

Infrared and Ultraviolet Spectroscopic Studies on Intramolecular Hydrogen Bonding of Poly(itaconic acid)

Seigou KAWAGUCHI,* Masashi KAMATA, and Koichi ITO

*Department of Materials Science, Toyohashi University of Technology,
Tempaku-cho, Toyohashi 441, Japan*

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ABSTRACT: UV and IR absorption spectra of poly(itaconic acid) (PIA) were measured on salt-containing aqueous solutions of various degree of neutralizations (a), to confirm the existence of intramolecular hydrogen bonds between ionized and un-ionized carboxyl groups. Two kinds of isosbestic points were observed in UV spectra at $\lambda=218$ nm and $\lambda=213$ nm in the region of $a \leq 0.5$ and $a \geq 0.5$, respectively. A stretching vibration frequency of C=O of un-ionized carboxyl groups and an asymmetric stretching vibration frequency of COO⁻ shifted to lower wavenumbers by 20 cm^{-1} and by 8 cm^{-1} , respectively, with increasing a above 0.5. Peak separations for the IR spectra were successfully carried out over a whole a , by assuming four species, free COOH, free COO⁻, hydrogen-bonded COOH, and hydrogen-bonded COO⁻. It was concluded that PIA forms an ionic intramolecular hydrogen bond between α - and β -carboxyl groups in a single monomeric unit during neutralization. The strength and extent of hydrogen bonds were compared with those of the polyelectrolytes having maleic acid units reported previously. The anti- and gauche-staggered conformers in the monomeric unit of PIA at $a=0.5$ could be determined to be $16 \pm 2\%$ and $84 = 2\%$, respectively.

KEY WORDS Polyelectrolyte / Poly(itaconic acid) / Hydrogen Bonding / Infrared / Ultraviolet / Conformation / Dissociation /

It is well-known that electrostatic interactions are decisive in controlling solution behavior of highly charged polyelectrolytes, such as dissociation, ion condensation, conformation and organization.¹ A great number of theoretical and experimental studies have been performed to elucidate such characteristic solution behavior of polyelectrolytes. Ionization equilibrium is a direct result of the electrostatic interaction between the charges on a polyelectrolyte chain and the surrounding small ions.² Various theories for dissociation behavior of polyelectrolytes have been reported, including Debye–Hückel approximation,³ counterion condensation theory,⁴ and analytical Poisson–Boltzmann approximation⁵ for a uniformly charged cylindrical model. The

reason why the model in which many discrete charges on a polymer chain can be smeared over the surface of a rod has been accepted so far is based on the fact that this could be successfully applied to the dissociation of weak polyacids, such as poly(acrylic acid) (PAA) and poly(methacrylic acid).^{6,7}

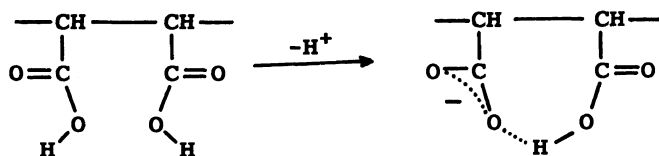
It also has been known, however, that the radius of the rod for fitting the experimental data sometimes must assume a physically unreasonable value.^{8–11} In addition, as reported in a previous paper, this model could be entirely inapplicable to polyelectrolytes having higher charge densities than PAA, such as poly(maleic acid) (PMA) and its stereoisomer, poly(fumaric acid) (PFA), both of which exhibit a two-step dissociation in the

* To whom correspondence should be addressed.

vicinity of half-degree of dissociation (α).² This strongly suggests that the short-range interaction plays a dominant role in the dissociation of the polyelectrolytes. In fact, our theoretical study on an alternating copolymer of isobutylene and maleic acid (PIM) which shows two-step dissociation more clearly than PFA and PMA, allowed us to conclude that the apparent two-step dissociation results from the strong short-range electrostatic interaction between the nearest neighboring ionizable groups, but not from the long-range one.¹² Therefore, the discrete charge model, that considers the difference in configuration and conformation of a macromolecule and the *additional interactions*, should be used to

interpret the dissociation behavior of polyelectrolytes by assuming a suitable electrostatic potential between the densely fixed charges on a polymer chain. We stress here that some additional interactions, strongly depending on the configuration of the polyelectrolyte, may exist when the distance between the carboxyl groups becomes shorter than that in PAA, just as in the cases of PFA, PMA, and PIM.

