Macromolecules 1992, 25, 7317-7323

Analysis of Polyelectrolyte Chain Conformation by Polarized Raman Spectroscopy

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Received July 27, 1992; Revised Manuscript Received September 15, 1992

ABSTRACT: Conformational changes of the weak polyelectrolyte, poly(acrylic acid), are monitored by polarized Raman spectroscopy as the polymer undergoes ionization in salt-free, semidilute solution. Persistence lengths are obtained by interpreting the depolarization ratio for CH stretching in terms of the relative number of gauche and trans conformers and by then inserting these conformer statistics into a simplified rotational isomeric state model. The results show that the polymer stiffens only slightly as it is ionized, a conclusion consistent with earlier scattering and NMR investigations conducted under comparable solution conditions. The data agree best with wormlike chain models that incorporate the full Poisson–Boltzmann equation; they do not follow Manning condensation inasmuch as the persistence length increases at ionizations above the condensation threshold.

Introduction

The structure and dynamics of neutral polymers in solution are reasonably described by the class of two-parameter theories, which characterize the global chain conformation in terms of a persistence length and an excluded volume parameter. This global description, in turn, must properly reflect chain conformation at the scale of a repeat unit. For example, the rotational isomeric state model provides a framework for predicting the persistence length using knowledge of bond lengths, bond angles, and torsional potentials. With polyelectrolytes the prescription for describing chain structure is less complete, presumably because electrostatic interactions act at all pertinent length scales, from the very local to the size of the entire chain; it is not obvious that global and local interactions can be separated in the same manner as with neutral polymers. Nonetheless, the most widely accepted theory for polyelectrolyte solutions, that of Odijk[1,2] and Skolnick and Fixman,[3] falls into the two-parameter class. Locally, the chain is modeled as a flexible line of smeared charge, and the persistence length is divided into two parts. One, the bare persistence length, describes the intrinsic stiffness of the chain backbone in the absence of electrostatic interactions and can be analyzed as for neutral polymers. The second, termed the electrostatic persistence length, characterizes the stiffness attributable to the energy differences as the line charge is bent. This component is predicted to depend strongly on the solvent conditions and the density of charge along the chain backbone. The two-parameter theory for polyelectrolytes does not attempt to describe local molecular structure and dynamics: it provides no insight into the conformational changes that underlie the predicted variations in the persistence length. The purpose of this work is to partially close this gap in our understanding of polyelectrolytes by measuring conformational changes as chain stiffness is varied.

Here, we describe the use of vibrational spectroscopy to probe the local structure of poly(acrylic acid) as electrostatic interactions are "tuned" by varying ionization. Our goal is to understand how local structure is modified as electrostatic interactions are introduced. Most previous solution characterizations of polyelectrolytes have employed methods such as viscometry and light scattering that provide only global structural information. These studies have been interpreted to show that chain stiffness increases with ionization, and it has been suggested that in the extreme case the chain becomes fully extended. Vibrational spectroscopy is ideally suited to address issues of local structure and thus complements the previous work. For the disordered chain conformations typically found in solution, the various vibrational bands associated with specific chain conformations overlap, making it difficult to precisely characterize spectral features. Consequently, we focus on the information provided by polarization studies, which are sensitive to changes in the conformational distribution, i.e., to changes in the distribution of torsional angles among the various rotational states permitted in a vinyl chain backbone. These changes are ultimately the ones responsible for variations in the persistence length. Similar approaches have been pursued to study conformational changes in neutral polymer solutions, for example, to identify the Θ condition or to quantify the enthalpy or entropy of helix formation.[4-8] Direct calculation of the persistence length from depolarization data has been hampered, though, by the absence of polarizability derivative values for different conformations, even in small molecules. Recent literature results,[9-11] however, make it possible, in conjunction with a simplified form of the rotational isomeric state model, to calculate the persistence length using the CH stretching depolarization ratio of poly(acrylic acid). For comparison and verification, the analogous polarized vibrational data for small model compounds are also presented.

Most polyelectrolyte theories rigorously apply only in dilute solution, and unfortunately, the sensitivity of the spectroscopic technique makes it difficult to apply at low concentration. Our study thus focuses on salt-free solutions in the semidilute regime, corresponding to mass concentrations in the 10% range. At such large polymer concentrations, the bare persistence length is always greater than the electrostatic persistence length; thus, changes in chain stiffness with ionization are limited. Improved instrumentation should eventually permit application of the same method to dilute solutions, and there is a strong incentive to push in this direction as electrostatic effects in dilute solution are expected to be much greater, especially for salt-free solutions. The persistence lengths for poly(acrylic acid) from the vibrational method will be compared to those obtained by scattering and also to those predicted by various wormlike chain theories.

