Laser-Excited Raman Studies of the Conformational Transition of Syndiotactic Polymethacrylic Acid in Water

J. L. Koenig, A. C. Angood, J. Semen, and J. B. Lando

Contribution from the Division of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106.

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Abstract: The Raman spectra of syndiotactic polymethacrylic acid were investigated in the solid state, and in water solution as a function of neutralization. The Raman and infrared spectra of the solid polyacid indicate a helical conformation with a pitch of 3:1 or greater. The Raman spectra at various degrees of neutralization indicate progressive changes in C–COOH motions in a neutralization range from 0.1 to 0.4, superimposed on the expected changes occuring as a function of ionization. The changes from 0.1 to 0.4 neutralization can be explained in terms of the breakup of hydrophobic methyl–methyl interactions, but unlike the denaturization of globular proteins this transition is progressive, not cooperative.

Protein denaturation in aqueous solution occurs by a process that is not well understood. A study of the behavior of simple synthetic polyelectrolytes may cast some light on the behavior of proteins. A conformational transition of polymethacrylic acid (PMAA) in aqueous solution occurs within a critical interval of the degree of neutralization of the polyelectrolyte.[1–5] This transition occurs at a degree of neutralization of approximately 0.2–0.3. It has been suggested that at very low degrees of ionization, the polymethacrylic acid molecules have very compact globular structures stabilized by internal hydrophobic methyl–methyl interactions.[1] Although the external COOH groups are preferentially ionized as base is added, the fewer COOH groups in the interior are also ionized but at a slower rate. When the charge created in the interior by the titration reaches a critical value, a cooperative transition occurs to a more extended form.[1] This effect marks the conformational transition.

It is our intention in this paper to report some laser-excited Raman spectroscopic studies of this transition of PMMA in water. Since water scatters in only one region of the Raman spectrum (1650 cm^{-1}), detailed structural information can be obtained concerning the mechanics of the transition. In addition, some information about the conformation of syndiotactic PMAA and the salt in aqueous solution is obtained.

Experimental Section

Syndiotactic polymethacrylic acid was synthesized at −78° by irradiating a 20% (by volume) solution of distilled methacrylic acid in dry 1-propanol with 10 Mrads of cobalt-60 γ radiation. The polymer contained 88% syndiotactic triads as determined from 60-Mc proton resonance spectra of the methylated (with diazomethane) polymer.

Aqueous solutions of polysodium methacrylate were prepared by dissolving 3 g of the polyacid in 27 g of an equivalent amount of aqueous carbonate-free sodium hydroxide. Solutions of the polymer at degrees of neutralization between 0 and 1 were prepared by mixing the salt solution with appropriate volumes of a 10% (by weight) aqueous solution of the polyacid. Laser–Raman spectra of the polymer solutions and of the solid polyacid and its sodium salt were obtained with a spectrometer which has been previously described.[6] Infrared spectra of the two solids in potassium bromide pellets were obtained using a Perkin-Elmer Model 521 spectrometer.

Results and Discussion

A. Structure of PMAA in Aqueous Solution. The Raman spectra of PMAA in the solid state and in aqueous solution are shown in Figures 1 and 2. The ir and Raman frequencies are compared in Table I for the polyacid. Examination of Figures 1 and 2 reveals a striking similarity in the Raman spectra of the solid and aqueous solution. Only two frequency shifts are observed upon dissolution. The band at 764 cm^{-1} in the solid moves to 772 cm^{-1} in aqueous solution, while the band at 1673 cm^{-1} moves to 1685 cm^{-1}. The similarity in Raman spectra suggests that little, if any, detectable conformational change in the PMAA structure occurs with dissolution. Presumably the local structure in aqueous solution is similar to the solid-state structure.

