Infrared and Ultraviolet Spectroscopic Studies on Intramolecular Hydrogen Bonding in an Alternating Copolymer of Isobutylene and Maleic Acid

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Received October 12, 1990; Revised Manuscript Received June 27, 1991

ABSTRACT: IR and UV absorption spectra of poly(isobutylene-*alt*-maleic acid) (PIM) in aqueous salt solutions were measured as a function of the degree of neutralization (a) to examine hydrogen bonding during dissociation in comparison with those of poly(acrylic acid) (PAA). In the UV spectra the absorbance of PIM in the vicinity of wavelength $\lambda = 215$ nm was found to increase with a, attain a maximum near $a = 0.5$, and then decrease, while that of PAA showed a clear isosbestic point at $\lambda = 213$ nm over a whole range of a. The IR spectra of PIM revealed that, above $a = 0.5$, a stretching vibration band of C═O of COOH shifts to shorter wavenumbers by 50 cm^{-1} and an asymmetric stretching vibration band of COO$^-$ also shifts to shorter wavenumbers by 27 cm^{-1}. Moreover, IR bands of PIM were successfully resolved into those of four species, that is, free COOH, free COO$^-$, hydrogen-bonded COOH, and hydrogen-bonded COO$^-$. The absorbance of a hydrogen-bonded carboxyl group was found to show a maximum just at $a = 0.5$ while free COO$^-$ did not appear until $a = 0.5$. It is thus concluded that PIM has intramolecular ionic hydrogen bonding between the ionized and the un-ionized carboxyl groups during the dissociation.

Introduction

Previous studies on potentiometric titration have shown that poly(fumaric acid) (PFA) and poly(maleic acid) (PMA), both of which have charge densities exactly twice as high as poly(acrylic acid) (PAA), dissociate apparently in two steps.[1] Also an alternating copolymer of isobutylene and maleic acid (PIM), which has the same average charge density as PAA but two carboxyl groups of which reside locally closer to each other as a pair, shows also a remarkable jump in apparent dissociation constant (pK_a) just at the degree of dissociation $\alpha = 0.5$.[2] In addition, the intrinsic viscosity, $[\eta]$, of these polyacids strangely decreases at higher α than 0.5, and the solutions of PFA and PMA even become turbid at higher α, contrary to the behavior of the usual polyacids like PAA.[1,2] To understand the nature of such polyacids with higher charge densities in terms of the electrostatic interaction in polyelectrolyte solutions, we carried out model calculations, which suggested that the apparent two-step dissociation should result from the strong short-range electrostatic interaction from the carboxyl groups in the proximity as expected.[3] That is, the difference in the local charge distribution of charges plays a dominant role in the dissociation behavior of the polyacids. The rod model with a smeared charge density is not always applicable to the dissociation behavior of some polyacids.[4]

The apparent two-step dissociation suggests that there are two kinds of ionizable carboxyl groups in these polyacids, although they are essentially indistinguishable from each other when the polyelectrolyte chain has no charge.[4] Half of the carboxyl groups may first dissociate in the same way as the usual polyacids, while the dissociation of the other half above $\alpha = 0.5$ is suppressed by the strong electrostatic interaction from the neighboring ionized groups. This apparent regularity of dissociation leads to a large deviation from random mixing, i.e., uniform charging,[3] which is assumed to be reasonable for the usual polyelectrolytes with comparatively lower charge densities such as PAA. It is true, however, that this effect must also be present in the dissociation of any polyelectrolytes even for PAA, but the nature of the rapid decrease of the electrostatic interaction with the separation between charges may lead to the fact that the dissociation behavior of PAA can be expressed approximately in terms of the average electrostatic interaction between charges on a polymer chain. On the other hand, as the distance between charges becomes shorter, the short-range electrostatic interaction becomes strong enough that it must be taken into account, for example, in the case of PIM.

In the previous model reported[2,3] this effect was introduced as the short-range interaction through the activity ratio of an ionized to an un-ionized carboxyl group. Assuming the local dielectric constant between the ionized groups to be lower than that in bulk or introducing the possibility of the intramolecular hydrogen bonding, we succeeded in reproducing the potentiometric titration curves quantitatively.[2-4] The local dielectric constant in the vicinity of the ionized groups[5] or between the ionized groups[6] is presumed to be much lower, but we do not have any tools to measure it directly. On the other hand, methods to detect the hydrogen bonding in low molecular weight compounds by various methods including UV, IR, and Raman spectroscopy are well established.[7-11] The various kinds of hydrogen-bonding types are known in aqueous solution, i.e., a linear or cyclic dimer between carboxyl groups, between carboxyl groups and water,[12] and between ionized and un-ionized carboxyl groups.[13-15] The spectroscopic studies on polyelectrolyte solutions also can provide valuable information about the change in the state of carboxyl groups during the neutralization. Roughly speaking, the previous spectroscopic studies can be classified into three categories; (1) counterion binding,[16-19] (2) conformational transition of polyelectrolyte chains,[20-25] and (3) hydrogen bonding.[26,27]