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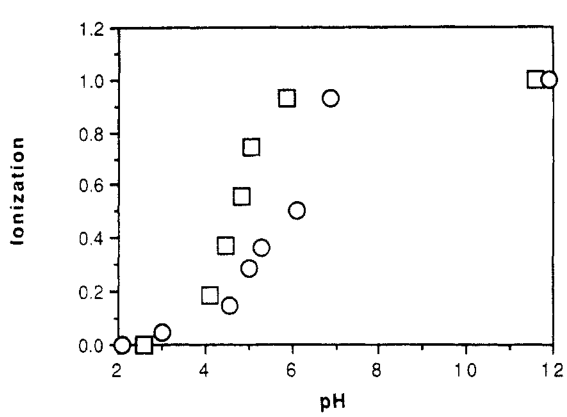

Figure 1. PAA (circles) and propionic acid (squares) titration curves.

Procedures

Experiment. Solutions of poly(acrylic acid) (PAA) were prepared by dissolving 0.1 g of 450 000 molecular weight polymer (Polysciences Lot No. 36320, Catalog No. 3312) in 1.0 mL of distilled water. The purity of the polymer sample was checked via elemental analysis, which found 49.5 wt % carbon and 5.6 wt % hydrogen, close to the theoretical values of 50.0 wt % carbon and 6.0 wt % hydrogen. Solutions were titrated with successive amounts of sodium hydroxide (Fisher Scientific Lot No. 746540 Catalog No. S-320) using a digital pH meter (Cole Parmer Solution Analyzer Model No. 5800-05 with Model No. L-05997-10 pH electrode). A typical titration curve is shown in Figure 1. Ionization I is calculated from

$$I = \{(-[\mathrm{OH}^-] + [\mathrm{H}^+] + [\mathrm{MOH}])/C_p\} \quad (1)$$

where $[\mathrm{OH}^-]$ and $[\mathrm{H}^+]$ are hydroxide and hydrogen ion concentrations determined from the pH of the solution, and [MOH] and C_p are the concentrations of the ionizing agent and polymer, respectively.[12]

Depolarized Raman spectra were obtained using the incident intensity of a vertically polarized Spectra Physics Model 165-08 argon ion laser tuned to the 5145-Å excitation line. A Newport Model RSA-2 polarizer selected scattered light of the appropriate linear polarization state, and this light was subsequently converted to circular polarization by a scrambler, ensuring that gratings of the detection system would not induce polarization artifacts into the spectra. Photons of the desired wavelength were subsequently passed to a photomultiplier tube by an ISA Ramanor U-1000 double monochromator. Photon counts were acquired by a personal computer operating Spectra-Link software. Attention focused on the CH stretching region, from 2850 to 3050 cm^{-1}, which was scanned at 10 s/point at 0.5-cm^{-1} increments.[13] During scanning, solutions were contained in a 10-mm × 10-mm × 50-mm rectangular quartz cuvette positioned to maximize the scattered intensity passing through the double monochromator. The four horizontal slits of the monochromator were opened to 300 μm, and the four vertical slits were opened completely. With these modifications, the signal to noise was much improved over conventional arrangements. Before a scan, samples were allowed to equilibrate in the 100-mW incident beam for ca. 12 h.

Spectra were initially treated with the Savitsky–Golay smoothing option (sensitivity = 25) in the Spectra Calc program (Galactic Industries). Obvious minima on each side of the appropriate peak were then hand-picked, a two-point baseline correction was performed, and the peak area was calculated. Duplicate measurements on the same sample were performed to estimate the reproducibility of the method; this reproducibility is indicated by the error bars in each figure. Inhomogeneities that produce multiple scattering have often been blamed for errors in the measurement of the depolarization ratio.[14] To determine if multiple scattering was important, PAA solutions were placed in the incident beam in front of a capillary filled with CCl_4, from which depolarized spectra were taken. If the PAA solutions scrambled the incident light's polarization state, the apparent depolarization spectra of CCl_4 would change from the expected value. The depolarization ratio of the 459-cm^{-1} band of CCl_4, however, remained zero whether or not PAA solutions were in place. For example, the depolarization ratio for the 459-cm^{-1} band of CCl_4 changed on average from 0.0027 ± 0.0012 to 0.0022 ± 0.0011 when PAA solutions were placed before it. Multiple scattering was thereby discounted.

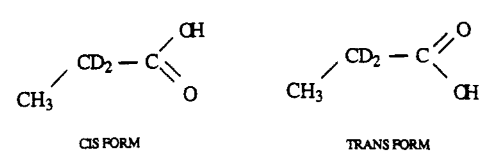

Figure 2. Cis and trans forms of propionic-*2,2*-d_2 acid.

To verify that the depolarization ratio was sensitive to conformational change in the backbone, and not to the ionization of the acid group, the depolarization ratio of the CD stretching vibration of a model compound, propionic-*2,2*-d_2 acid (Aldrich Catalog No. 37,792-9), was also examined as a function of ionization. CD stretching rather than CH stretching in the fully protonated acid was measured to avoid interference from CH_3 stretching. Solutions of the acid in distilled water at 50.0 wt % were studied in the same manner as the PAA solutions. A typical titration curve for propionic acid is shown in Figure 1. If one considers the acid carbon and oxygen part of a side group, as in PAA, no conformational changes occur in propionic acid since there are only two "backbone" carbons. Cis–trans isomerization can occur, however, if the acid carbon and oxygen are considered part of the backbone, as shown in Figure 2 and as studied by Umemura in the crystalline state;[15] no distinctions have been made in the literature between the conformers of propionic acid in the liquid state.[16-19] We presume that none exist and interpret spectral differences entirely in terms of ionization.