Recently, IR and UV spectroscopic studies on some polyelectrolytes carrying maleic acid units have definitely shown that ionic intramolecular hydrogen bonds are formed only between an ionized carboxyl group and the nearest neighboring un-ionized carboxyl group *in the course of neutralization*.^{13,14} Here, this

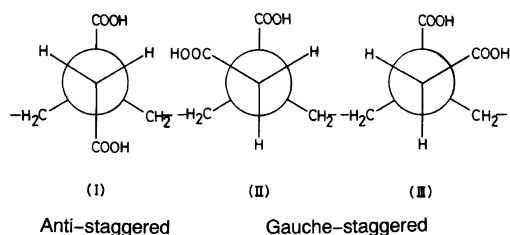


requires some comments. Various kinds of hydrogen bondings exist usually in aqueous solutions of carboxylic acids, forming cyclic and linear dimers, and polymers, along with the solvated species.¹⁵ However, beside such intermolecular hydrogen bonds, we claim that intramolecular hydrogen bonds are formed between COOH and COO⁻ in polyelectrolytes containing maleic acid units *on neutralization*.^{13,14} This type of hydrogen bond was not formed between the carboxyl groups of PAA.^{13,16} This means that not only a simple separation between the donor (COO⁻) and acceptor (COOH) but a relative position of each atom constructing this bonding, might be crucial. That is, this type of hydrogen bond can be formed only when the nearest neighboring COOH and COO⁻ may lie on the same plane and H of COOH can approach O⁻ of COO⁻.¹⁴ Constructing a molecular model, it could be easily understood that polyelectrolytes having maleic acid units such as PIM and PMA have a favorable configuration

to form hydrogen bonding but not PAA. Further, this is strongly dependent on the local configuration of carboxyl groups on a polyelectrolyte, as for the cases of PMA and PFA, representing a possible reason why the dissociation behavior of PMA and PFA is different from each other and the polyelectrolytes with maleic acid units show apparent two-step dissociation.

Poly(itaconic acid) (PIA) is a polyelectrolyte with the same average charge density as PFA and PMA but with the carboxyl groups spaced differently from those of the latter two, that is, one lying on the main chain and the other on the side chain. We reported in the previous paper that PIA also dissociates apparently in two steps and shows a symmetrical titration curve at $\alpha = 0.5$, suggesting that the carboxyl groups on the main chain (α -COOH) and on the side chain (β -COOH) of PIA may dissociate almost independently, due to the weaker interaction between α -COOH and β -COOH than between α -COOH's in PMA and PFA.¹⁷

Along with dissociation properties, it is particularly interesting to clarify whether the hydrogen bonds formed in PIM and PMA exist also in PIA, because the internal rotation of β -COOH in PIA will allow both the gauche conformation in which hydrogen bonding can form easily and trans conformation in which hydrogen bonding can form with difficulty. Some Newman's projections for a monomeric unit of PIA chain are shown below, where



$-H_2C$ and CH_2- represent the methylene of the main chain of PIA. It has been recognized that conformer-I is thermodynamically the most stable. However, when either of two carboxyl groups dissociates, hydrogen bonding will stabilize and favor conformers-II and III. Therefore, determination of the extent of hydrogen bonding may give information about the energy difference among the rotational isomers or the energy of hydrogen bonding.

The present study presents the details of UV and IR spectra of PIA in salt-containing aqueous solution as a function of degree of neutralization (a) and determines the extent and strength of hydrogen bonds by peak separation and to compare with the dissociation properties of the related polyelectrolytes.