The present study is aimed at proving that intramolecular hydrogen bonding presumed in the previous paper[2,3] occurs during the dissociation of PIM, directly by

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0024-9297/91/2224-6030$02.50/0

UV and IR spectroscopy, since the carboxyl group has so strong an absorption band in these wavelength regions that the hydrogen bonding may cause any detectable changes in the spectra different from those of PAA, which was confirmed not to have any intramolecular hydrogen bonding.[18]

Materials and Methods

Samples of PIM and PAA were the same as those used in the previous papers.[1,2]

UV spectra of aqueous polyelectrolyte solutions were recorded at 24 ± 1 °C in the wavelength λ range of 185–250 nm with a Hitachi Model 330 spectrophotometer using a deuterium lamp. The accuracy of the wavelength was ±0.2 nm. Oxygen was eliminated from the optical path of the instrument by flushing nitrogen during the measurement. The polymer solutions were prepared by passing through a mixed bed of ion-exchange resins and adding a required amount of NaOH and $NaClO_4$ to set a given degree of neutralization a and salt concentration. Throughout the present paper, we will use the degree of neutralization a for the degree of dissociation α used in the titration studies previously reported since there is little difference between a and α except in low- and high-pH regions. The polymer and salt concentrations, C_p and C_s, were 6.46–9.24 mN and 50 mN $NaClO_4$, respectively. It should be noted that $NaClO_4$ was used as an added salt in the UV spectroscopic measurement instead of NaCl because of its transparency in this wavelength region.[20]

IR spectra were obtained with a JEOL JIR-40X FT-IR spectrophotometer under a nitrogen atmosphere at 24 ± 1 °C. The most characteristic absorption frequencies in the spectra are a stretching vibrational frequency of C=O in COOH and asymmetric and symmetric stretching vibrational frequencies of COO^-. These absorptions appear in the region from 1400 to 1750 cm^{-1},[28] where ordinary water also shows a strong absorption. Thus, deuterated water as well as deuterated base was used for IR spectroscopic measurement. The carbon dioxide-free NaOD solution was prepared by dissolving freshly cut sodium in D_2O (99.85% D) purchased from Commissariat àL'energie Atomique (France) under argon atmosphere. The concentration of NaOD was determined by potentiometric titration. The freeze-dried samples were dissolved in D_2O, and NaOD and NaCl were added to the solution. C_p and C_s were 0.982–1.11 N and 5.0 mN NaCl, respectively. The solutions were held between two CaF_2 plates separated by a spacer of thin lead film. An average cell length (d) was determined by an interference method before each measurement. Recording conditions were as follows: resolution, 2.0 cm^{-1}; accumulation, 40 scans. The spectra were little affected by interference fringes in the present study. We obtained the net IR spectra of PIM by subtracting the spectrum of D_2O from those of PIM, taking into account C_p.

Results

UV spectra of PIM and PAA in aqueous $NaClO_4$ solutions at various a for reduced C_p are shown in Figure 1. UV spectra of low molecular weight monocarboxylic acid and its salt are generally known to have two main bands ascribed to COOH and COO^-. The UV spectra of PAA also have two main bands ascribed to COOH ($n \rightarrow \pi^*$, λ_{max} = 210 nm) and to COO^- ($\pi \rightarrow \pi^*$, λ_{max} = 183 nm).[20,27] Since the absorbance of the band of $n \rightarrow \pi^*$ decreases while that of $\pi \rightarrow \pi^*$ increases with a, as shown in Figure 1a, a clear isosbestic point appears as a result at λ = 213 nm over a whole range of a. Compared with the spectra of the typical low molecular weight monocarboxylic acid, i.e., acetic acid, which has a maximum at 204 nm with a molar extinction coefficient of about 40 L mol^{-1} cm^{-1}, in both hexane and water,[20] the band for PAA at a = 0 is clearly red-shifted and has about 3 times stronger intensity. The existence of an isosbestic point of the PAA spectra suggests that only two kinds of species, COOH and COO^-, exist during the neutralization, just as in the case of acetic acid. It is noted here that the UV spectrum is not sensitive enough to detect a change in the water structure or in the ion binding during neutralization. In contrast to the UV spectra of PAA, those of PIM are much more complex, as shown in Figure 1b, where absorbance at λ = 215 nm increases with a up to a = 0.5 and beyond it decreases in turn with a as in the same way as those of PAA. The spectra of PIM also show an isosbestic point at λ = 213 nm only in the limited region above a = 0.5. This fact suggests that the electronic states of the carboxyl groups of PIM must be different from those of PAA during the neutralization. We can thus conclude from UV spectra of PIM that there may exist more than two kinds of species of the carboxyl groups of PAA during the neutralization. However, further analysis of UV spectra is difficult at present, while IR spectra will provide more definite information about the species.