Fermi resonance can affect the measured intensity of CH stretching by borrowing intensity from an overtone or combination band of a second vibration of the same symmetry and chemical group. Since we are using CH stretching intensity as a conformational probe, we must understand how this intensity is affected by other vibrations. Therefore, unpolarized FT Raman spectra of both PAA and the deuterated model compound were taken to probe the CH or CD stretching region, respectively, as well as to uncover any vibrations which would interact with this region via Fermi resonance. Spectra were collected in the 180° scattering geometry using 1.06-μm incident light from an unpolarized CVI Nd/YAG laser and a Bruker IFS 88 FTIR equipped with a FRA 106 Raman sample module. One thousand scans were taken at 4-cm^{-1} resolution, with ca. 1.3 W applied at the sample. The spectrum of the solvent-filled, silvered quartz cuvette was subtracted using the Spectra Calc program to attain the true polymer spectrum.

Conformational Analysis Using Depolarized Scattering Data. The depolarization ratio ρ of a Raman band for 90° scattering geometry and parallel polarized incident light is defined as the ratio of perpendicularly polarized scattered intensity to that which is parallel polarized or

$$\rho = (I_\perp / I_\parallel) \quad (2)$$

Focusing on the conformationally sensitive bands of a vinyl polymer, the depolarization ratio can be equated to the number ratio of gauche and trans isomers that exhibit perpendicular and parallel polarized scattering:[20]

$$\rho = \frac{x I_{\perp g} + I_{\perp t}}{x I_{\parallel g} + I_{\parallel t}} \quad (3)$$

Here, x is the isomeric gauche to trans ratio, $I_{\perp g}$ and $I_{\perp t}$ are the scattered intensities for gauche and trans isomers analyzed by perendicular polarization, respectively, and $I_{\parallel g}$ and $I_{\parallel t}$ are these intensities analyzed by parallel polarization.

To reduce eq 3 to a more useful form, we first explore the separate depolarization ratios for the gauche and trans isomers of PAA, ρ_{gauche} $(=I_{\perp g}/I_{\parallel g})$ and ρ_{trans} $(=I_{\perp t}/I_{\parallel t})$, respectively. We rely on a literature analysis of the symmetric and asymmetric CH_2 stretching vibrations of n-butane, the simplest model compound possessing gauche and trans isomerism. The depolarization ratios can be written in terms of each isomer's overall polarizability tensor α and its derivative α' with respect to the normal coordinate of vibration Q

$$\rho = \frac{3\gamma'^2}{45\bar{\alpha}'^2 + 4\gamma'^2} \tag{4}$$

where γ' is the derivative of the anisotropy of α and $\bar{\alpha}'$ is the derivative of the trace of α, both with respect to Q.[21] Therefore, γ' can be expressed more explicitly as

$$\gamma'^2 = \left(\frac{\partial\gamma}{\partial Q}\right)^2 = \frac{1}{2}[(\alpha'_1 - \alpha'_2)^2 + (\alpha'_2 - \alpha'_3)^2 + (\alpha'_3 - \alpha'_1)^2] \tag{5}$$

where α'_1, α'_2, and α'_3 are the partial derivatives of the principal polarizability elements, and $\bar{\alpha}'$ is given

$$\bar{\alpha}' = \left(\frac{\partial\bar{\alpha}}{\partial Q}\right) = \frac{1}{3}(\alpha'_1 + \alpha'_2 + \alpha'_3) \tag{6}$$

The needed derivatives of the polarizability tensor are estimated using the Wolkenstein approximations

$$\alpha' = \frac{\partial\alpha}{\partial Q} = \sum_j \frac{\partial\alpha^j}{\partial r_j}\frac{\partial r_j}{\partial Q} \tag{7}$$

where $\partial\alpha^j/\partial r_j$ is the derivative of the polarizability tensor of the jth bond with respect to its internal coordinate r_j and $\partial r_j/\partial Q$ is the derivative of this coordinate with respect to Q. The form of eq 7 implies the independence of each bond's polarizability tensor; the sum is over all bonds associated with the vibration. To calculate the depolarization ratio for CH stretching, we use the diagonalized $\partial\alpha^{CH}/\partial r_{CH}$ elements for gauche and trans n-butane obtained by Gough via a self-consistent field analysis and assume values for $\partial r_j/\partial Q$ consistent with symmetric and asymmetric stretching.[9] Substitution yields ρ_{gauche} for the sum of the CH symmetric and asymmetric stretching vibrations as 0.7718 (the maximum value of this sum is 1.5 since the maximum value of individual vibration is 0.75) and ρ_{trans} as 0.0552.

