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RAMAN SPECTROSCOPIC STUDIES ON THE INTERACTION BETWEEN COUNTERION AND POLYION

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The interaction between alkali metal ions and the polyacrylate ion was investigated by means of Raman spectroscopy, in comparison with the Raman spectra of propionate salts. The Raman bands due to the metal-oxygen bond were not apparent and no significant difference was observed among the Raman spectra of several univalent salts of polyacrylate, except in the case of the lithium salt. The apparent degree of dissociation of lithium polyacrylate, as determined from the relative intensity of a specific band characteristic of the carboxylate ion, was lower than those of the other alkali metal salts. It is concluded from the Raman data that the electrostatic interaction between counterions and a polyion is not specifically modified by forces of a nonionic nature. Moreover, it is pointed out that the local conformation of polyacrylate changes gradually with the degree of neutralization, but that the change is not like a conformational transition between globular and random coil forms.

1. Introduction

It is well known that the thermodynamic properties of a polyelectrolyte solution, such as the activity coefficient and osmotic pressure, as well as transport phenomena of polyelectrolytes can, at least qualitatively, be well explained by the idea of counterion binding. Direct observation of the nature of the interaction between counterions and polyions has also been carried out by using the methods of potentiometry, ultraviolet, Raman, polarography, NMR, etc. Discussions concerning the theories and experimental results of counterion binding are presented in various reviews [1–5]. To data, however, the nature of the interaction between a counterion and a polyion is still obscure. The term counterion binding (or association, condensation, fixation, etc.) is used in different terminologies. It may sometimes imply the nonionic binding of counterions on the fixed groups or a simple electrostatic attraction between a polyion and a small ion. The nature of interaction is naturally different with different combinations of counterion and fixed ion [1].

With respect to the interaction between alkali metal ions and polyions, some investigators [6,7] have interpreted their experimental results by using the idea of site binding or specific binding, such as chemical association. On the other hand, Mandel [8] and Leyte [2] concluded from the measurement of absorption spectra and NMR that in a solution of sodium polyacrylate, complex formation between a polyion and counterion does not occur and that a physical association due to electrostatic attraction, i.e., a kind of ion atmosphere binding may be assumed.

A powerful laser Raman spectrometer can give useful information not only about the molecular structure but also about the intra- and intermolecular interactions through analysis of vibrational frequencies, intensities and half-widths. The strong intermolecular binding should give rise to new Raman bands. Even if the intermolecular interac-

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tion is weak, the interaction may affect the intensities and half-widths. Raman studies of aqueous solutions of simple electrolytes have been summarized in a few papers [9,10] in which it is known that Raman study is useful for studying the interionic interaction. A pioneering study on a polyelectrolyte by Raman spectroscopy was carried out by Lapanje and Rice [11] and, recently, a few papers [12–14] have been published in which conformational changes of poly(acrylic acid) and poly(methacrylic acid) with respect to the degree of neutralization were studied.

The main purpose of this paper is to investigate the nature of the interaction between alkali metal ions and the polyacrylate ion by means of Raman spectroscopy. The conformational change of poly(acrylic acid) is also discussed.

2. Experimental

2.1. Sample

Poly(acrylic acid) samples used were commercially supplied from Scientific Polymer Products Inc. (sample A and C) or prepared by degradation of a commercial sample ($M_r = 2.0 \times 10^6$) using an ultrasonic technique (sample B). Their molecular weights, determined by viscosity measurements in 0.1 mol/l NaCl [15], are (A) 1.8×10^3, (B) 2.0×10^4 and (C) 9.0×10^4. All simple salts used were of guaranteed reagent grade and were used without further purification. All aqueous solutions were prepared using deionized water.

2.2. Raman spectroscopy

The spectrometer used consisted of a laser Raman Spectrometer JRS-U1 (Japan Electron Optic Laboratory Co., Ltd.) and an argon ion laser produced by Coherent Radiation Co., Ltd., operating at 488 nm (800 mW). All measurements were carried out in pure aqueous solution at room temperature.

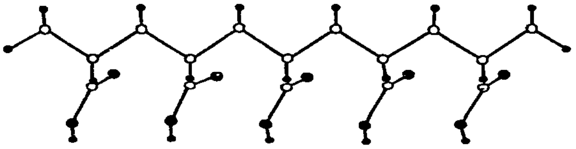

Fig. 1. Structure of the model polymer of poly(acrylic acid) in the TTT form. ○, C atom; ●, O atom, •, H atom.