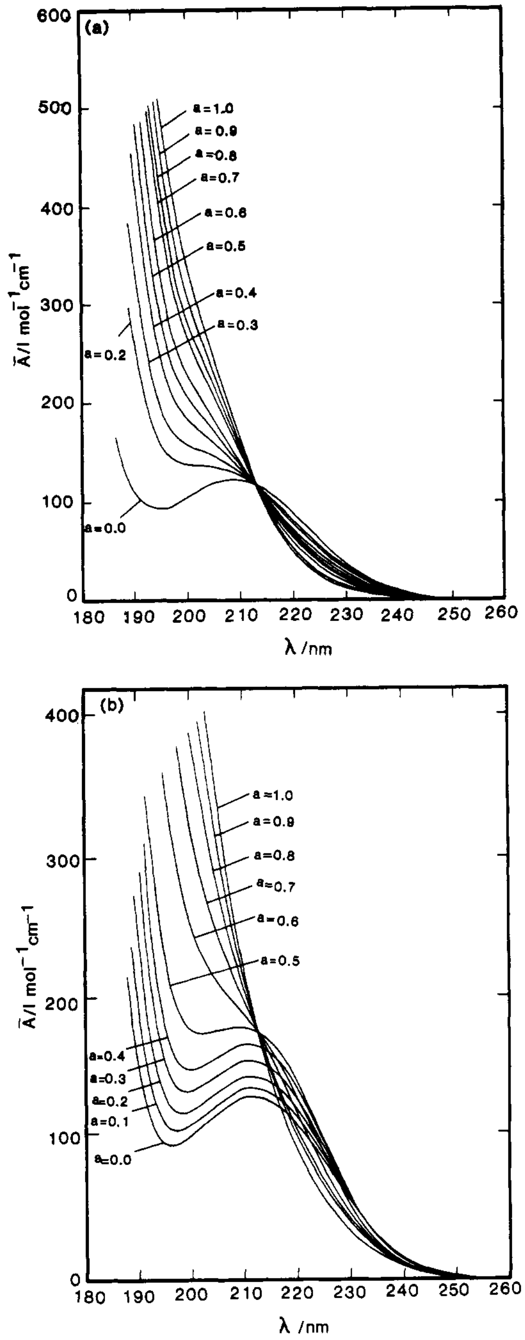

Figure 1. UV spectra at various a: (a) PAA, C_p = 6.46 mN, C_s = 50 mN; (b) PIM, C_p = 9.24 mN, C_s = 50 mN.

IR spectra of PIM and PAA in NaCl deuterated water at various a for fixed C_p are shown in Figure 2, where the

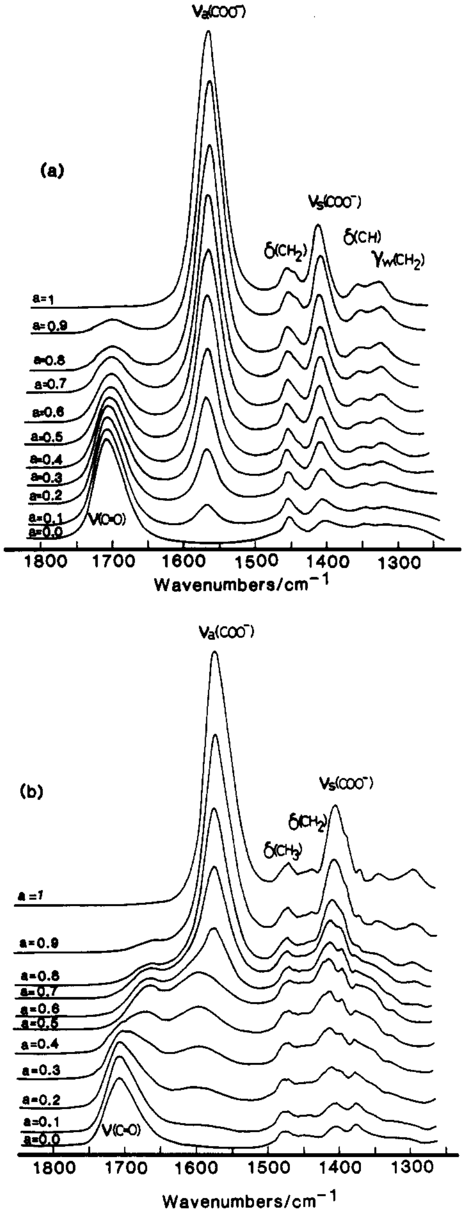

Figure 2. IR spectra at various a: (a) PAA, C_p = 1.11 N, C_s = 5 mN, d = 28.7 μm; (b) PIM, C_p = 0.982 N, C_s = 5 mN, d = 18.8 μm.