To explicitly relate ρ to x, one additional relationship is required. We now relate the total intensity scattered by the gauche isomer I_{gauche} ($=I_{\perp g} + I_{\parallel g}$) to that scattered by the trans isomer I_{trans} ($=I_{\perp t} + I_{\parallel t}$). The intensity of scattered light when the incident light is plane polarized can be obtained by[22]

$$I = KI_0 \frac{(\nu_0 - \nu)^4}{m\nu(1 - e(-h\nu/kT))}[45\bar{\alpha}'^2 + 7\gamma'^2] \tag{8}$$

where K is a constant, I_0 is the incident intensity, ν and ν_0 are the absolute frequencies of the normal vibration and incident light, respectively, and m is the reduced mass. Using the above calculated values of $\bar{\alpha}'$ and γ' for gauche and trans isomers of n-butane and the frequencies of the symmetric and asymmetric CH stretching vibrations given by Snyder[23] for the same isomers, we find

$$0.648 I_{gauche} = I_{trans} \tag{9}$$

This relationship, along with the values for ρ_{gauche} and ρ_{trans}, allows eq 3 to be rewritten in its most useful form

$$x = \frac{0.0601 - 1.0887\rho}{\rho - 0.7718} \tag{10}$$

which serves as the key operating tool to analyze polymer conformations from our spectroscopic data.

Method To Calculate the Persistence Length. To relate the isomeric ratio x to the persistence length L_t, we assume a rotational isomeric state model with one low-energy trans state of statistical weight one and two higher, equal-energy gauche states of statistical weight σ. The isomeric ratio is then

$$x = 2\sigma \tag{11}$$

with σ defined

$$\ln \sigma = -\Delta E/RT \tag{12}$$

where ΔE is the energy change between the two states, R is the gas constant, and T is the temperature. The persistence length is calculated from σ in the usual manner. We first calculate the average of cos ϕ, the cosine of the dihedral angle

$$\langle \cos \phi \rangle = z^{-1}\sum u\eta \cos \phi\eta \tag{13}$$

where z is the partition function or the sum of statistical weights, $u\eta$ is the statistical weight of state η, and $\phi\eta$ is the dihedral angle of that state. If the three rotation states are described by ϕ = 0, +120, and −120°, of statistical weight 1, σ, and σ, respectively, eq 13 becomes

$$\langle \cos \phi \rangle = (1 - \sigma)/(1 + 2\sigma) \tag{14}$$

The limiting characteristic ratio at high molecular weight, C_∞, can then be written

$$C_\infty = \left(\frac{1 - \cos\theta}{1 + \cos\theta}\right)\left(\frac{1 + \langle\cos\phi\rangle}{1 - \langle\cos\phi\rangle}\right) \tag{15}$$

where θ is the valence angle between bonds.[24] The persistence length is finally obtained

$$L_t = (L/2)(C_\infty + 1) \tag{16}$$

where L is the carbon–carbon bond length.

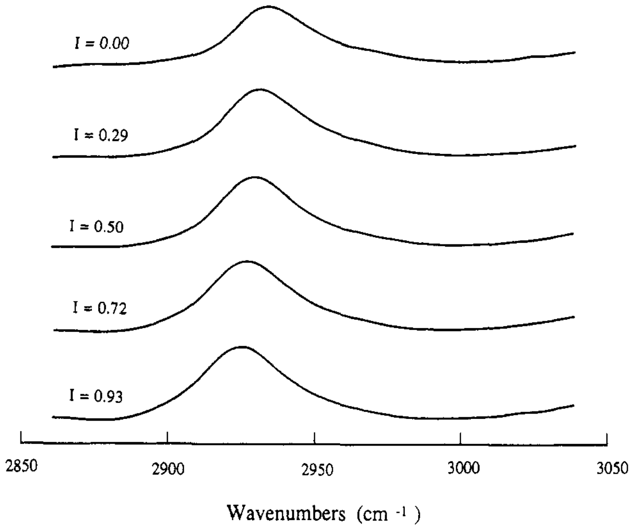

Figure 3. X(ZZ)Y spectra of 10.0 wt % PAA as a function of I.

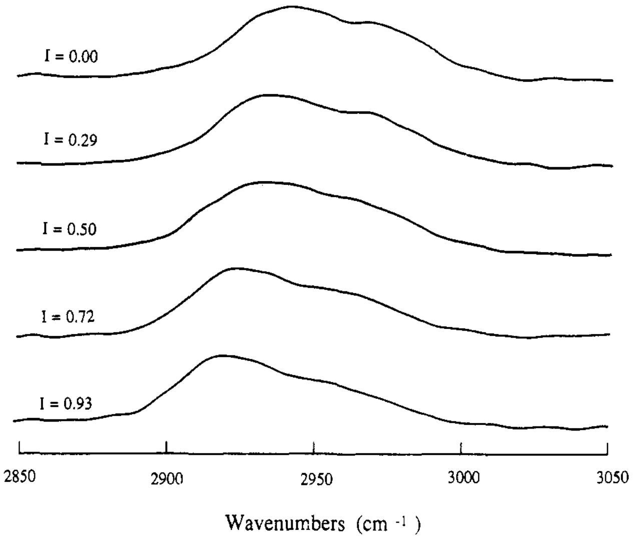

Figure 4. X(ZX)Y or anisotropic spectra of 10.0 wt % PAA as a function of I.