The Raman spectrum of the solid-state polymer shows a broad band centered at 1673 cm^{-1} in the region associated with the carbonyl stretching frequency. This carbonyl frequency is below the value of 1709 cm^{-1} expected for free carboxylic acid groups. The frequency of 1673 cm^{-1} for PMAA is quite close to the value for the hydrogen-bonded carboxylic acid groups of glacial acetic acid, indicating that the carboxyl groups in PMAA are nearly completely involved in hydrogen bonding in the solid state. On dissolving PMAA, there is an increase in intensity of the carbonyl peak and a shift in frequency to 1685 cm^{-1}. The increase in intensity is partially a result of the superposition of the broad Raman scattering peak of water. However the spectrum of PMAA in water is different from the spectrum of polyacrylic acid in water where there is an intense peak at 1720 cm^{-1} related to the free carboxylic acid.

Hydrogen bonding persists in aqueous solution of PMAA but is weaker than in the solid state as indicated by the increase in frequency and must involve intramolecular hydrogen bonding since intermolecular hydrogen bonding would be expected to decrease the frequency of the carboxyl band. The increase in the frequency from 1673 to 1685 cm^{-1} must reflect a loosening of the intramolecular hydrogen bonds probably as a re-

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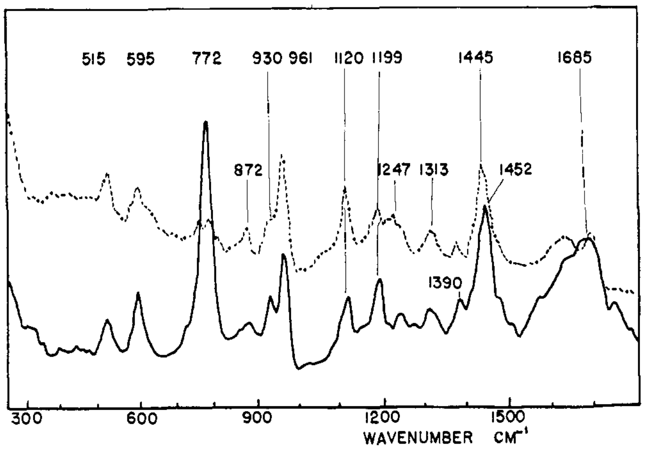

Figure 1. Raman depolarization spectrum of polymethacrylic acid in aqueous solution. (—) Electric vector of incident beam 1 to scattering plane. (····) Electric vector of incident beam 2 to scattering plane.

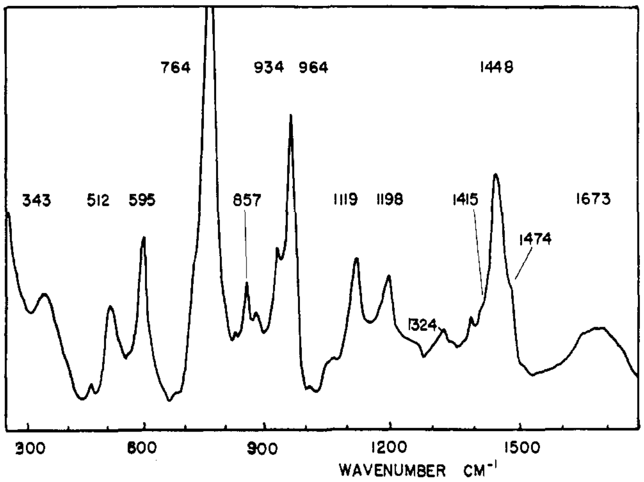

Figure 2. Raman spectrum of solid polymethacrylic acid.

sult of the swelling of the molecule by water. However, intramolecular hydrogen bonding persists or the carboxyl frequency would be expected at 1709 cm^{-1} as observed for acetic acid in aqueous solution.

The band at 764 cm^{-1} is highly polarized and occurs in the region expected for the symmetric C–C stretching mode of the C–COOH group. This band is sensitive to the environment of the carboxyl group, and the change on dissolution apparently produces a slight shift in the frequency of the band. Changes in the bonding of the carboxyl group as a result of ionization produce frequency shifts in this band also. For example, the corresponding vibrational mode is found at 890 cm^{-1} in acetic acid and shifts to 926 cm^{-1} in sodium acetate. The shift from 764 to 772 cm^{-1} upon dissolution arises from the different bonding, previously discussed, of the carboxyl groups in solution. It is also possible that the hydrophobic methyl–methyl interactions suggested by Liquori[1] are also changing slightly and are having some effect on this frequency. It is difficult to predict the magnitude or direction of the frequency shifts for hydrophobic interactions of this type.