absorption bands ascribed to C=O of COOH decrease while those to COO⁻ increase with a. The assignments of each band and a dependence of the frequencies of their bands are shown in Figure 3. In PAA, as shown in Figures 2a and 3a, the frequency of the stretching vibration of C=O, ν(C=O), and those of the asymmetric and the symmetric stretching vibration, ν_a(COO⁻) and ν_s(COO⁻), as well as the shapes of these bands are independent of a. It was already confirmed that, in deuterated water solutions, the substitution of deuterium for hydrogen in a carboxyl group does not significantly affect the locations of these frequencies.[25,29,30] However, the situations are more complex in PIM as shown in Figures 2b and 3b. ν(C=O) shifts even by 50 cm⁻¹ to lower frequencies above a = 0.4 and ν_a(COO⁻) in the region $a < 0.5$ are higher by 27 cm⁻¹ than that of PAA and then approach to the same value as that of PAA beyond a = 0.5.

Discussion

In the case of a simple dissociation equilibrium such as acetic acid, where only two species represented by free

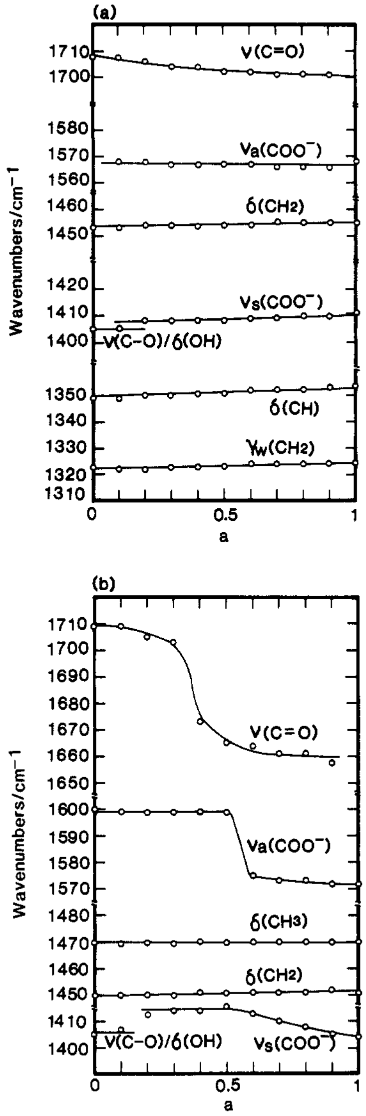

Figure 3. Plots of characteristic absorption frequencies against a: (a) PAA and (b) PIM. ν, δ, and γ_w represent stretching, bending, and wagging vibrations, respectively.

COOH and free COO⁻ are present, the absorbance at a given λ, $A(\lambda)$, should depend linearly on α, according to the equation

$$A(\lambda) = dC[E_{\mathrm{COOH}}(\lambda) + \alpha(E_{\mathrm{COO^-}}(\lambda) - E_{\mathrm{COOH}}(\lambda))] \quad (1)$$

where $E_i(\lambda)$ represents a molar extinction coefficient of species i at λ, C, the total concentration of acid, and d, the path length of a cell measured. For a poly(carboxylic acid) at equivalent molar concentration, C_p, we can define a reduced absorbance $\bar{A}(\lambda)$ by

$$\bar{A}(\lambda) = A(\lambda)/dC_p = E_{\mathrm{COOH}}(\lambda) + \alpha[E_{\mathrm{COO^-}}(\lambda) - E_{\mathrm{COOH}}(\lambda)] \quad (2)$$

Equations 1 and 2 lead to the prediction of an isosbestic point at a certain λ where $E_{\mathrm{COOH}} = E_{\mathrm{COO^-}}$, since, $A(\lambda)$ and $\bar{A}(\lambda)$ become independent of α. As shown in Figure 1a, PAA has a clear isosbestic point over a whole range of a at λ = 213 nm. The plots of $\bar{A}(\lambda)$ against a at various λ's for PAA are shown in Figure 4a, where $\bar{A}(\lambda)$'s are proportional to a as expected from eq 2. This supports a simple conversion of COOH to COO⁻ during the neutralization of PAA. In contrast to PAA, the dependence of $\bar{A}(\lambda)$ of PIM on a in Figure 4b seems not to be represented by eq 2. Namely, an isosbestic point is found at $a > 0.5$ while not at $a < 0.5$. This suggests that the