Results

Depolarized Spectra and Deduced Conformational Parameters. Polarized Raman spectra of PAA in the CH stretching region are plotted in Figures 3 and 4, respectively, with PAA ionization I as a parameter. The

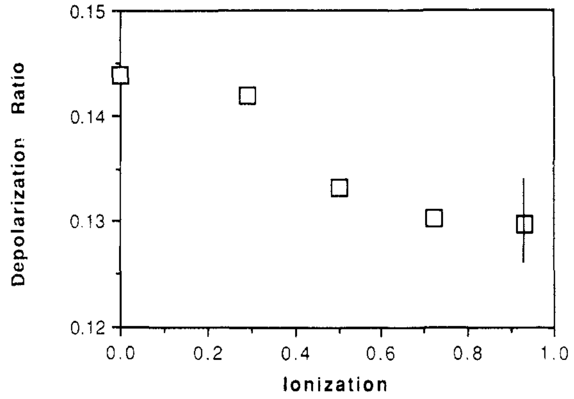

Figure 5. Depolarization ratio of the CH stretching region of PAA vs *I*.

Table I
Conformational Analysis of Depolarized Raman Data

ionization	ρ	ΔE (cal/mol)	C_∞	L_t (Å)
0	0.1438	1471	18.0	14.6
0.29	0.1418	1486	18.5	15.0
0.50	0.1332	1553	20.7	16.7
0.72	0.1303	1578	21.6	17.4
0.93	0.1296	1584	21.8	17.6

CH stretching region obviously consists of two or more components, a feature especially notable in Figure 4. The components include the CH symmetric and asymmetric stretching vibrations, along with the possible Fermi resonance interactions that occur between the above and overtone or combination bands. With resolution of the components difficult, the area underneath the full peak is used to calculate the depolarization ratio ρ. These ratios are plotted as a function of *I* in Figure 5. This figure indicates that ρ is a weakly decreasing function of *I*. A decrease is expected if more trans conformer is generated upon ionization, because the trans conformer has a lower depolarization ratio than the gauche conformer, as argued earlier for the case of *n*-butane and as inferred for other vinyl polymers.[6]

The ΔE, C_∞, and L_t values calculated from the depolarization data are assembled in Table I. The energy difference between isomers grows by ca. 8% from its initial value of 1471 cal/mol for the un-ionized polymer to 1584 cal/mol for the fully ionized sample. In comparison, the energy change between the same isomers is 600 cal/mol for polyethylene at room temperature and reportedly is 1100–2300 cal/mol for PTFE.[24] The smallness of the change in conformer energy upon PAA ionization seems to indicate that the polymer does not stiffen appreciably as it ionizes. The associated C_∞ values range from 18.0 when PAA is unionized to 21.8 when fully ionized. Newman et al. reported $C_\infty = 6.3$ for un-ionized PAA in dioxane,[25] while Takahashi et al. reported $C_\infty = 11.3$ for fully ionized PAA in 1.5 M NaBr at the Θ condition;[26] both values were derived from intrinsic viscosity data. Using a light-scattered method, Takahashi et al. also reported $C_\infty = 21$ for PAA in 1.5 M NaBr at the Θ condition.[27] Allegra et al. performed a calculation of the unperturbed dimensions of ionized PAA as a function of tacticity and found $C_\infty \sim 10$ when the chain was atactic.[28] According to the present analysis, L_t changes from 14.6 to 17.6 Å upon ionization. Muroga et al. studied persistence length changes for PAA in similar semidilute solutions using SAXS and found $L_t = 8$–15 Å.[29] These authors failed to see a consistent change in L_t with increasing ionization, however. The lack of change in local conformation was also seen by Muroga via NMR for isotactic PAA upon ionization.[30] In this instance, vicinal coupling constants of the methylene protons of PAA, which are sensitive to the chain backbone dihedral angle, were not observed to vary as the polymer ionized.

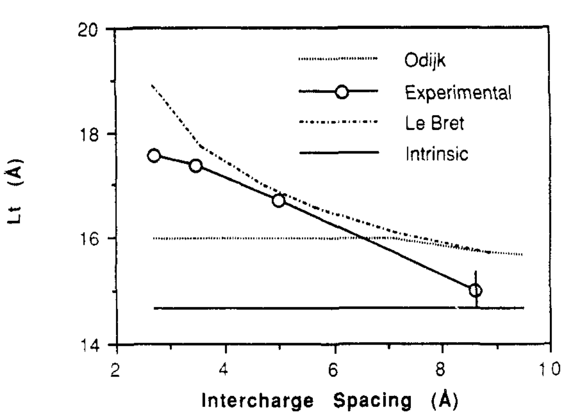

Figure 6. Comparison of experimental and theoretical persistence lengths. The Le Bret curve is plotted for the case where the ratio of the dielectric constant inside the wormlike cylinder to that outside is zero.