An investigation by X-ray crystallography has not resulted in any conclusive evidence for the conformation of PMAA due to the inability to obtain fiber patterns. Some structural information can be obtained from the spectroscopic results. The various helical conformations of a syndiotactic polymer have different infrared and Raman selection rules and dichroic behavior.[7] These differences allow one to differentiate between planar, 2_1, 3_1, and $>3_1$ helical conformations. If syndiotactic PMAA assumes a planar conformation, the model will have C_{2v} symmetry and the vibrational spectra can be classified into (p,σ), (d,π), (d,σ), and d,0) where p and d represent Raman bands which are polarized and depolarized, respectively. The π and σ represent parallel and perpendicular infrared polarizations, respectively. The zero means that the mode is inactive in either Raman or infrared. Thus, a vibrational mode of the type (p,σ) means the mode has polarized scattering in Raman spectra and has perpendicular dichroism in the infrared.

If the syndiotactic PMAA has a 2_1 helical conformation, it has a D_2 symmetry and its vibrational modes may be classified (p, 0), (d, π), and (d, σ). If the syndiotactic PMAA has a 3_1 conformation, it has a D_3 symmetry and its vibrational modes have (p, 0), (d, 0), and (d, σ). If the helical conformation is greater than 3_1, the symmetry belongs to the D_n dihedral group where n is the number of turns in the helix. The vibrational modes for D_n are (p, 0), (0, π), (d, 0), and (d, σ).

The vibrational modes for each of these conformations are characteristic of the structure, and in principal, allow the possibility of differentiating between the various conformations. For the PMAA system, this method is limited in application because of the inability to produce the stretched films necessary for infrared dichroism measurements. It is possible to obtain Raman depolarization data by using the aqueous solutions as the local conformations do not seem to change drastically from the solid state to solution.

The polarized Raman bands at 595, 764, and 1198 cm^{-1} do not appear in the infrared. Five depolarized bands at 857, 872, 1044, 1067, and 1119 cm^{-1} also do not appear in the infrared. Depolarized Raman bands at 934, 964, 1391, 1415, 1448, and 1474 cm^{-1} have corresponding frequencies in the infrared. Finally, there are four infrared modes at 533, 800, 1176, and 1266 cm^{-1} which are found only in the infrared, not in the Raman. Data suggest that the vibrational modes of PMAA be classified at (p, 0), (d, 0), (d, ir), and (0, ir) where ir means the modes occur in the infrared but their polarizations are not known. Caution must be exercised in accepting the (p, 0), (d, 0), and (0, ir) classifications since the inherent weaknesses of certain modes and the limitations in instrumental sensitivity make these classifications slightly arbitrary. However, it would be highly fortuitous if all 12 of the bands which are unique to either the Raman or infrared would exhibit this behavior. The weight of the current evidence suggests that these modes correspond to the D_n symmetry which requires the syndiotactic PMAA to exist as a helix with pitch greater than 3_1. We would suggest, on the basis of this evidence, that PMAA exists as a helix containing more than six monomer repeat units per two turns of the helix. A locally planar model has been suggested in solution but[8] is definitely ruled out since the polarized Raman