EXPERIMENTAL

The sample of PIA was the same as that used in the previous work.¹⁷ Every measurement was carried out at 25°C under N_2 atmosphere. UV spectra of PIA in aqueous solution were measured in the wavelength λ ranged from 185 to 260 nm with a Hitachi Model 330 spectrophotometer. The details were presented in the previous paper.^{13,14} The polymer and salt

($NaClO_4$) concentration, C_p and C_s , were 8.03 mN and 50 mN, respectively. The error of C_p was not over 0.5%.

FT-IR spectra were measured on samples dissolved in heavy water with a JEOL JIR-40X FT-IR spectrophotometer. C_p and C_s ($NaCl$) were 0.502 N and 5.0 mN, respectively. The carefully freeze-dried PIA sample was dissolved in D_2O containing $NaCl$ and neutralized with $NaOD$ to a selected value of a . The error of C_p and a were within 0.5% over all measurements. The path length of CaF_2 cell used was determined to be 27.6 μm with the interference method just before the measurement and was within error of 0.2% over whole a . The resolution and accumulation were 2.0 cm^{-1} and 40 times, respectively. Net spectra of PIA were obtained by subtracting the spectrum of D_2O from the spectra of the solutions containing PIA, as reported in the previous papers.^{13,14} Throughout the present paper, we use the degree of neutralization (a) instead of the degree of dissociation (α).

RESULTS

The UV spectra are shown in Figure 1. Usually, partially neutralized carboxylic acid in aqueous solution gives rise to absorption at two different wavelengths which are ascribed to $n \rightarrow \pi^*$ of COOH ($\lambda = 210$ nm) and $\pi \rightarrow \pi^*$ of COO^- ($\lambda = 183$ nm), respectively.¹⁸ Therefore, UV spectra must have an isosbestic point at a certain wavelength, if the two species change stoichiometrically with variation of a , as in the cases of low molecular weight monocarboxylic acid¹⁸ and PAA.¹³ Two points should be noted in this figure. One is the existence of two isosbestic points, at $\lambda = 218$ nm in the region of $a \leq 0.5$ and at $\lambda = 213$ nm in $a \geq 0.5$. The other is the fact that little absorption appears in the region above $\lambda = 220$ nm ascribed to the intramolecular hydrogen bonding as found in PIM and PMA.^{13,14} Therefore, judging from the UV spectra alone, it is likely that the carboxyl groups of PIA do not form any

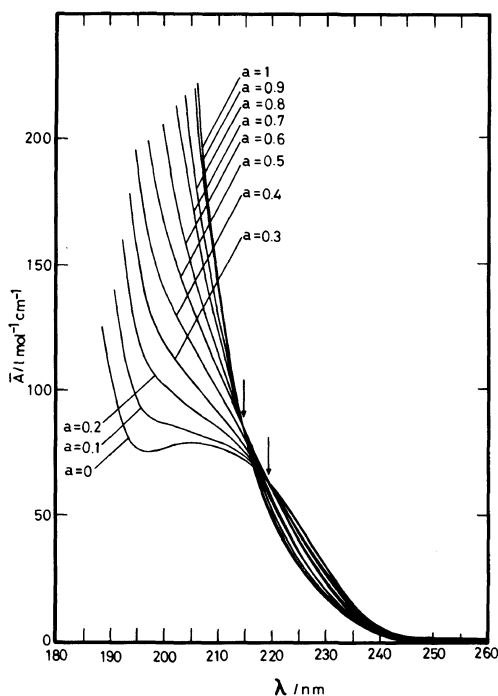


Figure 1. UV spectra reduced for C_p and path length at various a : $C_p = 8.03 \text{ mN}$, $C_s = 50 \text{ mN}$, where the arrows represent an isosbestic point.

hydrogen bonds and they dissociate independently from each other in the course of neutralization. The existence of the two isosbestic points may be due to difference in electronic behavior between the α - and β -carboxyl groups, as will be discussed later.