It is widely known that the presence of an asymmetric center in a vinyl polymer complicates the rotational isomeric state analysis of the dihedral angle.[24] Only the simplest analysis was performed here, one that ignores such complication. The reasonable agreement between the present results and those of earlier investigations thus might not have been expected. That our analysis apparently works may suggest that conformer energy differences partly arise from short but nonlocal interactions, making the proper dihedral angle choice of little import. The Debye–Huckel screening length, a scale for the reach of electrostatic forces in an ionic solution, never falls below 6 Å, which is greater than the PAA monomer length of about 2.5 Å. We are currently attempting to understand nonlocal force effects further using molecular simulations.

Comparison to Theory. In Figure 6 we compare the measured persistence lengths as a function of *I* to the predictions of various wormlike chain models. To draw the different curves on a single figure, it is assumed that the intrinsic and electrostatic components of L_t are additive and that L_e disappears at zero ionization. Our experimental L_t at zero ionization is thus the intrinsic persistence length. We first discuss comparisons to single-chain models or those that neglect any interchain contributions to chain stiffening. Odijk's model employs the linearized Poisson–Boltzmann equation to balance thermal motion with the electrostatic energy to bend a line of charge, obtaining L_e through the general relation between the bending force constant and the persistence length.[1] Skolnick and Fixman independently derived the same L_e formula.[3] Although rigorously valid only at low charge density, it has been suggested that Odijk's model can be extrapolated to high charge densities by asserting Manning type ion condensation[2,31] even for salt-free solutions.[32] For our case of a salt-free polyelectrolyte whose charge density varies with ionization, we can write $L_e \approx (16\pi \mathbf{Q} L_m C_p)^{-1}$ for $A > \mathbf{Q}$ and $L_e \approx (16\pi A L_m C_p)^{-1}$ for $A \leq \mathbf{Q}$. Here $\mathbf{Q}$ is the Bjerrum length $(= e^2/\epsilon kT)$, L_m is the repeat unit length (=2.5 Å), and backbone charges are separated by average distance A $(= L_m/I)$. The figure reveals a major discrepancy between Odijk's theory and experiment at intercharge spacings less than the Bjerrum length, a discrepancy rooted in the assumption of Manning condensation. This assumption eliminates the influence of *I* above the condensation threshold at $A = \mathbf{Q}$. The data clearly show electrostatic chain stiffening above the threshold.

Line charge models can be improved by incorporating both nonlinear electrostatic effects and a finite chain radius; ion condensation then is not assumed at high charge densities. We are aware of only one salt-free persistence length prediction, that by LeBret, and he considered less concentrated solutions than ours.[33] We extrapolated his tabulated values to our C_p using the excellent power law correlation between C_p and L_e noted in his calculations. Figure 6 shows this extrapolation for PAA modeled as a cylinder of 2-Å radius and of smeared charge density L_m/I. These improved calculations fall closest to our data at low intercharge spacings. The cause for the better agreement is clear: the low-potential approximation implicit in the linearized Poisson–Boltzmann equation underestimates the potential near the surface of the charged backbone, and the potential in this region is crucial in establishing L_e for highly charged polymers.

The correlation length in these semidilute solutions is of the same order as the measured persistence length.[32] It may seem unreasonable to ignore, as in the theories just discussed, the influence of interchain interactions on L_e. Witten and Pincus[34] and Hayter et al.[35] present theories that attempt to incorporate chain–chain interactions in semidilute polyelectrolyte solutions and, more specifically, their effect on chain stiffness. Both approaches assume that L_t is dominated by L_e. As a result, the theories are unable to provide predictions for our system.

Combining the Odijk theory with the formalism developed here, it is interesting to calculate how ρ changes as the concentration of a salt-free PAA solution is reduced. For the 10.0 wt % solution of this study, we observe a 5% change in ρ as I varies from 0 to 100%. However, if this 100% ionized solution could be examined at 0.10 wt % PAA, the predicted change in ρ is over 50%. The full utility of our method to monitor conformational changes in polyelectrolytes will not be known until experiments at lower C_p are performed.

Analysis of Fermi Resonance and Ionization Effects on the CH Stretching Vibration. As noted earlier, both Fermi resonance and acid group ionization could interfere with the CH stretching bands critical to our conformational analysis. These two effects will now be assessed by a more detailed study of the relevant PAA and model compound spectra.

The only possibility for a Fermi resonance interaction is between an overtone of the $\delta(CH_2)$ bend at 1456 cm^{-1} and a CH stretch of the same symmetry and chemical group. We probe this interaction using the isotropic and anisotropic spectra of PAA, a format which will most effectively separate the symmetric and antisymmetric CH stretching vibrations, due to their different contributions to the trace and anisotropy polarizability derivatives. Isotropic and anisotropic spectra are calculated

$$I_{\text{iso}} = I_{\parallel} - \frac{4}{3}I_{\perp} = 45K'\left(\frac{\partial\bar{\alpha}}{\partial Q}\right)^2 \qquad (17)$$

$$I_{\text{aniso}} = I_{\perp} = 3K'\left(\frac{\partial\gamma}{\partial Q}\right)^2 \qquad (18)$$

respectively.[36] Figures 4 and 7 display these spectra for PAA. We assume that the lower frequency component can be assigned to $\nu_{\text{sym}}(CH)$ and that this vibration is of the same symmetry as the overtone of the $\delta(CH_2)$ bend in propionic acid.[17] A Fermi resonance interaction should be most apparent in the isotropic spectra, as these are dominated by symmetric CH stretching.[37] The isotropic spectra in Figure 7 show one asymmetric peak, which shifts from 2934 to 2926 cm^{-1} upon ionization. We cannot distinguish a component attributable to a Fermi resonance interaction. The anisotropic spectra in Figure 4 show two components, one at 2940 cm^{-1}, which shifts to 2921 cm^{-1} upon ionization, and one at 2962 cm^{-1}, which shifts to 2951 cm^{-1} upon ionization. No features can clearly be assigned to Fermi resonance interactions.