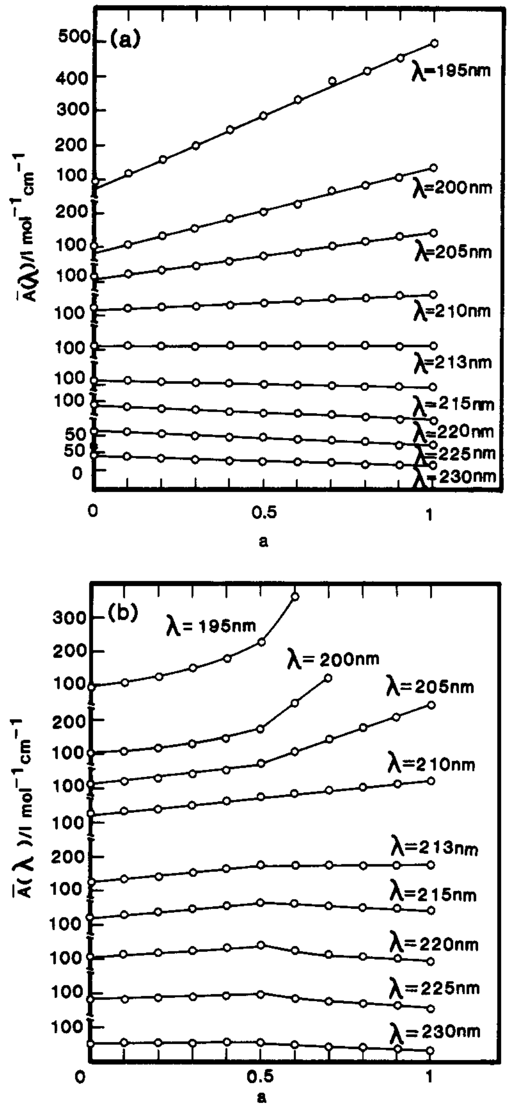

Figure 4. Plots of $\bar{A}(\lambda)$ against α at various λ's: (a) PAA and (b) PIM.

dissociation process of PIM is not a simple dissociation equilibrium between COOH and COO^- like PAA. Accordingly, it is concluded that PIM may have other electronic states of the carboxyl groups in addition to free COOH and free COO^- of PAA.

The appearance of the new electronic states of the carboxyl group in PIM may be explained by either conformational transition or hydrogen bonding. Poly(methacrylic acid) (PMeA) is well-known to undergo a conformational transition by competitive electrostatic and hydrophobic interactions. UV spectra of PMeA did not show, in fact, any isosbestic point and are quite different before and after the conformational transition.[20-22] Although PIM has also two methyl groups in the repeat unit, PIM does not show any evidence for conformational transition in the other solution properties reported previously,[2] and the change in UV spectra of PIM with α is quite different from that of PMeA. We may assume, therefore, that this new absorption band of PIM should not be due to any conformational transition but rather to hydrogen bonding. With respect to hydrogen bonding, it may be possible that there are three kinds of hydrogen bonds, between the un-ionized carboxyl groups, between the un-ionized and the ionized one, and between the carboxyl groups and water. It is highly likely that the hydrogen bonding between the un-ionized COOHs is present at lower α. If the new band is due to this hydrogen bonding, the absorbance should decrease with α. Figure 1b shows, however, that the bands of PIM increase with α up to $\alpha = 0.5$. Moreover, even PAA might have such hydrogen bonds between the un-ionized COOHs at lower α. UV spectra of PAA do not show any band in Figure 1. It can be concluded, therefore, that this band should not be the absorption of hydrogen bonding between the un-ionized COOHs. This new absorption band at about $\lambda = 215$ nm seems the same as that reported by Nagakura in hydrogen maleate anion,[11] who concluded that this may be regarded as the charge-transfer band pertinent to the $-OH\cdots O^-$ hydrogen bonding systems, that is, as the band due to the transition between the ground and the excited energy levels caused by the following resonance:

$$-OH\cdots O^- \leftrightarrow O^-\cdots HO^-$$

Taking into account the above observations including Nagakura's results, it is concluded from the UV spectroscopic data that some of the carboxyl groups of PIM may form the ionic hydrogen bonding between COO^- and COOH during the neutralization.

The studies on IR spectroscopy of a substituted succinic acid and its salts, which are assumed as a low molecular weight model compounds of a maleic acid unit in PIM, show that in certain salts strong intramolecular hydrogen bonding is found,[13-15] where two remarkable shifts were observed: $\nu_a(COO^-)$ of a hydrogen-bonded COO^- shifts always to a higher wavenumber by 35 cm^{-1} than that of free COO^- and $\nu(C{=}O)$ of hydrogen-bonded COOH shifts to a lower wavenumber by 30 cm^{-1} than that of free COOH. The present results on the frequency shifts of PIM seem to be consistent with those on succinic acid. It can be concluded again that PIM has extra species, hydrogen-bonded carboxyl groups during the neutralization, in addition to free COOH and free ionized COO^- existing in PAA. This must be the reason for rather complex spectral change of PIM in Figures 2 and 3.