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Table I

Polymethacrylic acid							Poly(sodium methacrylate)					
Raman					Infrared		Raman			Infrared		
Solid		Solution			Solid		Solution			Solid		Tentative assignment
cm^{-1}	RI[a]	cm^{-1}	RI[a]	P[b]	cm^{-1}	RI[a]	cm^{-1}	RI[a]	P[b]	cm^{-1}	RI[a]	
343		343	vb									
					404	w						
					413	w				410	m	
										420	w	
512		512	m		515	m						
										518	w	
					533	m	528	m		530	w	
										555	vw	
595		595	s	P								Skeletal δ_{C-C-C} 204
							603	s	P			Skeletal $\delta_{C-C-C}COH^-$
					631	w				615	w	
					636	w						
721		721	sh							720	vw	
764												
										755	m	
		772	vvs	P								C–COOH ν(C–C)
					800	s						
										812	vw	
					826							
							832	vvs	P			C–COONa ν(C–C)
857		857	w				859	m		857	s	$C-CH_3$
		872	vw									
934		930	s		933	s						
							938	m		938	s	$C-CH_3$
964		961	s		967	s	967	s		967	s	$C-CH_3$
					1006	s						
							1058	w		1057	w	COO^-
		1067	w									
1119		1120	m									
							1122	m		1128	vw	
					1176	vs						COOH
1198		1199	m	P			1205	s		1204	s	
		1247	m	P								COOH
		1313					1319	w				CH_2
1324												
							1341	m	P	1345	s	COO^-
										1365	s	COO^-
		1390			1389					1392	vs	COO^-
1415		1415			1413		1418	m	P			
1448		1445	m		1449		1447	s		1443	s	CH_2
		1452								1465	s	
1474					1475	m						OH
					1487							
							1541					COO^-
										1550	vvs	
							1645					COO^-
1673												
		1685										COOH

[a] RI = relative intensity. [b] P = polarized.

bands do not appear in the infrared and the twofold helix is eliminated since the depolarized lines do not appear in the infrared. The 3_1 helix is a possibility if the four infrared bands which are not found in the Raman are bands which are intrinsically weak and therefore not observable in the Raman effect.

It is also of interest to determine the structure of the poly(sodium methacrylate) (PNaMA) relative to the PMAA. The Raman spectrum of PNaMA in water shown in Figure 3 exhibits polarized and depolarized lines in the same frequency regions as PMAA (Table I). Since the chemical structure is the same except for the removal of the hydrogen atom, the vibrational modes should have similar character, and the polarized Raman mode must have a similar vibrational and structural basis and differ in frequency only in terms of the conformational differences and the effects of the ionization. The largest frequency shift for a polarized symmetric mode is from 772 cm^{-1} in PMAA to 832 cm^{-1} in PNaMA. This large frequency shift is, in large part, due to differences in ionization as previously indicated but must also reflect an uncoiling of the helix. A comparison of the shift as a result of the uncoiling can be made with polybutene-1. When the helix angle is 120°, for polybutene-1 (3_1 helix) a band is observed at 774 cm^{-1}; at 108°, 781 cm^{-1}; at 103°, 784 cm^{-1}; at 98°, 786 cm^{-1}; and at 90° (4_1 helix), 790 cm^{-1}. The frequencies have been calculated by normal coordinate-analysis procedures and suggest that this vibrational mode in the polyacid is sensitive to conformational as well as ionization differences. Another polarized band which shifts is the band at 595 cm^{-1} in PMAA which shifts to 603 cm^{-1} in PNaMA. This band is probably associated with the C–C–C bending of the polymer backbone and

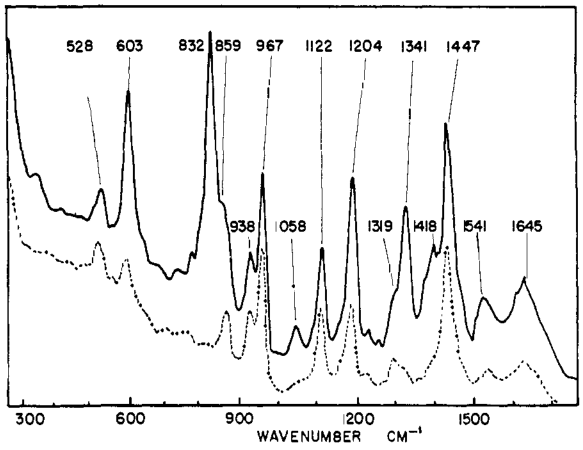

Figure 3. Raman depolarization spectrum of poly(sodium methacrylate) in aqueous solution. (—) Electric vector of incident beam 1 to scattering plane. (····) Electric vector of incident beam 2 to scattering plane.

this shift results from a conformational change between the un-ionized and ionized acid.

