no correction for the free acid or free hydroxyl was needed, and α was calculated as $[C_{A^+}]/[C_{HA}{}^0]$, where $[C_{A^+}]$ is the molarity of the dissociated carboxylic acid (equal to the amount of NaOH added, $[C_{Na^+}]$), and $[C_{HA}{}^0]$ is the total amount of carboxylic acid. If the pH was below 5 or above 9, correction for free H^+ or OH^- was needed because some of the titrant added was consumed to create free H^+ or OH^- in the solution. The correction for free acid or base was determined directly by a blank titration, which recorded the amount of NaOH required to bring the solvent alone to the same pH value. The corrected titration curve was obtained by subtracting the blank curve from the solution curve. Titration data thus obtained are presented in Figure 2 as $pK_a = pH + \log[(1 - \alpha)/\alpha]$ *vs.* α. In most measurements in the present work, the correction was negligible. Titrations in media with ionic strengths greater than 0.01 *N* did not show characteristic transition curves and hence are not reported here. Even though the final concentration of NaOH in the titration sample was about 0.003-0.005 *N*, the contribution to the ionic strength by the unbound, mobile Na^+ ions was assumed to be much smaller than 0.001 *N*. As the actual values of ionic strength of the media were not used in any of the quantitative analysis in this report, only the concentration of the added NaCl was used to describe each titration run.

B. Viscosity. Measurements of intrinsic viscosity as a function of the degree of ionization under conditions identical with those of the titrations presented in Figure 2 were originally planned in order to observe changes in hydrodynamic volume with changes in α. However, it was found to be very difficult experimentally to maintain constant pH and therefore constant α during the dilutions required for the Huggins extrapolation to zero polymer concentration. As an alternative, inherent viscosities $\{\eta\} = \ln \eta_{rel}/c$, where η_{rel} is the relative viscosity and c is the polymer concentration) at a polymer concentration of 0.2 g/dl were obtained. Since the slopes of $\{\eta\}$ *vs.* c for all the experimental conditions are not expected to vary greatly, the values of $\{\eta\}$ represent a valid apmedia using Cannon-Fenske viscometers at 25 ± 0.002°. These given degree of ionization. The inherent viscosities for copolymer F4 were measured in the mixed isopropyl alcohol-water (4:1) mixture at various values of α and in different ionic strength media using Cannon-Fenske viscometers at 25 ± 0.002°. These results are presented in Figure 3.

C. Hydrolysis. In addition, a portion of the same copolymer sample was subjected to basic hydrolysis in order to convert some of the ester groups into carboxylic acid units. An excess of NaOH was added to a polymer solution and the reaction was allowed to continue for several days. After the addition of a known amount of HCl sufficient to neutralize both the excess base and the polymer, the samples were titrated with NaOH in a manner similar to that described previously. No attempt was made to isolate the products. The ionic strength of each solution was calculated knowing the amount of acid added to each sample; additional NaCl was added when necessary to obtain the desired ionic strength. The acid contents of the new copolymers were determined from the resulting titration curves, and the curves were analyzed in a manner similar to that of the original polymer. The mole ratios of ester to acid for the copolymers studied were 3:1 (F4), 2:1 (F4A), and 1:1 (F4B).

II. Results and Discussion

A. Potentiometric Titration and Inherent Viscosity. The dissociation of a carboxylic acid may be described by a single dissociation constant, K_0, as expressed in the following two equations

$$\mathrm{pH} = \mathrm{p}K_0 - \log\left(\frac{1-\alpha}{\alpha}\right) \tag{1}$$

$$\mathrm{p}K_0 = 0.434\Delta G^\circ/RT$$

where α is the degree of ionization and ΔG° is the free-energy change for the ionization process. In the dissociation of polyelectrolytes, additional work is required to ionize the charge groups against the existing charges on the chain and hence[14,15]

$$\mathrm{pH} = \mathrm{p}K_0 - \log\left(\frac{1-\alpha}{\alpha}\right) + \frac{0.434}{RT}\left(\frac{\partial G_{\mathrm{ion}}}{\partial\alpha}\right) \tag{2}$$