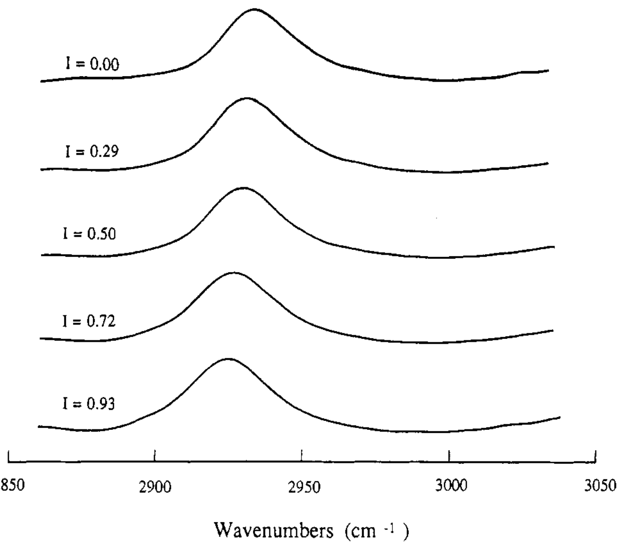

Figure 7. Isotropic spectra of 10.0 wt % PAA as a function of I.

The shifts to lower frequency and closer proximity to the overtone of the $\delta(CH_2)$ bend could suggest that the unverified Fermi resonance interaction grows with ionization. We assume that the overtone of the $\delta(CH_2)$ bend does not shift in frequency as a function of ionization because our unpolarized FT Raman data of PAA as a function of ionization show that the $\delta(CH_2)$ fundamental does not. If this assumption is true, the shifts serve to lower ρ beyond that expected from conformational change alone, based on their effect on the parallel polarized spectra. On the other hand, the frequency shifts could also indicate increasing chain order. For example, Snyder et al. calculate that the symmetric/asymmetric CH stretches for poly(ethylene) shift upward about 6 cm^{-1} in unpolarized spectra as chains become disordered.[37] As seen in Figure 8, the corresponding vibrations in our unpolarized FT Raman spectra shift from 2935 to 2921 cm^{-1} as a function of ionization. A final possibility, discussed below, is that the frequency shift is related directly to ionization.

To assess whether ionization affects ρ, we first analyze the relevant bands for propionic-2,2-d_2 acid. The depolarized spectra, shown in Figures 9 and 10, exhibit multiple bands in the CD stretching region, as did the CH stretching vibrations in PAA. Although resolution of the components into CD symmetric and asymmetric stretches is possible for the model compound, ρ is calculated from the area underneath all CD stretching vibrations, maintaining the procedure used for PAA. The depolarization ratio of propionic-2,2-d_2 acid increases from 0.191 to 0.200 with ionization, a trend opposite to that seen for PAA with ionization. Inasmuch as no conformational transition occurs for propionic acid, its ρ depends only on ionization. Analogous ρ increases have been tabulated in compounds with substituents of increasing electronegativity on the carbon involved in CH stretching,[38,39] and we believe the same phenomenon is operative here. If ρ for PAA is sensitive to this effect and if conformational and ionization effects are additive, the changes in ρ due to conformational changes are greater than considered earlier (0.144–0.121 rather than 0.144–0.130). The ensuing minor changes in

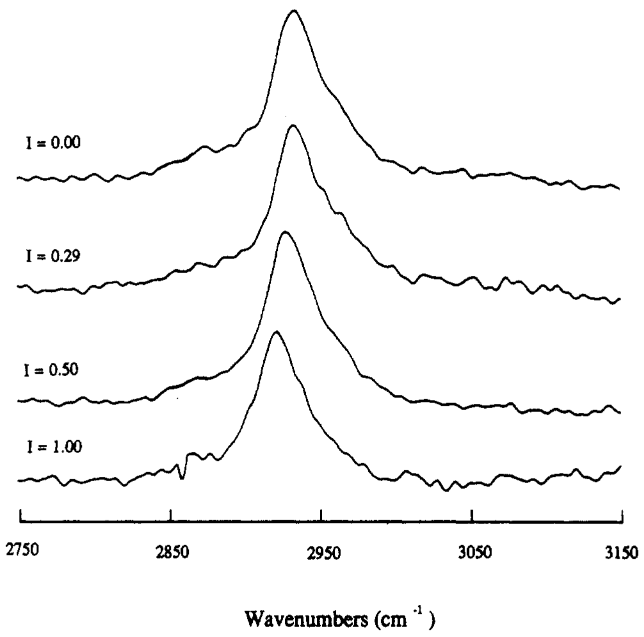

Figure 8. Unpolarized FT Raman spectra of 10.0 wt % PAA as a function of *I*.