The vibrational spectra of PNaMA can be classified according to (p, 0), (d, 0), (d, ir), and (0, ir) in a manner similar to PMAA. There is one band which is polarized at 1341 cm^{-1} in the Raman and occurs at 1345 cm^{-1} in the infrared; the experimental precision is insufficient to indicate whether these are the same or different bands. It is possible that an accidental degeneracy has occurred. The number of bands in the (0, ir) classification is 11 (only four for PMAA) which suggests that the pitch of the helix is greater than 3_1, whereas for PMAA it was possible for the helix to be 3_1 but more likely to be greater.

One must conclude that the PMAA and PNaMA have slightly differing helical conformations with the PNaMA having the more open conformation. This is acceptable since the highly charged carboxylate ions would repulse each other, and these electrostatic forces can be minimized by allowing the helix to uncoil slightly so that the carboxylate ions are further apart.

B. Changes in the Raman Spectra with the Degree of Neutralization. The neutralization process is reflected by changes in the C═O stretching mode. The band at 1685 cm^{-1} in the un-ionized acid, shown in Figure 1, decreases in intensity with increase in α. The band at 1645 cm^{-1}, shown in Figure 3, associated with the salt increases in intensity with increase in ionization. The relative intensity of these two peaks is a reflection of the state of neutralization. The changes in this region are apparently linear with the degree of neutralization.

The greatest changes in the spectrum of PMAA with degree of ionization occur in the C–C stretching region of the spectra. This is shown in Figure 4. In order to determine the nature of the changes in this region which are a result of ionization of the carboxylic acid group, we compared the observed changes with those for glacial acetic acid. In the neutralization of acetic acid only two distinct peaks are observable, one corresponding to the un-ionized acid and one to the carboxylate ion. As the ionization proceeds, the changes in these C–C stretching bands occur in a manner similar to the carboxyl stretching mode.

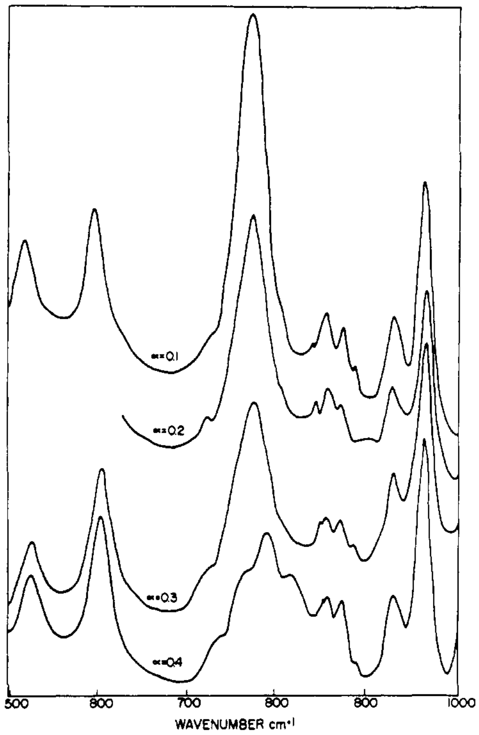

Figure 4. Raman spectra of polymethacrylic acid in water solution at various degrees of neutralization with sodium hydroxide.

When the spectrum of syndiotactic PMAA at various degrees of neutralization is examined (Figure 4), it is clear that simple ionization cannot explain these data. The band at 774 cm^{-1} is unchanged in going from α = 0.0 to 0.1. Considerable broadening of this band is observed at α = 0.2 and 0.3, suggesting a number of component peaks present under the band envelope. Since the Raman polarization properties are the same, this suggests that multiple structures are contributing to this broadening. At α = 0.4, there is a shift of the band center to 789 cm^{-1}. In addition to the band broadening, new bands appear as shoulders at 735, 768, 811, and 822 cm^{-1}. These peaks are also polarized and must be associated with asymmetric vibrations.