In the case of polyions which do not undergo conformational transition during ionization, *e.g.*, poly(acrylic acid) (PAA), $(\partial G_{\mathrm{ion}}/\partial\alpha)$ is simply the additional free-energy change required to remove H^+ against the strong electrostatic repulsive forces of the chain. In the case of polyions which undergo conformational transition during ionization, *e.g.*, poly(methacrylic acid) (PMAA) and poly(glutamic acid) (PGA), another additional contribution to free-energy change due to conformational change should also be included in the quantity $(\partial G_{\mathrm{ion}}/\partial\alpha)$. The apparent p*K* can then be defined as

$$\mathrm{p}K_a = \mathrm{pH} + \log\left(\frac{1-\alpha}{\alpha}\right) \tag{3}$$

Plots of the observed pK_a against α have been found very useful in recognizing a pH-dependent conformational transition. For a polyelectrolyte such as PAA which does not undergo a conformational transition during ionization, pK_a is a monotonic increasing function of α.[2,9] In the cases of PMAA and PGA, and other distinctive polyelectrolytes, the curve of such a plot has a sharp rise at low α, followed by a maximum, or plateau region, and rises again at high α. The abnormal shape of the curve reflects additional work required for a conformational change in the chain brought about by ionization, *e.g.*, the globular coil-extended coil transition in PMAA[2,7-9] or the helix-coil transition in PGA.[2-5]

Figure 2 shows the plots of pK_a *vs.* α for the copolymer of this study (F4) in isopropyl alcohol-water (4:1) with ionic strengths of 0.0, 0.001, 0.005, and 0.01 *N* NaCl. A conformational transition is clearly indicated from the shape of these curves. In Figure 4 similar plots are presented for copolymers F4, F4A, and F4B of different acid

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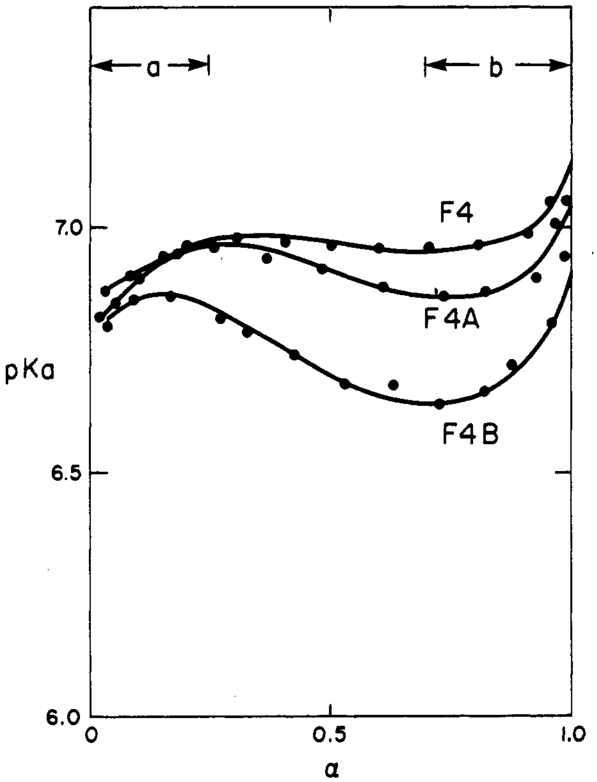

Figure 4. Potentiometric titration curves for fractions F4, F4A, and F4B in isopropyl alcohol-water (4:1) at 0.01 N NaCl.

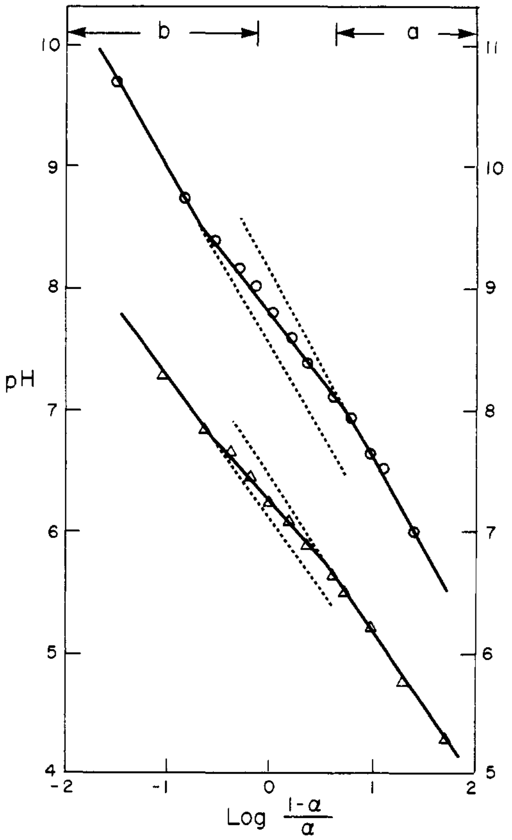

Figure 5. Henderson-Hasselbalch plots for F4. Circles and left-hand scale for isopropyl alcohol-water (4:1); triangles and right-hand scale for isopropyl alcohol-water (4:1) and 0.005 N NaCl.

