Dissociation Behavior of Poly(fumaric acid) and Poly(maleic acid). 3. Infrared and Ultraviolet Spectroscopy

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ABSTRACT: Infrared (IR) and ultraviolet (UV) absorption spectra of poly(fumaric acid) (PFA) and its stereoisomer, poly(maleic acid) (PMA), in aqueous solution at various degree of neutralization (a) were measured to study their dissociation behavior and to compare with those of an alternating copolymer of isobutylene and maleic acid (PIM), whose carboxyl groups show a definite intramolecular ionic hydrogen bonding between nearest-neighbor carboxyl groups during neutralization as reported in the previous paper. In UV spectra, the absorbance of PFA and PMA in the vicinity of $\lambda = 220$ nm was found to increase with a up to $a = 0.6$ and then decrease with a. The IR spectra of PFA and PMA revealed that, above $a = 0.5$, a stretching vibration band of C=O of COOH shifts to lower wavenumbers by about 25 cm^{-1} and an asymmetric stretching vibration band of COO^- also shifts to lower wavenumbers by about 24 cm^{-1}. The IR bands ascribed to carboxyl groups of PFA were resolved into those of four species, that is, free COOH, free COO^-, hydrogen-bonded COOH, and hydrogen-bonded COO^-. It was shown that PFA has both free and hydrogen-bonded COO^- as well as both free and hydrogen-bonded COOH at $a = 0.5$. The IR bands of PMA, however, could not be resolved by those only four species over a whole a. It appears that PMA has the hydrogen bonding formed over four adjacent COOH's which can resonate each other. The difference in the dissociation process between PFA and PMA was discussed from a viewpoint of their configurational difference. The most probable dissociation process for PFA and PMA was proposed and discussed in view of the results of potentiometric titration.

Introduction

In a previous paper, we found that poly(fumaric acid) (PFA) and its stereoisomer, poly(maleic acid) (PMA), both of which have charge densities exactly twice as high as a conventional vinyl carboxylic polyelectrolyte such as poly(acrylic acid) (PAA), dissociate apparently in two steps, at a degree of dissociation (α) = 0.5, and that PMA shows a more definite two-step dissociation than PFA.[1] Because PFA and PMA do not necessarily show a definite pairing of carboxyl groups on a polymer chain, that is, the molecular structure of both acids are represented by –(CH(COOH))–, it is particularly interesting to clarify the cause of why these polyelectrolytes show apparent two-step dissociation. The difference in dissociation behavior between them should be attributed only to their configurational difference. That is, PMA must have a more regular configuration in the nearest neighbors than PFA, because PMA was prepared via poly(maleic anhydride) whose carboxyl groups are fixed in the cis form. We have presented previously some possible configurations for PFA and PMA.[2] Theoretical studies on the potentiometric titration of PFA and PMA suggested that strong short-range electrostatic interaction for these polyelectrolytes having a high charge density plays a dominant role in the dissociation behavior and that their dissociation behavior can be qualitatively interpreted by the configurational difference.[2] The agreement of the calculation with the experimental data, however, was not necessarily quantitative, since the experimental titration curves showed an asymmetric nature for the electrostatic interaction part, ΔpK, i.e., a lower increase for $\alpha < 0.5$ and a higher increase for $\alpha > 0.5$.[1,2]

The effect of the configuration of polyelectrolytes on the dissociation properties has been known since Nagasawa et al.[3,4] reported that isotactic PAA and poly(methacrylic acid) (PMeA) showed larger ΔpK than their syndiotactic counterparts because of the difference in the local conformation. They successfully applied a rodlike model with a smeared charge density, where the difference in the local conformation of polyelectrolyte was assumed as that in the average charge density and radius of rod. However, the large difference in ΔpK between PFA and PMA above $\alpha = 0.5$ in addition to their two-step dissociation cannot be definitely elucidated by only the simple Coulombic electrostatic interaction. That is, it seems reasonable that there may exist any additional interaction such as hydrogen bonding whose extent and type vary with the difference in the configuration of carboxyl groups on a polyelectrolyte chain.