3. Calculation of normal modes

To see the effect of polymer conformation on the Raman spectra, calculation of the vibrational frequencies of a model polymer of the poly(acrylic acid) type having four different conformations was carried out by means of the GF matrix method [16]. The model polymer consists of five acrylic acid monomers and one methyl group at a terminal end of the chain. Four different conformations were assumed which consisted of three segments of TTT, TTG, TGT and TGG, respectively, where T and G indicate *trans* and *gauche* forms, respectively. For simplicity we consider the clockwise *gauche* form only. As an example, the conformation consisting of three segments of TTT is represented in fig. 1.

The molecular parameters and force constants used in this calculation are listed in tables 1 and 2, respectively. The model polymer contains 49 atoms and the number of the vibrational frequencies is 141. However, all the calculated vibrational modes are not necessarily observed because of the inherent width of bands and their overlap.

The same structures as for poly(acrylic acid) were assumed for the corresponding model polymer of sodium polyacrylate, except that the –COOH group was replaced by the –COO⁻ group. The force constants used for these model polymers are also given in table 2.

Table 1

Molecular parameters

Bond length (Å)		Bond angle (°)	
C–C	1.54	<CCC	109.5
C═O	1.19	<HCH	109.0
C–H	1.09	<OCO	118.0
C–O	1.29		
$C–O^-$	1.24		

Table 2

Force constants (md/Å)

K, H and F: stretching, bending and repulsive terms, respectively.

Poly(acrylic acid)					
K(CC)	1.92	K(CH)	4.45	K(CO)	6.20
K(C=O)	9.03	K(OH)	5.95	H(HCH)	0.43
H(CCH)	0.24	H(CCC)	0.28	H(CC=O)	0.55
H(OC=O)	0.60	H(COH)	0.26	F(HCH)	0.02
F(CCH)	0.36	F(CCC)	0.24	F(CC=O)	0.70
F(OC=O)	2.52	F(COH)	0.60	F(CCO)	0.60
H(CCO)	0.28				
Sodium polyacrylate					
K(CC)	1.92	K(CH)	4.45	K(CO)	9.10
$K(CCO_2^-)$	6.23	H(HCH)	0.43	H(CCH)	0.24
H(CCC)	0.28	H(CCO)	0.55	H(OCO)	0.60
F(HCH)	0.02	F(CCH)	0.36	F(CCC)	0.24
F(CCO)	0.70	F(OCO)	2.52		

The vibrational frequencies calculated for the model polymers having different conformations are not given in section 4 and are used for discussing the effect of conformation on the Raman spectra in section 5.

4. Results

4.1. Raman spectra of poly(acrylic acid) and sodium polyacrylate

The Raman spectra of poly(acrylic acid) of different molecular weights are compared with respect to the data of propionic acid in fig. 2A, while the corresponding spectra of their sodium salts are shown in fig. 2B. Concerning the frequencies and their intensities, no difference is observed among the spectra of the samples of different molecular weights. The only difference is that as the molecular weight increases, the Raman spectral line in the region from 700 to 1000 cm^{-1} becomes obscure. In this work, therefore, most measurements were carried out using sample A. The observed frequencies for sample A and their assignments are summarized in table 3. The assignment was carried out taking into account the spectra of propionic acid [17] and succinic acid [18].