contents but the same chain length in isopropyl alcohol-water (4:1) with 0.01 N NaCl, in which a transition is also evident. The regions labeled a and b in Figures 2 and 4 can be associated with the form a at a low degree of ionization and the form b at high degree of ionization existing after the conformational transition, respectively. The conformation at a low degree of ionization may be described as a compact globular coil with the possibility of hydrogen bonding between -COOH groups. The coil begins to open and extend on further ionization and goes through a transition region between $0.2 \simeq \alpha \simeq 0.6$. Ionization beyond this region does not alter the structure but merely requires more work for ionization, and the potentiometric titration curves continue to rise.

The above interpretation has been confirmed independently by viscosity measurements for F4 samples at the corresponding degree of ionization and ionic strength. Results of the inherent viscosity work are shown in Figure 3. Viscosity increases as α increases in the region a which corresponds to (a) region in Figure 2. The viscosity continues to increase through the transition region up to approximately $\alpha = 0.6$, where region b begins. Beyond $\alpha = 0.6$, the curves either show plateau regions or a downward trend. The downward trend of the curves can be explained by the fact that the titration medium becomes a poor solvent for the ionized polymer at high α, and also because the effective ionic strength of the solution resulting from counterion mobility increases as the titration proceeds.

B. Free-Energy Change. As was stated earlier, extra free energy is required to ionize a polyion which undergoes a conformational transition during ionization. The change in free energy for the process (un-ionized state a) → (un-ionized state b) is given by[16]

$$\Delta G_c = 2.3RT\int_0^1 (pK - pK_b)d\alpha \qquad (4)$$

$$= 2.3RT\int_0^1 (pH - pH_b)d\alpha \qquad (5)$$

The pK and pH in the equations above represent the observed values at α, and pK_b and pH$_b$ represent the hypothetical values for pure state b at the same α. It is evident that if curves of pK (or pH) against α and pK_b (or pH$_b$) against α are constructed, ΔG_c can be estimated from the area between the two curves. In the case of the helix-coil transition of PGA in certain ionic strength solutions, the plot of pK_b against α can be obtained by a linear extrapolation of the pK against α plot from the high-α region to $\alpha = 0$, as was done by Zimm and Rice.[16] Other workers studying PGA, including Olander and Holtzer,[5] and Nagasawa and Holtzer,[3] found it necessary to use a curved extrapolation to $\alpha = 0$, since the high-α region was not linear in their cases. For a polyelectrolyte such as PMAA, linear extrapolation is not possible. Nekrasova *et al.*[2] and Nagasawa *et al.*[9] were able to use a curved extrapolation to evaluate their data on PMAA. However, Leyte and Mandel,[7] whose data extend to higher α values, found even this technique unusable. Instead, they used the empirical Henderson-Hasselbalch plots to extrapolate their data through the transition region. Mandel and Stadhouder[8] in their studies of PMAA and partially methylated PMAA, and Nekrasova *et al.*[17] in their study of PMAA, also used this approach to extrapolate their titration data from high α to $\alpha = 0$. Being unable to use the linear extrapolation suggested by Zimm and Rice[16] for the present data, an alternative treatment using Henderson-Hasselbalch plots has been applied here to estimate the values for ΔG_c.

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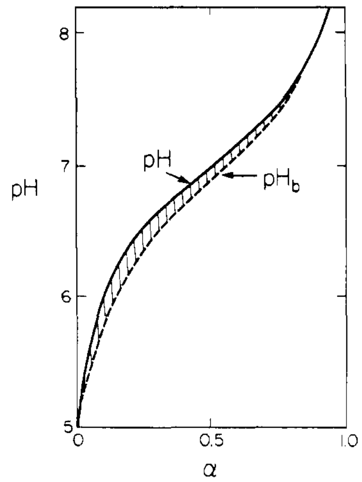

Figure 6. pH *vs.* degree of ionization for F4 in isopropyl alcohol-water (4:1) at 0.01 *N* NaCl. Curve marked $\mathrm{pH_b}$ is a curvilinear extrapolation obtained from Figure 5.