We reported previously that an alternating copolymer of isobutylene and maleic acid (PIM), which has a number of isolated maleic acid residues, each flanked by isobutylene residues in a backbone, resulting in a definite pairing of the carboxyl groups, shows a clear two-step dissociation at $\alpha = 0.5$.[5] Theoretical study also suggested that apparent two-step dissociation results from the strong short-range electrostatic interaction. If one assumes either a lower dielectric constant or hydrogen bonding between the nearest-neighbor carboxyl groups, the agreement of theoretical curves with observed ones was quantitative. It was thus concluded that both strong short-range electrostatic interaction and hydrogen bonding affect appreciably the dissociation behavior of PIM.

Very recently, in order to confirm the existence of hydrogen bonding during neutralization, infrared (IR) and ultraviolet (UV) spectra for PIM and PAA in aqueous solution were measured as a function of the degree of neutralization (a).[6] They revealed that the nearest-neighboring carboxyl groups of PIM form quantitatively an ionic intramolecular hydrogen bonding between COOH and COO^- when either of the paired carboxyl groups dissociates. That is, the amounts of both hydrogen-bonded COOH and COO^- attain maxima at $a = 0.5$ and show symmetrical shapes about their maxima. In addition, no free COO^- exists below $a = 0.5$ and free COOH exists above

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$a = 0.5$. On the other hand, all carboxyl groups of PAA did not form such ionic intramolecular hydrogen bonding over whole a. This fact strongly suggests that all ionized COO^-'s of PIM are hydrogen-bonded below $a = 0.5$ and then above $a = 0.5$ and all $COO^- \cdots HOOC$ pairs are destroyed by further neutralization. Taking into account the effect of hydrogen bonding, the agreement of the observed titration curve with the theoretical curve was quantitative. Therefore, the ionizable groups of PIM are strongly affected not only by simple Coulombic interaction but also by ionic hydrogen bonding between nearest-neighbor carboxyl groups. This is one of the main reasons for a definite two-step dissociation at $a = 0.5$ for PIM.

While the various types of hydrogen bonding are known in aqueous solution, i.e., linear or cyclic dimer between carboxyl groups or between carboxyl groups and water,[6] such hydrogen bonding does not largely affect the dissociation behavior of polyelectrolyte, taking into account the case of PAA.

It seems reasonable to assume that carboxyl groups of PFA and PMA also form such a hydrogen bonding during dissociation, since the nearest-neighbor carboxyl group is completely in the β-position in a polymer chain, like PIM. Judging from cooperative natures of hydrogen bonding, however, equivocal pairing of carboxyl groups due to the complicated configurations for PFA and PMA may lead to an increase in the number of pairings of hydrogen bonding.[2] Therefore, the extent and types of hydrogen bonding of PFA and PMA should be determined spectroscopically as a function of a, in order to clarify the dissociation behavior.

The present study is aimed at proving whether intramolecular hydrogen bonding for PFA and PMA occurs during neutralization, by means of UV and IR spectroscopy, and at clarifying the effect of the configurational difference on the dissociation behavior. Since the configuration of the monomer of PFA is trans, it is reasonable to assume that hydrogen bonding cannot form between the two carboxyl groups in the original monomer. However, both UV and IR spectra of PFA showed the existence of hydrogen bonding. This strongly suggests that the cis addition mode in polymerization makes new pairs which can form hydrogen bondings. It is also reasonable that two carboxyl groups in the monomer units of PMA are capable of forming hydrogen bonding like those of PIM. IR and UV spectra of PMA indicated the formation of hydrogen bonding. However, the type of hydrogen bonding of PMA was different from that of PIM, because cis addition of the monomer to the chain terminal in polymerization may make four equivalent carboxyl groups which can resonate each other. Therefore, the type and extent of hydrogen bonding for PFA and PMA are more complex than those for PIM. In the present paper, we will fully discuss the relationship between the configuration and the dissociation behavior of polyelectrolytes and the most probable dissociation process for PFA and PMA.