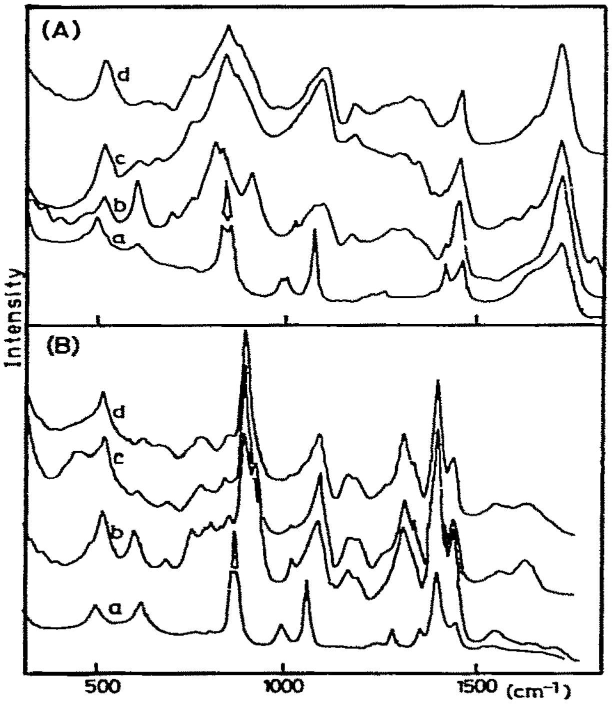

Fig. 2. Raman spectra of poly(acrylic acid) (A) and sodium polyacrylate (B) of different molecular weights. (a) Propionic acid, (b) ($M_r = 1.8 \times 10^3$), (c) poly(acrylic acid) ($M_r = 2.0 \times 10^4$), (d) poly(acrylic acid) ($M_r = 9.0 \times 10^4$). 25% aqueous solution.

Table 3

Raman frequencies of poly(acrylic acid) and sodium polyacrylate in aqueous solutions

Poly-(acrylic acid)	Sodium poly-crylate	Assignments
1710 vw	1710 vs	C=O stretching
	1555 w	CO_2
1453 m	1453 m	CH_2 bending
1422 sh		OH
	1412 vs	CO_2^-
1321 w	1322 m	CH_2 wagging
1283 w		
	1205 w	
1179 w	1180 w	CH_2 torsion
1105 m	1102 m	CH_2 bending+CCH bending
1089 w		
1029 w	1029 w	CH_2 rotation
	939 s	
917 m		C–C stretching
	904 vs	
	868 m	
840 m	840 vw	
816 m	816 m	
	798 w	
	765 m	C–CO_2^- stretching
753 sh		C–COOH stretching
699 w	699 w	CCO bending
604 m	604 m	CO_2 out of plane
509 m	509 m	CO_2 rotation
465 sh	475 sh	
393 vw	393 vw	
343 w	343 vw	
316 vw	316 vw	

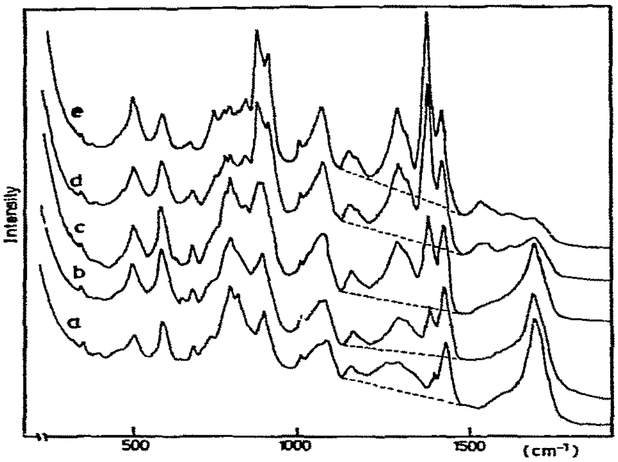

Fig. 3. Raman spectra of poly(acrylic acid) at different degrees of neutralization. Degree of neutralization, α: (a) 0, (b) 0.2, (c) 0.4, (d) 0.8, (e) 1.0. 25% aqueous solution. The dashed lines indicate the backgrounds.

Fig. 3 shows the Raman spectra of poly(acrylic acid) at different degrees of neutralization with NaOH. The results in fig. 3 are in agreement with those obtained by Lando et al. [13] and Bardet et al. [14]. Slight differences among three experiments are due to the difference between the molecular weights of the samples used by different authors. The changes in the spectrum of poly(acrylic acid) with the degree of neutralization are observed in the regions from 500 to 1000 cm^{-1} and from 1300 to 1750 cm^{-1}. Since the bands located at 509, 604, 1412, 1555 and 1710 cm^{-1} refer to the vibrational modes in –COOH or –COO$^-$ groups, it is reasonable that these band intensities vary with the degree of neutralization. As the band located at 1453 cm^{-1} is assigned as a –CH_2– bending mode and its band intensity should not vary with the degree of neutralization, the intensities of the above bands in –COOH or –COO$^-$ groups relative to that of the band at 1453 cm^{-1} must be linear with respect to the degree of neutralization. As the intensity of the band at 1412 cm^{-1} is relatively stronger than those of the other bands, the intensity ratio, R, of two bands located at 1412 and 1453 cm^{-1} ($R = I_{1412}/I_{1453}$) is plotted against the degree of neutralization, α, in fig. 4. The peak intensities, I_{1412} and I_{1453}, are estimated assuming that the background is a straight line as shown by dashed lines in fig. 3. The experimental errors in the intensity ratio, R, are within 10% of R through this experiment. For comparison, the same ratio, R, for propionic acid is also shown in fig. 4. It is found that R values thus estimated change linearly with the degree of neutralization up to $\alpha = 1$ in both cases.