In sharp contrast to the UV spectra, it was revealed in IR spectra that the C=O stretching vibrational frequency of the un-ionized carboxyl group and the COO⁻ asymmetric stretching vibrational frequency of the ionized one shift to lower wavenumbers by about 30 and 8 cm⁻¹, respectively, with increasing a above 0.5, as shown in Figures 2 and 3. It was also found that the spectral change of PIA with a is similar to that of PIM and PMA but different from that of PAA.^{12,13} That is, the C=O band is considerably broadened with increasing a and the COO⁻ band is sharpened above $a = 0.5$. This means the existence of any absorption species other than the free COOH

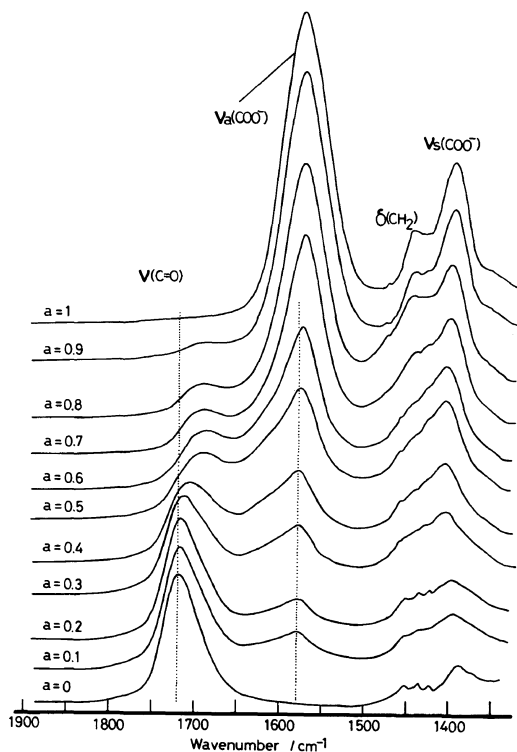


Figure 2. IR spectra at various a : $C_p = 0.502 \text{ N}$, $C_s = 5.0 \text{ mN}$, $d = 27.6 \mu\text{m}$, where the terms denoting each absorption are described in Figure 3.

and COO⁻ during neutralization. Therefore, we are allowed to conclude from the IR spectra that the carboxyl groups of PIA form the intramolecular hydrogen bonds between the ionized and un-ionized carboxyl groups *on neutralization*, as in the cases of PIM, PMA, and PFA. The apparent discrepancy between the conclusions from the UV and the IR spectra might be due to the fact either that the UV absorption of these groups was not so much sensitive as IR, or that the hydrogen bonding of PIA is weaker than that of PIM and PMA, as will be discussed later.

DISCUSSION

As already described in *Introduction*, the two carboxyl groups in a monomer unit of PIA chain have two kinds of conformational

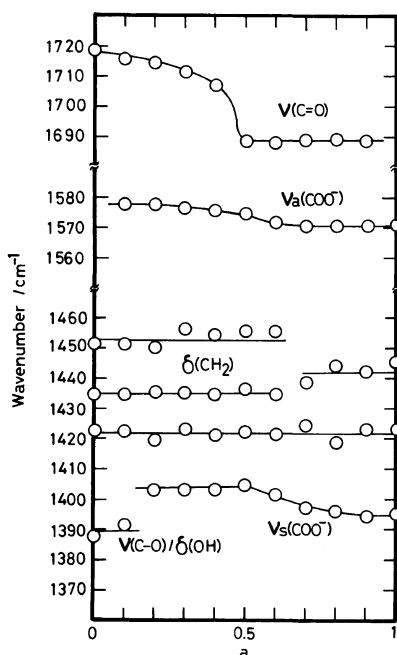


Figure 3. Plots of characteristic absorption frequencies against a , where ν , and δ represent stretching and bending vibration, respectively. The subscripts a and s mean an asymmetric and symmetric, respectively.

isomers, one anti and two gauche conformations, where the former can form hydrogen bonding with difficulty¹⁴ and the latter two can form as in PIM and PMA. Therefore, we are concerned with the concentration ratio of the conformers, the strength and extent of the hydrogen bonding in the course of neutralization, and their relation to dissociation behavior.