Materials and Methods

Samples of PFA and PMA were the same as those used in the previous paper.[1] UV spectra were measured in the wavelength λ range of 185–260 nm with a Hitachi Model 330 spectrophotometer. Details are presented in the previous paper.[6] The polymer and the salt ($NaClO_4$) concentrations, C_p and C_s, were 5.02–5.69 mN and 5 mN, respectively. It is noted here that turbidity was not observed under this condition.[7] As reported in the previous paper,[1] both solutions of PFA and PMA produce precipitation in the region of $\alpha > 0.5$ even at dilute C_s, $C_s < 0.1$ N NaCl. The cloud points may be largely dependent on the C_p, C_s, a, temperature, molecular weight, and type of counterion.[7]

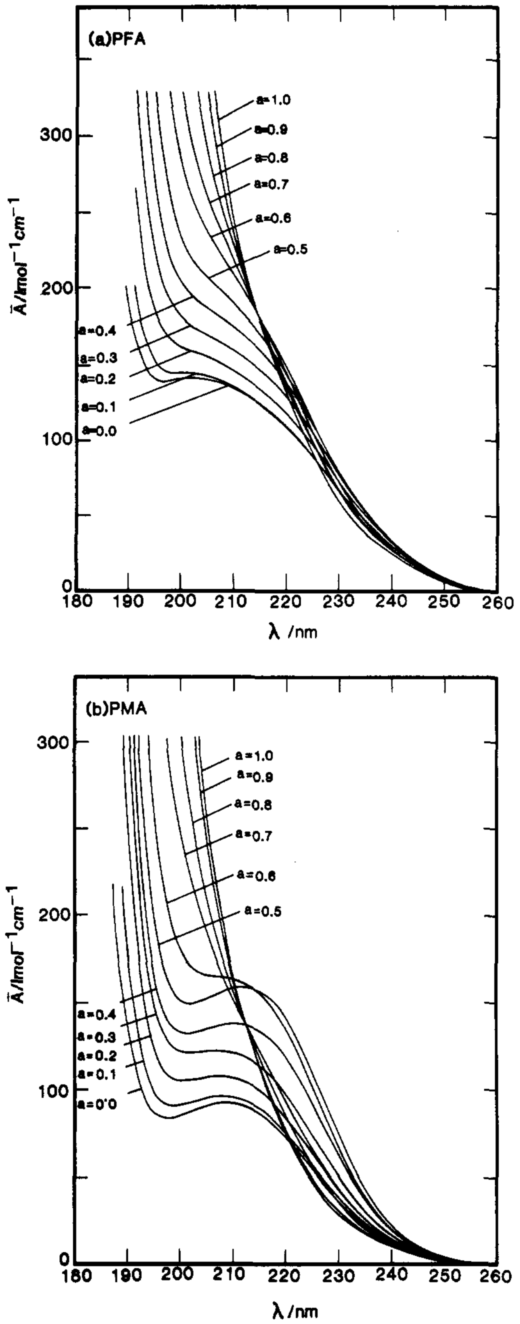

Figure 1. UV spectra at various a: (a) PFA, $C_p = 5.02$ mN, $C_s = 5$ mN; (b) PMA, $C_p = 5.69$ mN, $C_s = 5$ mN.

FT-IR spectra in the salt-free deuterated water were measured with a JEOL JIR-40X FT-IR spectrophotometer, as detailed in the previous paper.[6] C_p of PFA and PMA were 0.439 and 0.477 N, respectively. C_p or C_s dependence on IR spectra was confirmed to be negligibly small. Although a solution of PFA and PMA became turbid at a degree of neutralization (a) > 0.7 under this condition,[7] IR spectra were little affected. Since solutions of PFA and PMA produced precipitation even in salt-free solution, the turbid solution was rigorously stirred up to just before measurement. Throughout the present paper, we will use the degree of neutralization a instead of the degree of dissociation α.