The concentration dependence of R for sodium polyacrylate and sodium propionate at $\alpha = 1$ is shown in fig. 5. As the concentration of the solute

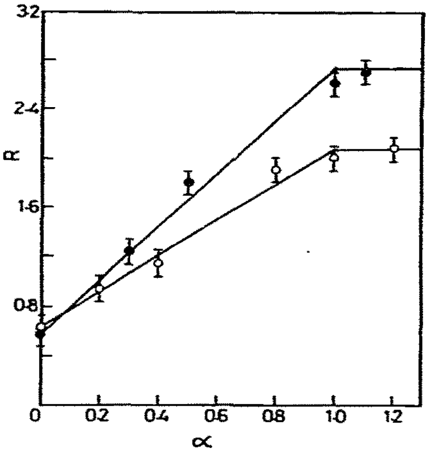

Fig. 4. The intensity ratio, $R = I_{1412}/I_{1453}$, at different degrees of neutralization, α. The values were estimated from the data in fig. 3. Data of (○) poly(acrylic acid) and (●) propionic acid. The experimental error is indicated in the figure.

decreases, the intensity ratio increases. The increase in R with dilution may be due to the decrease in screening of $-\mathrm{COO}^-$ due to its ionic atmosphere.

The spectrum in the region from 750 to 1000 cm^{-1}, which mainly shows the C–C stretching modes, is also sensitive to change in the degree of neutralization, as observed in fig. 3. In poly(acrylic acid), there are two kinds of C–C bond: one is the C–C bond in the backbone of poly(acrylic acid) (type A) and the other is the C–C bond in the C–COOH or $\mathrm{C{-}COO^-}$ group (type B). From the experimental results on succinic acid and its salt, Maury and Bardet [18] indicated that the vibrational frequency of the C–C stretching mode of type A is not affected by the degree of neutralization, while that of type B shifts to the higher frequency side by about 5 cm^{-1} with further neutralization [18]. The bands referring to the C–COOH and C–COO groups, therefore, may be at 753 and 765 cm^{-1}, respectively. The remaining bands in the C–C stretching region in fig. 3, where the vibrational frequencies do not shift with the degree of neutralization though their intensities vary, may be due to the C–C bond of type A.

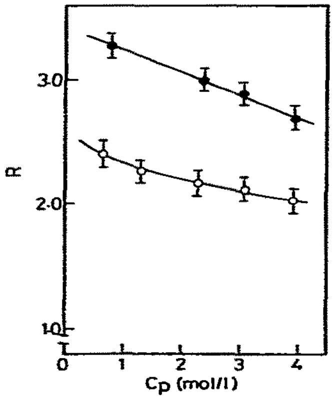

Fig. 5. Concentration dependence of the intensity ratio, R. (○) Poly(acrylic acid), (●) propionic acid.

4.2. *The effect of counterions on the Raman spectra of poly(acrylic acid)*

The Raman spectra of several univalent salts of poly(acrylic acid), neutralized with alkali metal hydroxides, are shown in fig. 6. The spectra are compared at the same degree of neutralization, α = 1. No significant difference is observed among the spectra, i.e., all vibrational frequencies of the Raman bands are observed at the same position. No band characteristic of a metal-oxygen bond,

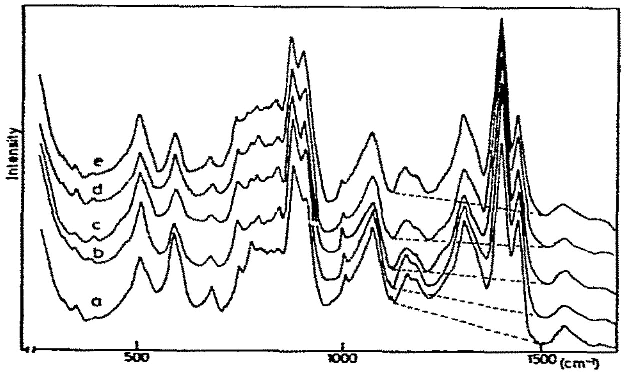

Fig. 6. Raman spectra of several univalent salts of polyacrylate: (a) lithium, (b) sodium, (c) potassium, (d) rubidium, (e) cesium. 25% aqueous solution. The dashed lines indicate the backgrounds.