Usually, the mole fractions of the anti (P_I) and gauche-staggered conformers (P_{II}) may be represented by the torsional strain energy difference between them, ΔE , using the following equations,

$$P_I = 1 - P_{II} = 1 / (1 + 2 \exp(\Delta E/kT)) \quad (1)$$

$$\Delta E = E_I - E_{II} \quad (2)$$

where E_I , E_{II} , k , and T are the strain energy of conformer-I and conformer-II, Boltzmann constant, and absolute temperature, respec-

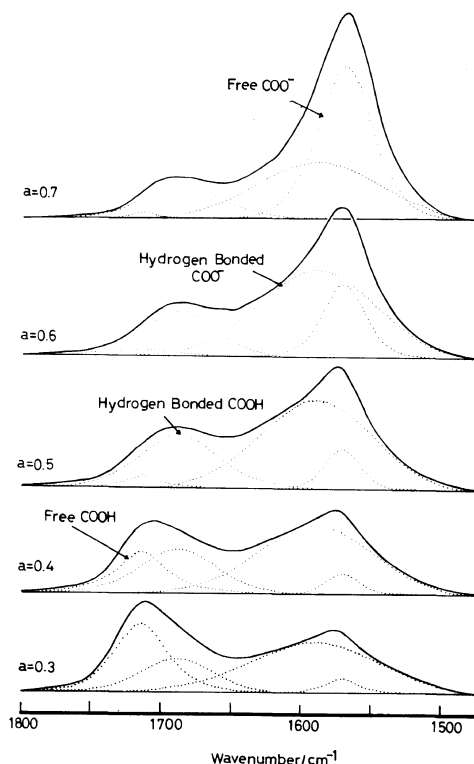


Figure 4. Expanded IR spectra ascribed to the ionizable groups at various a , where the solid and dotted lines were the observed spectra and the resolved bands, respectively.

tively.

The peak separations for the IR spectra from 1800 to 1450 cm^{-1} covering the stretching vibration of the un-ionized carboxyl group and asymmetric stretching vibration of the ionized carboxyl group were carried out by using the damped least-square for nonlinear least-square method, as reported in the previous paper,^{13,14} where each band was assumed to be expressed by Gauss-Lorentz (1:1) function. Figure 4 shows that the observed IR spectra are well reproduced over all a , by using the following four absorption species, 1712 cm^{-1} for the free COOH, 1571 cm^{-1} for the free COO^- , 1688 cm^{-1} for the hydrogen-bonded COOH, and 1590 cm^{-1} for the hydrogen-bonded COO^- . Here, it should be emphasized that the observed spectra cannot be completely resolved over whole a , if less than four species and any

frequencies different from the ones used here were used. It is noted in this figure that the free COO^- at $a < 0.5$ and free COOH at $a > 0.5$ exist together with the hydrogen-bonded species, in contrast to the case of PIM, where free COO^- below $a = 0.5$ and free COOH above $a = 0.5$ do not exist.¹³ This coexistence was also observed in the case of PFA having two kinds of carboxyl pairs, *i.e.*, racemic and meso diads. The former carboxyl pair can form but the latter pair cannot form hydrogen bonds.¹⁴

The areas of each resolved band, S_i , are shown as a function of a in Figure 5, where the areas of hydrogen-bonded species, $S_{\text{COOH}}^{\text{H}}$, and $S_{\text{COO}^-}^{\text{H}}$ attain maxima at $a = 0.5$ and vary symmetrically with a around the maximum. This should be distinguishable from the case of PFA,¹⁴ where S^{H} s increase with a up to $a = 0.5$ and keep constant to $a = 0.75$, and then decrease with a . The difference between PIA and PFA may be based on the fact that the carboxyl groups of PIA is capable of changing from the conformer-I to II or to III unlike PFA at room temperature.