In IR spectra, we will focus the stretching vibration band of C=O and the asymmetric stretching vibration band of COO^- since they are typical bands for un-ionized COOH and ionized COO^-, respectively. Equation 2 can be transformed to

$$\frac{A(\nu(C{=}O)) - A(\nu_a(COO^-))}{C_p d} = \bar{A}(\nu(C{=}O)) - \bar{A}(\nu_a(COO^-)) = E\nu(C{=}O) - \alpha[E\nu_a(COO^-) + E\nu(C{=}O)] \qquad (3)$$

where E, A, and $\bar{A}$ are the same as those in eq 2 and represent the stretching vibration band of C=O and the asymmetric stretching vibration band of COO^-, respectively. If eq 3 is applicable, that is, the assumption of the mixture of the two species is reasonable, the quantity of the left side of eq 3 should be a linear function of α. The plots of eq 3 for PIM and PAA are shown in Figure 5. PAA is found to obey eq 3; an increase in the electrostatic field and a change of hydration as well as an overall conformational change of a polymer chain during neutralization of PAA seem to have no appreciable influence on the variation of electric moments corresponding to both $\nu(C{=}O)$ and $\nu_a(COO^-)$.[18] From this plot, the ratio of $E\nu_a(COO^-)/E\nu(C{=}O)$ can be determined to be 2.4 for PAA. On the other hand, PIM is found to show a break point at $\alpha = 0.5$; that is, $\bar{A}(\nu(C{=}O)) - \bar{A}(\nu_a(COO^-))$ of PIM decreases gradually with α at $\alpha < 0.5$ and decreases more steeply at $\alpha > 0.5$.

The complex variation of the absorption band with α for PIM seems to result from a complex dependence of

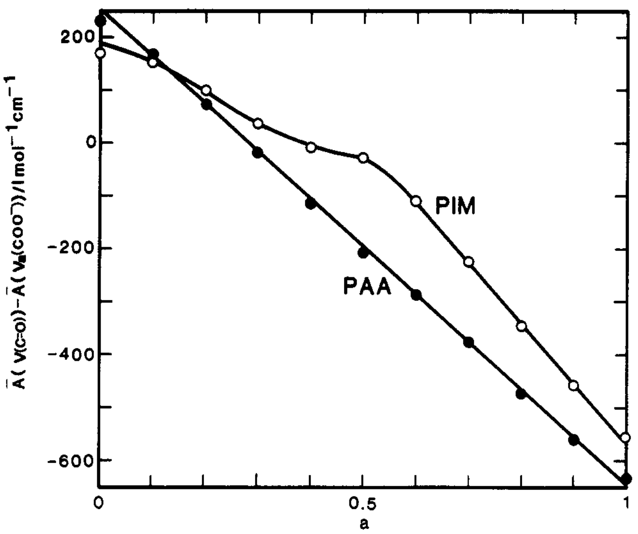

Figure 5. Plots of $\bar{A}(\nu(C{=}O)) - \bar{A}(\nu_a(COO^-))$ against a: PIM (○) and PAA (●).

hydrogen-bonded species on a. To carry out a quantitative analysis of IR spectra, we tried to resolve them into four component bands based on the following procedures:

1. The frequency assignments are 1702 cm^{-1} for free COOH, 1572 cm^{-1} for free COO$^-$, 1669 cm^{-1} for hydrogen-bonded COOH, and 1598 cm^{-1} for hydrogen-bonded COO$^-$.
2. The frequency of each component band is independent of a.
3. Each absorbance can be represented by a Gauss–Lorentz function as

$$F(\nu) = \frac{H \exp\left[-\ln 2\left(\frac{\bar{\nu}-\nu}{W_1}\right)^2\right]}{1+\left(\frac{\bar{\nu}-\nu}{W_2}\right)^2} \qquad (4)$$

where H is an intensity at ν, $\bar{\nu}$ is a band frequency assigned at the procedure 1, and W_1 and W_2 are Gaussian and Lorentzian bandwidth parameters.

4. The background between 1800 and 1300 cm^{-1} and the absorption of adjacent CH_3 and CH_2 of each spectrum can be subtracted from the original one.
5. The optimization is carried out by using the damped least-square for a nonlinear least-square method.[31]

Some examples of spectrum resolution of PIM are shown in Figure 6, where we can confirm more clearly the existence of the band due to hydrogen bonding extracted from the complex spectra of PIM. Spectra of PAA also could be expressed approximately over a whole range of a, in terms of this method including only two species, free COOH and free COO$^-$. The area, S_i, of band i was calculated approximately by

$$S_i = \int_{\bar{\nu}_i-5X_i}^{\bar{\nu}_i+5X_i} Fi(\nu)\,\mathrm{d}\nu \qquad (5)$$