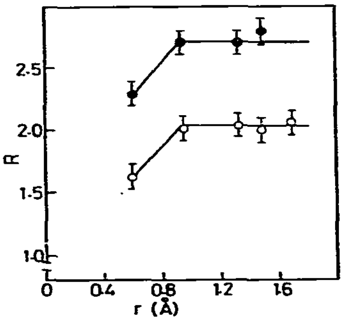

Fig. 7. The intensity ratio, R, as a function of ionic radius, r. (○) Polyacrylate salts, (●) propionate salts.

which is expected to appear in the region from 300 to 500 cm^{-1} [19], is observed. Moreover, their intensities are almost the same, except in the case of the lithium salt. The difference between the lithium salt and the other salts is particularly clear in the region 1400–1500 cm^{-1}. If the ratio of I_{1412}/I_{1453}, R, is plotted against ionic radius as in fig. 7, the R value for lithium polyacrylate is clearly lower than those for the other salts. The same tendency is also observed in solutions of propionate salts.

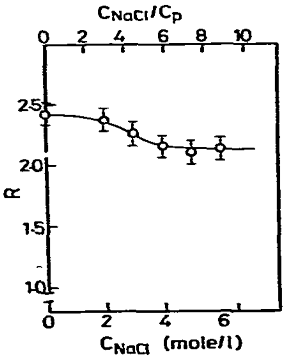

Fig. 8. The intensity ratio, R, as a function of NaCl concentration (C_{NaCl}) and of the concentration ratio (C_{NaCl}/C_p), where C_p is the concentration of polymer (C_p = 0.66 mol/l).

4.3. The effect of added salt on the Raman spectra of poly(acrylic acid)

The effect of NaCl on the Raman spectra of sodium polyacrylate in the region from 1400 to 1500 cm^{-1} was investigated in a wide concentration range of the simple salt. The R values obtained are shown as a function of NaCl concentration and also of the ratio, [NaCl]/[sodium polyacrylate], in fig. 8. A slight decrease in R is observed at higher salt concentration.

5. Discussion

5.1. The interaction between counterion and polyion

The appearance of a vibrational Raman band is dependent upon there being a change in bond polarizability with bond length, which in turn depends on the change in a finite electron density in the bond. In general, purely ionic or ion-dipole binding does not give rise to a Raman band characteristic of the bond. In the Raman spectra in fig. 6, we could not observe the Raman band due to the metal-oxygen bond.

Fig. 7 shows that the intensity ratio, R, of lithium polyacrylate as well as that of lithium propionate is lower than those of the other salts. This result appears to imply that Li^+ has an effect such as decreasing the apparent degree of dissociation of the –COOH group in both solutions of propionate and polyacrylate salts. However, the lower R value of Li^+ is not a specific feature of polyelectrolytes. The difference in R of the lithium salt from those of the other alkali metal salts is of the same magnitude in both solutions of polyacrylate and propionate salts within experimental error. Moreover, in a previous paper [20], we investigated the Raman line shape of the $\nu_1(A_{1g})$ mode of SO_4^{2-} for various salts and observed the asymmetric Raman band only for Li_2SO_4 in the case of univalent counterions. It is well known in the electrochemistry of simple salts that the thermodynamic properties of lithium salt solutions are different from those of the other alkali metal salt solutions. For example, the mean activity coefficient of lithium acetate shows a quite different concentration dependence from those of the other alkali metal salts of acetic acid [21]. In the viscosity behavior of polyacrylate, the behavior of the lithium salt is different from that of the other alkali salts [22].

The slight decrease in R with increasing concentration of added salt in fig. 8 implies that the environment around the $-COO^-$ groups may be influenced somewhat by added salts. However, the change does not appear to be significant enough for any specific interaction such as covalent binding between Na^+ and the $-COO^-$ group to be assumed.

Thus, the Raman data in this experiment indicate that the electrostatic interaction between a counterion and a polyion is not specifically modified by nonionic forces such as those of a covalent bond. The interaction may be similar to that of the ion pair defined by Bjerrum [23].