At α = 0.5, the position of the major peaks shifts to 828 cm^{-1} and remains at approximately this value during further neutralization. There is a narrowing of the band although shoulders are still apparent at 743, 758, and 778 cm^{-1}. As neutralization is continued the band narrows until at α = 1.0 the breadth of the band now at 832 cm^{-1} is equivalent to that observed at α = 0.0 at 774 cm^{-1}. It should be noted that the bands at 857 and 876 cm^{-1} are observable at all degrees of neutralization, while additional bands at 845 and 890 cm^{-1} are observed in the range α = 0.0–0.4.

These data suggest that when an aqueous solution of syndiotactic PMAA is partially neutralized, the symmetric C–COO stretching mode which is sensitive to the conformation of the repeat unit scatters over a range of frequencies while in the neutralized or completely un-ionized acid form it scatters at 824 and 774 cm^{-1}, respectively.

The broadening is considerably different from that expected from the simple overlap between two strong peaks with the position of maximum intensity being determined by the relative concentrations of the two components. A portion of the changes in frequency may be explained simply by the ionization of the carboxylic acid group. This alone does not explain the large broadening actually observed. This inherent broadening of the Raman peaks and the multiplicity of shoulders at 0.4° of neutralization suggest a multiplicity of different structures exists at this degree ionization. When the degree of ionization is either increased or decreased, the number of structures decreases. This multiplicity of structures would normally be characteristic of a randomization of the structure.

Thus the Raman solution data would suggest a locally regular helical conformation, unaffected by neutralization, up to a degree of neutralization of 0.1. In the region $\alpha = 0.1$ to 0.4 an increasing multiplicity of structures is present. As neutralization proceeds in the range $\alpha = 0.4$ to 1.0, the number of structures decreases until an ordered structure characteristic of the polysalt is obtained. This interpretation is consistent with the observations of Liquori and his coworkers that PMAA undergoes a transformation from a tight coil, characterized by hydrophobic interactions, to an extended structure during neutralization. However, our results suggest that this transformation is not cooperative as is postulated for the denaturation of globular proteins, since our data indicate a progressive randomization of structure in this neutralization range.

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Heat Capacity Changes Associated with the Solvolysis of *t*-Butyl Chloride in Binary Alcohol–Water Systems[1]

R. E. Robertson[2] and S. E. Sugamori

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Abstract: The heat capacity of activation for the solvolysis of *t*-butyl chloride in the high water range of alcohol-water mixtures shows dramatic changes in value over the alcohol concentration range where quasi-aqueous structure is replaced by other solvent interactions. The corresponding changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were found to be less complex than previously reported. The mechanistic implications of the changes in quasi-thermodynamic terms are discussed. A brief description is given for an automatic, random-access system for rate determination by conductance.

The work reported here is a natural extension of our systematic search for relationships between structure, mechanism, and the accompanying solvent reorganization attending the activation process for hydrolyses in water.[3] The point of departure was the suggestion that evidence of solvent reorganization was more likely to be apparent in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ than in $\Delta F^{\ddagger}$. While this is undoubtedly true, experience soon proved that for solvolyses in water, the temperature dependence of $\Delta H^{\ddagger}$ ($\Delta C_p^{\ddagger}$) was a much more sensitive indicator of solvent reorganization[4] than either $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$.[6] That such a correlation exists can be related to the special nature of initial state solvation of nonelectrolytes in aqueous solutions.[7-12]

In water, weakly polar solutes such as the reactive halides may be pictured as surrounded by a hydrogen-bonded solvent shell in which

$$\text{water–water interaction} > \text{water–solute interaction} \quad (1)$$

There is no implication here as to the "thickness" of the shell; modification of the adjacent water molecules is the major effect. Nor do we imply that water–solute interaction is absent.[13] While admittedly an abstraction, we choose to discuss the temperature effects on this system in terms of the stability of the solvent shell. We neglect any speculation as to the exact nature of the solvent shell where we are dealing with mixed solvents. Our system does not provide an answer to such questions. We do assume that the stability of this solvent shell is temperature dependent, decreasing as the temperature increases. A similar trend is found for the structure of the bulk solvent with which the molecules in the solvent shell are in equilibrium. Granted that the breakdown of the initial state solvation shell determines in part the enthalpy required in the activation process, then this

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