The compositions of the hydrogen-bonded and free COOH or those of COO^- at $a = 0.5$ were evaluated as $84 \pm 3\%$ and $16 \pm 3\%$, respectively, using the values of S_{COOH} at $a = 0.5$ and at $a = 0.0$ or S_{COO^-} at $a = 0.5$ and at $a = 1.0$. These compositions correspond to the mole fraction of the conformers, if one assumes that the conformers-II and -III necessarily form the hydrogen bonding. The energy difference, ΔE , could be estimated to be 2.4 kJ mol^{-1} by using eq 1. This positive value of ΔE in $a = 0.5$ should be noted, since this means that the conformers-II and -III are more stable than the conformer-I, contrary to the common knowledge.

This value, however, is consistent with that reported by Nunes *et al.*,²⁰ who determined $\Delta E = 2.5 \text{ kJ mol}^{-1}$ in the region of $0 \leq a \leq 0.5$, and $\Delta E = -3.3 \text{ kJ mol}^{-1}$ in $0.5 < a \leq 1$ from the vicinal H---H coupling constant of succinic acid aqueous solution as a function of pH. They

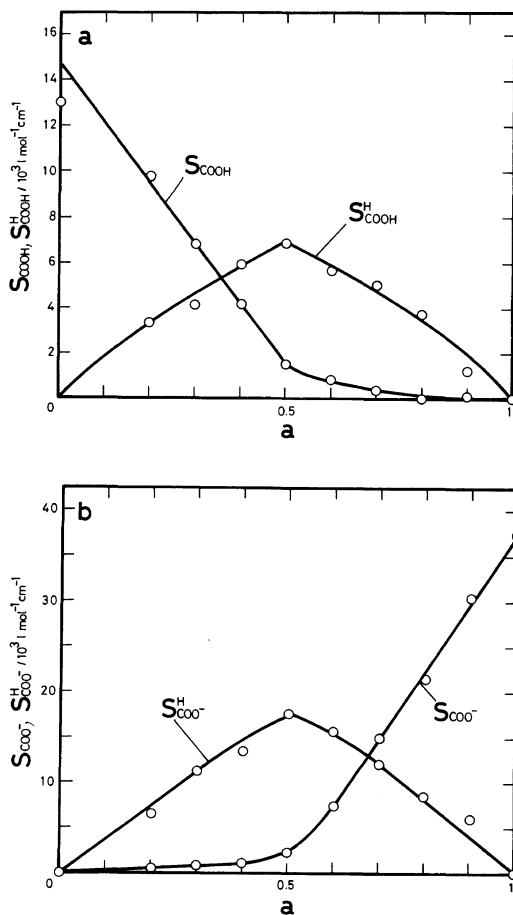


Figure 5. Plots of areas of the resolved bands reduced for C_p and path length against a , where the areas were calculated by using a common Simpson method: (a) S_{COOH} and $S_{\text{COOH}}^{\text{H}}$; (b) S_{COO^-} , and $S_{\text{COO}^-}^{\text{H}}$. S_i and S_i^{H} describe the areas of free and hydrogen-bonded species i , respectively.

also have reported that the high composition of conformer-II and -III was maintained constant in the region of $0 < a < 0.5$.²⁰ Although they did not show any explanation with respect to this positive value, two reasons for the high stabilization and constant composition of conformers-II and -III in the region of $a \leq 0.5$ may be anticipated. One is the effect of hydration at $a = 0$. Consider the difference in the solubility between fumaric acid and maleic acid at $a = 0$. Maleic acid is about 100 times more soluble than fumaric acid,²¹ indicating