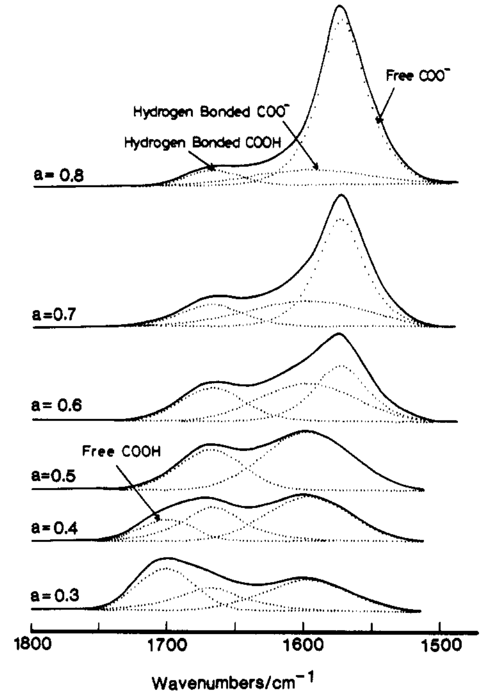

Figure 6. Expanded IR spectra of PIM at various a. Solid and dotted lines represent observed and resolved spectra, respectively.

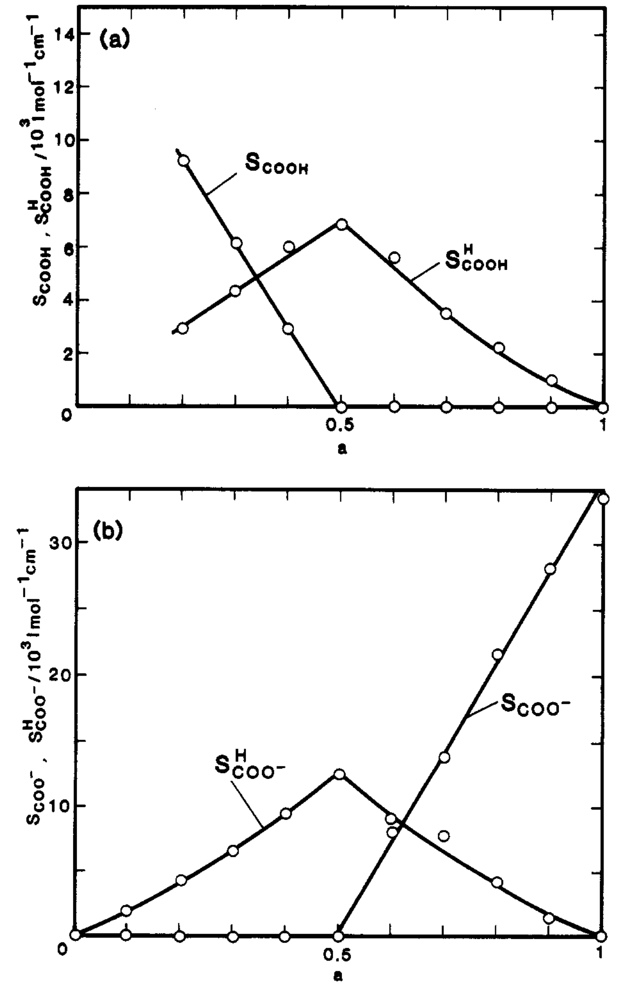

Figure 7. Plots of the area of a resolved band against a: (a) S_{COOH} and $S^H{}_{COOH}$; (b) S_{COO^-} and $S^H{}_{COO^-}$.

where X_i is a half-width of band i. The calculations of eq 5 was carried out by a common Simpson method. The plots of the area of free COOH, S_{COOH}, hydrogen-bonded COOH, $S^H{}_{COOH}$, free COO$^-$, S_{COO^-}, and hydrogen-bonded COO$^-$, $S^H{}_{COO^-}$, against a are shown in Figure 7. It is quite clear that the amounts of hydrogen-bonded COOH and COO$^-$ estimated from $S^H{}_{COOH}$ and $S^H{}_{COO^-}$ attain maxima at a = 0.5, respectively, and show symmetrical shapes concerning each maximum point. In addition, it is noted that neither free COO$^-$ exists below a = 0.5 nor free COOH exists above a = 0.5. These results mean that all ionized COO$^-$s are immediately hydrogen-bonded below a = 0.5