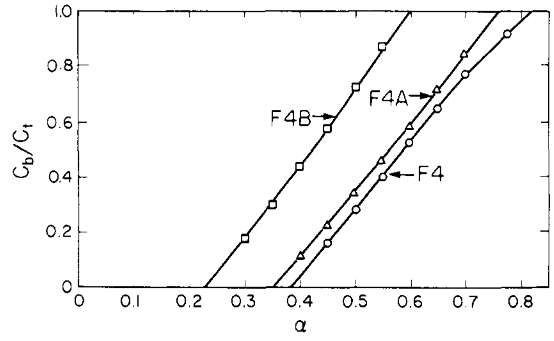

Figure 7. Fraction of state b *vs.* degree of ionization for fractions F4, F4A, and F4B at 0.01 *N* NaCl.

Experimental observations (for examples, see Katchalsky and Spitnik,[18] Strobel and Gable,[19] and Fischer and Kunin[20]) reveal that many polyelectrolytes conform to the empirical Henderson-Hasselbalch equation

$$\mathrm{pH} = \mathrm{p}K' - n \log \left(\frac{1-\alpha}{\alpha}\right) \tag{6}$$

where $\mathrm{p}K'$ and n are empirical constants depending on the polymer-solvent system. Since two conformational forms of the polymer are indicated by the titration data, it is expected that two distinct regions should be observed when the Henderson-Hasselbalch equation is applied. Representative plots of pH against log $[(1 - \alpha)/\alpha]$ for F4 are presented in Figure 5. These plots show two linear regions at low and high α separated by a transition region. By extrapolating the linear portions marked a and b into the transition region, it is possible to determine pH values for form a and form b in the transition region. The observed pH and extrapolated $\mathrm{pH_b}$ obtained in this manner are plotted against α for F4 at an ionic strength of 0.01 *N* in Figure 6 as an example of the procedure. ΔG_c has been estimated from the area of the shaded portion between the curves. Values of ΔG_c determined using the titration data presented in Figures 2 and 4 applying the graphical procedure are listed in Table I.

It is realized that the procedure for estimating ΔG_c using the Henderson-Hasselbalch plot is only empirical and the values derived are not very reliable. While there is no other precise method available for the present data, this procedure appears to be useful in estimating the values for ΔG_c. Although the average value of 70 cal/mol obtained here is only a rough estimate, its magnitude is comparable to values of 110 cal/mol for PMAA in 0.01 *N* NaCl[2,17] and 180 cal/mol for PMAA in H_2O.[21]

Table I
Calculated Values of ΔG_c, cal/mole

Polymer	Ester:Acid, Mole Ratio	ΔG_c, 0.0 *N*	ΔG_c, 0.001 *N*	ΔG_c, 0.005 *N*	ΔG_c, 0.01 *N*
F4	3:1	90	50	40	60
F4A	2:1				90
F4B	1:1			60	100

Table II
Transition Parameters for F4, F4A, and F4B

Copolymer	Ester:Acid, Mole Ratio	α_0	$f_{\alpha=1.0}$	$f_{\alpha=\alpha0}$
F4	3:1	0.38	0.25	0.10
F4A	2:1	0.35	0.33	0.11
F4B	1:1	0.22	0.50	0.11

C. Transition Parameters. The fraction of state b present in the transition region can be estimated as follows[19]

$$[C_b]/[C_t] = (\alpha - \alpha_a)/(\alpha_b - \alpha_a) \tag{7}$$

where

$$\alpha[C_t] = \alpha_a[C_a] + \alpha_b[C_b] \tag{8}$$

Here $[C_a]$, $[C_b]$, and $[C_t]$ are the concentrations of the states a and b and the total polymer, respectively, and α_a and α_b are the hypothetical values for α for the two states a and b during the transition at α. By extrapolating the linear portion of the curve described in Figure 5 into the transition region, values of α_a and α_b can be obtained at a given pH. The fractions of state b ($[C_b]/[C_t]$) are plotted against α in Figure 7 for the three copolymers studied. These curves show that the transition begins at the lowest α for F4B and begins at higher α values with decreasing acid content of the copolymers. Using the α values representing the start of the transition for the three polymers (α_0), it is possible to calculate the fraction of charge per residue existing at the beginning of the transition, $f_{\alpha=\alpha0}$ from the following relationship