that the hydration to the nearly carboxyl groups may be much favored over the distant ones. At $a=0$, stabilization due to the intramolecular cyclic hydrogen bondings *between un-ionized carboxyl groups* should be also considered. The other is an ionic intramolecular hydrogen bonding between the ionized and un-ionized carboxyl groups, when the acid is partially neutralized. This also may lead to stabilizing of the conformers-II and -III, as expected before. The effect of the ability of hydration on the configurational difference decreases with neutralization, taking into account the fact that the difference in the solubility between maleic acid and fumaric acid at $a=0.5$ is negligibly small.²² The effect of ionic intramolecular hydrogen bonding increases with a up to $a=0.5$, and then decreases with a , as shown in Figure 5. Therefore, we can conclude that the value of ΔE at $a=0.5$ is mainly ascribed to the conformational stabilization energy resulting from the hydrogen bonding formed between COO^- and COOH . Further, the constant value of ΔE in the region of $0 \leq a \leq 0.5$, which was reported by Nunes *et al.* may result from balance between the hydration and intramolecular hydrogen bonding, and the fact that the energy of hydration effect on conformational difference between anti- and gauche-conformation is nearly identical with that of conformational stabilization of hydrogen bonding. 'On the other hand, the effect of Coulombic repulsion between the charges becomes larger at $a > 0.5$, so that the *trans* becomes more stable conformer than the *gauche*. We will clarify further the effect of hydration and hydrogen bonding, using the experimental data of low molecular weight organic dibasic acids and the calculation of molecular orbital.²³

As shown in Figure 3, the frequency shifts of COOH and COO^- of PIA at $a=0.5$ are relatively small, compared with those of PIM. Here, we can discuss about relative strength of the hydrogen bonding, using the frequencies used to resolve the spectra. It is reasonable to

assume that the strength of hydrogen bonding can be relatively determined by the difference in the frequencies between the hydrogen-bonded and free species, since the original force constants of free COOH and COO^- can be regarded to be perturbed by hydrogen bonding. The relative strength of hydrogen bonding was estimated using the following equation,

$$\Delta k_i = \mu_i | (v_H^i)^2 - (v_f^i)^2 | \quad (3)$$

$$i = \text{COOH or COO}^-$$

where v_H and v_f are the frequencies of hydrogen-bonded and free species and μ , a reduced mass. The value of Δk for COOH and COO^- of PIA estimated by eq 3 was smaller than that of PIM by $26 \pm 2\%$. This allows us to conclude that the hydrogen bonding of PIA is weaker than that of PIM by about 26%. The difference in the strength of hydrogen bond between PIA and PIM may result from the difference in the extent of resonance stabilization of this bond, in addition to the difference in their molecular structures. When either of definitely paired carboxyl groups of PIM dissociates, the resulting charge can be uniformly distributed into them through the hydrogen bonding, so that a considerably stabilized resonance structure can be formed. On the other hand, in the case of PIA, hydrogen bonding will occur and break invariably by the internal rotation of β -carboxyl group. In addition, considering the dissociation process of PIA, the β -carboxyl group dissociates at first because the effect of the electric potential of the polyion is weaker than that of α -carboxyl group.¹⁷ This displaces the charge to the β -carboxyl group. As a result, the resonance stabilization effect on the hydrogen bonding of PIA is smaller than that of PIM.

The relative strength of hydrogen bonding obtained can be compared with the potentiometric titration behavior. As mentioned earlier, the carboxyl groups of PIA can form hydrogen bonding, only when they are in *gauche* position. Taking into account such effect into our

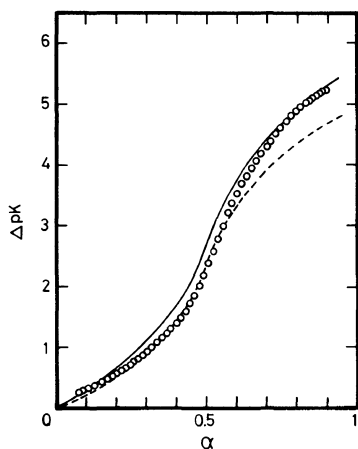


Figure 6. Comparison of observed titration curves (\circ)¹⁷ with calculated ones, where the energy of hydrogen bonding was assumed to be 12.6 kJ mol^{-1} . The details of model were described in the text. The solid, and broken lines show the calculated ΔpK and ΔpK_{short} , respectively.