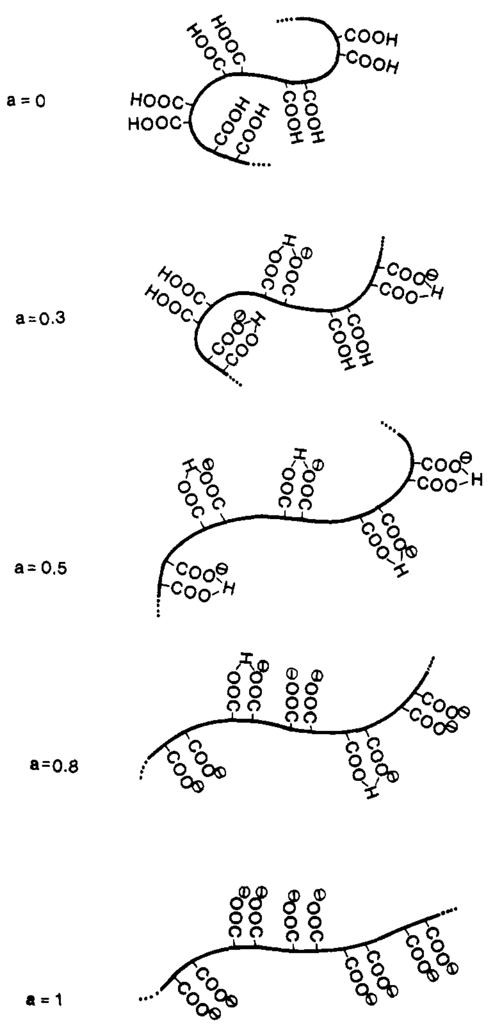

Figure 8. Schematic process of the dissociation of PIM.

and then above a = 0.5, and the $COO^-\cdots HOOC$ pair is destroyed by the neutralization.

Even at this stage, we cannot determine definitely which pair of COOH and COO^- can be hydrogen bonded, (1) between adjacent pairs of the unit of maleic acid, (2) between intramolecular pairs separated far along the same polymer chain, or (3) between intermolecular pairs of two different chains. Judging from the facts that a simple quantitative relationship holds between a and the amount of hydrogen bonding, which has a maximum just at a = 0.5, and especially that PAA does not show any evidence for hydrogen bonding, intermolecular hydrogen bonding between COOH and COO^- may not occur to any detectable extent. Also it is reasonable to presume that the adjacent pair of COOH and COO^- in the same maleic acid unit separated from each other in an alternating copolymer PIM chain forms quantitatively intramolecular hydrogen bonding. Therefore, we can represent schematically the dissociation process of PIM as shown in Figure 8. At $a < 0.5$, all ionized COO^-s are completely hydrogen bonded with COOHs, while at $a > 0.5$, all COOHs are completely hydrogen bonded to COO^-s, and an extra amount of neutralized COO^-s become free. This is one reason why PIM dissociates apparently in two steps.

Finally, the difference, $\Delta\nu$, in frequency between the asymmetric and symmetric vibrations is shown in Figure 9, where at $a < 0.5$, $\Delta\nu$ of PIM gradually decreases, keeping the value by 25 cm^{-1} as high as that of PAA, drops steeply at a = 0.5, and then above 0.5 increases again gradually with a, in contrast to PAA. $\Delta\nu$ is generally used as a measure of the degree of the covalent character of metal bonding in carboxylate groups; i.e., if $\Delta\nu$ is larger than 225 cm^{-1}, the binding is regarded as covalent.[32] For PIM and PAA, $\Delta\nu$'s are always less than 225 cm^{-1} at any a, and therefore the interaction between Na^+ and COO^- is regarded as ionic.[33] The larger values of $\Delta\nu$ for PIM seem to reflect hydrogen bonding as noted above. We do not have any reasonable interpretation for the increase in $\Delta\nu$ of PIM at $a > 0.5$.

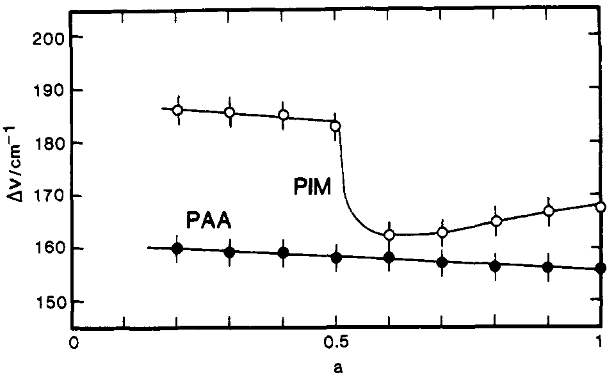

Figure 9. Plots of $\Delta\nu$ against a: PIM (○) and PAA (●).

Conclusion

From detailed analysis of UV and IR spectra of PIM in comparison with PAA, we have clarified the ionic intramolecular hydrogen bonding quantitatively between the adjacent pair of the ionized and the un-ionized carboxyl groups in the same maleic acid unit of PIM in the course of neutralization. To our best knowledge, this is the first work to confirm the existence of hydrogen bonding of polyacids directly by spectroscopic methods and to establish a quantitative analytical method of the hydrogen bonding. We will have to discuss in the future about the reason why only PIM forms the hydrogen bonding between COOH and COO^- but not PAA.

Acknowledgment. We are indebted to Professor A. Minakata of the Hamamatsu University school of medicine and Dr. S. Koda of Nagoya University for many valuable comments and helpful discussions. This work was supported in part by the Ishida Foundation and by a Grant-in-Aid for Encouragement from the Ministry of Education, Science and Culture of Japan (01750823).

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Registry No. PIM (alternating copolymer), 135639-46-2; NaOH, 1310-73-2; $NaClO_4$, 7601-89-0.