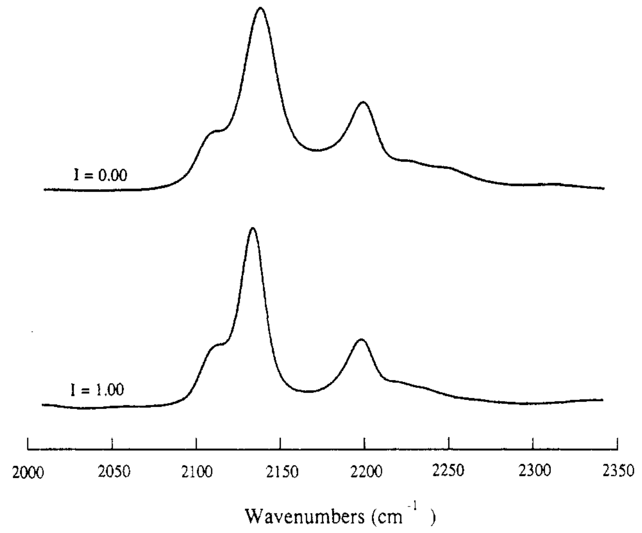

Figure 9. X(ZZ)Y spectra of 50.0 wt % propionic-2,2-d_2 acid as a function of *I*.

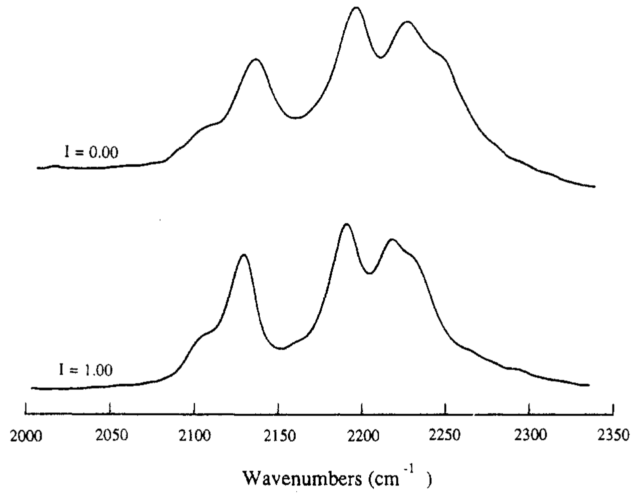

Figure 10. X(ZX)Y spectra of 50.0 wt % propionic-2,2-d_2 acid as a function of *I*.

ΔE, C_∞, and L_t are given in Table II. As for PAA, Fermi resonance can affect the CD stretching vibrations of propionic-2,2-d_2 acid and, hence, our measure of how ionization changes the CD depolarization ratio. Unfortunately, it is difficult to assess this affect from our FT Raman and dispersive Raman data without a full normal coordinate analysis.

Table II
Ionization Correction to PAA Depolarization Data

ionization	ΔE (cal/mol)	C_∞	L_t (Å)
0.00	1471	18.0	14.6
0.93	1662	24.9	20.0

The Raman spectra of propionic-2,2-d_2 acid can also be analyzed for frequency shifts with ionization to determine if the corresponding shifts for PAA are interpretable solely in terms of conformation, as suggested before, or in terms of ionization as well. The symmetric CD_2 stretches in both the isotropic and anisotropic spectra shift from 2138 cm^{-1} when un-ionized to 2134 cm^{-1} when ionized. No change is seen in the asymmetric CD_2 band of the isotropic spectra, and only a small shift from 2197 to 2194 cm^{-1} in the anisotropic spectra is seen. Unpolarized FT Raman spectra show a 2198–2196-cm^{-1} shift for the CD_2 asymmetric stretch and a 2136–2133-cm^{-} shift for the CD_2 symmetric stretch upon ionization. The shifts for PAA upon ionization are all much larger, but it is clear from the model compound data that we cannot unambiguously correlate frequency shifts with a disorder to order transition.

Conclusion

We have used polarized Raman spectroscopy and a simplified form of the rotational isomeric states model to calculate a persistence length for PAA as it is ionized with sodium hydroxide. The persistence length changes from 14.6 Å when the molecule is un-ionized to 17.6 Å when it is ionized. The small change indicates that the molecule does not stiffen appreciably as it ionizes in a salt-free, semidilute solution. The lengths calculated fall within the range of persistence lengths determined via SAXS by Muroga et al.[29] Our data agree best with wormlike chain models that incorporate the full Poisson–Boltzmann equation for determining the potential around the polyion; the data do not follow Manning condensation. This investigation clearly demonstrates that Raman spectroscopy can help sort out the confusing interplay of local and nonlocal forces in polyelectrolytes. Efforts are underway to extend the method to lower polymer concentrations, where electrostatic forces become more dominant and the persistence length becomes a more sensitive function of ionization.

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Registry No. PAA, 9003-01-4; $EtCO_2H$, 79-09-4.