previous model, the transition matrixes, \mathbf{M} and \mathbf{M}' , can be written as shown in Appendix. The quantitative agreement of the titration data with the calculated curves could be achieved using $E_{\text{H}} = 12.6 \text{ kJ mol}^{-1}$, as shown in Figure 6, where the dielectric constant was used as a bulk value. The value of energy used to fit was small by 40%, compared with that of PIM.¹² This means that the effect of the dielectric constant also must be considered to interpret

the dissociation behavior of these poly-electrolytes in addition to the hydrogen bonding.

Any absorption bands ascribable to hydrogen bonding did not appear in the UV spectra of PIA, as shown in Figure 1. The absorption of this type of hydrogen bonding in UV spectra may be regarded as a special application of Mulliken's charge-transfer theory, in the sense the energies of the no-bonded and charge-transfer structures are equal to each other.²⁴ The pairs of carboxyl groups of PIA do not have symmetry in contrast to those of PIM, PMA, and PFA. The transition between the ground and excited energy levels caused by resonance interaction may be not take place, because of free rotation at room temperature. The two kinds of isosbestic points are presumably due to the electronic difference between α - and β -COOH. The isosbestic point at $\lambda = 218 \text{ nm}$ may be due to the dissociation of β -COOH, and the other to the dissociation of α -COOH.¹⁷

APPENDIX

Transition matrixes, \mathbf{M} and \mathbf{M}' for the 2nd nearest neighbor interaction in Ising model are shown in this Appendix. See our previous papers for details.^{12,17,25}

$$\mathbf{M} = \begin{pmatrix} H & 0 & 0 & 0 & 0 & 0 & Ha & 0 & 0 & 0 & 0 \\ H & 0 & 0 & 0 & 0 & 0 & Ha & 0 & 0 & 0 & 0 \\ H & 0 & 0 & 0 & 0 & 0 & Hwa & 0 & 0 & 0 & 0 \\ H & 0 & 0 & 0 & 0 & 0 & Hwa & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & a & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & a & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & wa & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & wa & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & a & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & a & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & wa & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & wa & 0 \\ 0 & H & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & H & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & H & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}^T$$

Hydrogen Bonding of Poly(itaconic acid)

$$\mathbf{M}' = \begin{bmatrix}
 0 & H & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & u^t a & 0 \\
 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & u^t a & 0 \\
 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & u^t w a & 0 \\
 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & u^t w a & 0 \\
 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & u^g a \\
 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & u^g a \\
 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & u^g w a \\
 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & u^g w a \\
 \\
 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 \\
 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 \\
 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 \\
 a & z^{gg} a & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & a & a & z^{gt} a & z^{gt} a & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & v^g a & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & v^g a & v^g a & v^g z^{gt} a & v^g z^{gg} a \\
 a & z^{tg} a & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & a & a & z^{tt} a & z^{tg} a & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & v^t a & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & v^t a & v^t a & v^t z^{tt} a & v^t z^{tg} a \\
 a & z^{gg} a & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & a & a & z^{gt} a & z^{gg} a & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & v^g a & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & v^g a & v^g a & v^g z^{gt} a & v^g z^{gg} a
 \end{bmatrix}$$

where the superscript T means a transposed vector. H , u^g , u^t , w , v^g , v^t , z^{gg} , z^{gt} , z^{tg} , z^{tt} , and H are statistical weights defined as follows:

$$H = \exp(-E_H/kT),$$

$$u^i = u(R_i) = \exp(-e^2/DkTR_i)$$

$$v^i = u(R_i)$$

$$w = u(R)$$

$$z^{ij} = u(R_{ij})$$

The subscripts g and t mean *gauche* and *trans* conformation of β -COOH, respectively, and e , D , R , and E_H are electronic charge, dielectric constant, separation, and energy of hydrogen bonding, respectively.

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