$$f_{\alpha=\alpha_0} = \alpha_0(f_{\alpha=1.0}) \tag{9}$$

where $f_{\alpha=1.0}$ is the fraction of charge per residue at full ionization. The observed values of α_0, and the calculated values of $f_{\alpha=1.0}$ and $f_{\alpha=\alpha0}$ are listed in Table II. Again, application of the Henderson-Hasselbalch extrapolation technique was found necessary and the values derived here should be considered tentative. Nevertheless, the tabulation seems to indicate that although the transitions begin at different degrees of ionization (column under α_0), the fraction of charge per residue at the start of the transition (column under $f_{\alpha=\alpha0}$) is nearly the same for the three copolymers.

III. Conclusion

Potentiometric and viscometric studies of copoly(ethyl acrylate-acrylic acid) suggest that this polyelectrolyte

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undergoes a conformational transition during ionization in an isopropyl alcohol-water (4:1) mixture. Although the transition region is relatively broad compared with the range found for poly(methacrylic acid) in aqueous solution, the titration curve shows distinct characteristics of a polymer undergoing conformational change during ionization. This molecule probably assumes a compact globular coil structure at a low degree of ionization, possibly with some -COOH groups clustering together due to hydrogen bonding in the relatively nonpolar solvent. As the molecule dissociates, it transforms to a more extended state due to the breakdown of the hydrogen bonding and to the increasing repulsive forces of the charges along the chain. The free-energy change for this conformational transition has been estimated to range from 60 to 90 cal per mol; in view of the use of the Henderson-Hasselbalch equation to obtain the estimates they are regarded as tentative.

Three copolymers of the same chain length but different acid contents have been studied. A semiempirical treatment of the titration data indicated that although the start of titration region during ionization occurs at a lower degree of ionization for chains with higher acid content, the fraction of charge per residue at the onset of the titration seems to be the same for the three copolymers. This suggests that the distribution of charge may play little or no role in governing the onset of the transition.

Stress-Strain Isotherms and Stress-Temperature Coefficients of Poly(dimethylsiloxane) Networks in Compression

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ABSTRACT: Stress-strain isotherms at 30, 45, 60, 75, and 90° have been determined for compressed, unswollen poly(dimethylsiloxane) networks which had been prepared either in the undiluted state or in solution. For these networks in compression, deviations of the dependence of stress on strain from that predicted by the statistical theory of rubberlike elasticity are much less than is the case for polymer networks in elongation. The present data nonetheless give a value for the temperature coefficient of the unperturbed dimensions of the network chains which is in good agreement with published results on networks of poly(dimethylsiloxane) in elongation. This agreement thus seems to validate the intentional disregard of such deviations in analyses of stress-temperature measurements.

Most experimental studies of the elastic properties of rubberlike networks employ uniaxial elongation as deformation because of the relative ease with which such experiments may be carried out.[1-8] Comparatively little research has been done on networks in uniaxial compression because of difficulties due to the friction occurring between the compression plates and the sample surfaces in contact with them.[9,10] Since this friction interferes with the uniform expansion of the sample at these contact surfaces, a sample will frequently exhibit significantly nonuniform expansion ("barreling") in the direction perpendicular to that in which it is compressed. The corresponding uncertainty in the magnitude of the deformation of the sample obviously makes reliable interpretation of stress-strain data extremely difficult.

On the other hand, studies of networks in uniaxial compression have the very attractive characteristic of giving stress-strain relationships which exhibit much smaller deviations[3,10-20] ("Mooney-Rivlin C_2 terms"[21]) from the form predicted by the statistical theory[22,23] of rubberlike elasticity, than is the case for networks in uniaxial elongation. Such deviations from theory have in fact been held by some[24-29] to invalidate the interpretation of "thermoelastic" (stress-temperature) data carried out on elongated polymer networks at constant pressure, in particular the application of the statistical theory of rubberlike elasticity to such data in order to obtain the temperature coefficient of the unperturbed dimensions of the chains making up the network.[8,30-32] It is therefore obviously of very great

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(1) Surveys of experimental studies on rubberlike networks and related theory may be found in ref 2-8.

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(22) Reference 23 provides a list of references to papers in which the theory of rubberlike elasticity is developed.

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