5.2. *Conformational change of poly(acrylic acid) with degree of neutralization*

As described above, we calculated the vibrational frequencies of the model polymers of poly(acrylic acid) and sodium polyacrylate with different chain conformations. Assuming that the relative intensities of each band in the respective Raman spectra are equal to those of the corresponding vibrational modes of propionic acid and sodium propionate, and also that the half-width of each band is due to the slit-width, we can construct the expected Raman spectra of the model polymer of poly(acrylic acid) and sodium polyacrylate with different conformations, as shown in fig. 9. Although the Raman spectra of real polymers of poly(acrylic acid) and sodium polyacrylate (fig. 3) cannot be reproduced perfectly by this simple calculation, their features characteristic of the conformational change can be pointed out from comparison of the spectra in figs. 3 and 9. That is, fig. 3 shows that the Raman bands in the region of the C–C stretching modes from 750 to 1000 cm^{-1} vary with the degree of neutralization, whereas fig. 9 shows that the Raman bands in the same region are sensitive to the local conformation of the polymer chain. Therefore, it may be concluded that the change in the Raman spectra in the C–C stretching region with the degree of neutralization is ascribable to the randomization of the local conformation.

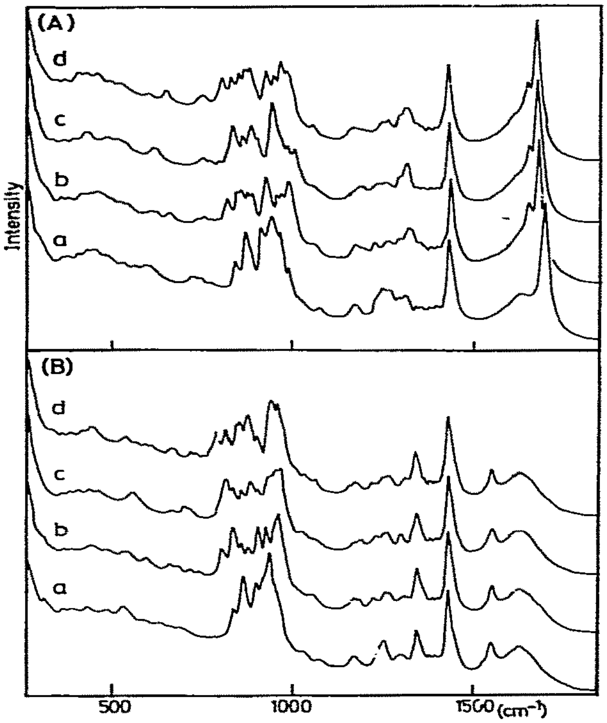

Fig. 9. The simulated Raman spectra of the model polymer of poly(acrylic acid) (A) and sodium polyacrylate (B), where the Raman spectrum of pure water is used as the background. (a) TTT, (b) TTG, (c) TGT, (d) TGG.

Many studies on the conformational change of poly(methacrylic acid) and poly(acrylic acid) with degree of neutralization have been carried out. It is well known that a clear conformational transition from a globular to a random coil form is found for poly(methacrylic acid) [24] but not for poly(acrylic acid) [25,26], though some workers [27,28] also reported a conformational change from a more tightly coiled to a less coiled structure for poly(acrylic acid). From potentiometric titration studies, Nagasawa et al. [29] pointed out that a conformational change of poly(acrylic acid) with the degree of neutralization must be taken into account but that the change is not like the conformational transition of poly(methacrylic acid) between the random coil and globular forms. This is consistent with the present Raman data. The change in the local conformation of poly(acrylic acid) with the degree of neutralization could not be detected by NMR [30].

Recently, Bardet et al. [14] indicated from the investigation of infrared and Raman spectra of syndiotactic poly(acrylic acid) that the progressive shift of the Raman line assigned to the vibrational mode of C–COOH between $\alpha = 0.2$ and 0.5 indicates a conformational transition near the degree of neutralization $\alpha = 0.2$. In the present work, we conclude that the Raman band which shows the progressive shift may be assigned to the vibrational mode of C–COOH as pointed by Bardet et al. [14], and that the shift is not due to the conformational transition, but due to the change in the vibrational frequences of $C\text{–}COO^-$ accompanying the dissociation.

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