Results

UV spectra of PFA and PMA in aqueous $NaClO_4$ solutions at various a for a fixed C_p are shown in Figure 1, where the absorbance of PFA and PMA in the vicinity of $\lambda = 220$ nm increases with a up to $a = 0.6$ and then decreases with a in a way similar to that of PIM reported in the previous paper.[6] An isosbestic point was observed at $\lambda = 214$ nm above $a = 0.6$ for PFA and at $\lambda = 213$ nm above $a = 0.7$ for PMA, respectively. Generally, UV spectra of organic carboxylic acids and their salts have two main bands ascribed to COOH ($n \rightarrow \pi^*$, $\lambda_{max} = 210$ nm) and to COO^- ($\pi \rightarrow \pi^*$, $\lambda_{max} = 183$ nm). If there exist only two kinds of absorption bands of COOH and COO^- which are in equilibrium with each other, an isosbestic point should appear at a certain λ over a complete range of a. We reported in the previous paper that UV spectra of PAA show a clear isosbestic point at $\lambda = 213$ nm over the whole range of a but PIM does not show any isosbestic point in the region $a < 0.6$.[6] It was concluded in the previous paper that the appearance of the new electronic states of the carboxyl groups of PIM results from the transition between the ground and the excited energy levels caused by the following resonance:[6]

$$-O-H\cdots O^- \leftrightarrow O^-\cdots H-O-$$

Therefore, the new absorption band in the UV spectra of PFA and PMA at $\lambda = 220$ nm which increases with a should also be closely related to an ionic hydrogen bonding. Thus, we concluded that carboxyl groups of both PFA and PMA form the ionic hydrogen bonding during neutralization, as in the case of PIM.[6] It is noted here that UV spectra of PFA are different from those of PMA. Thus a steep increase in the absorption band of PMA at $\lambda = 220$ nm with a was observed, while the UV spectra of PFA change intermediately between those of PAA and PMA or PIM.[6] This is consistent with the results of the potentiometric titration.[1] The difference in UV spectra between PFA and PMA may result from different extent and type of the formation of hydrogen bonding due to their configurational difference, as will be discussed.

IR spectra of PFA and PMA in deuterated water at various a for a fixed C_p together with the assignments of each band and the a dependence of frequencies of their bands are shown in Figures 2 and 3. It is noted here that IR spectra of PFA and PMA are similar to those of PIM reported previously.[6] That is, the frequency of the stretching vibration of C=O, ν(C=O), of PFA shifts by 30 cm^{-1} to lower frequencies above $a = 0.7$ and the frequency of the asymmetric stretching vibration of COO^-, $\nu_a(COO^-)$, in the region of $a < 0.5$ is higher by 24 cm^{-1} than that of PAA reported previously and then approaches the same value as that of PAA beyond $a = 0.5$. PMA also shifts ν(C=O) by 25 cm^{-1} to lower frequencies above $a = 0.5$, while $\nu_a(COO^-)$ in the region $a < 0.5$ is higher by 22 cm^{-1} than that of PAA[6] and then approaches the same value as that of PAA beyond $a = 0.5$. Therefore, we concluded that carboxyl groups of PFA and PMA also have the intramolecular hydrogen-bonded carboxyl groups during neutralization, as in the case of PIM.[6] However, it is noted here that the extent of the shift of PFA and PMA is smaller than that of PIM and that the change in the shift of the absorption bands of PFA and PMA with a is more gradual as compared with that of PIM.

Plots of $\bar{A}(\nu(C=O)) - \bar{A}(\nu_a(COO^-))$ against a are shown in Figure 4, where $\bar{A}$ represents the absorbance reduced for C_p. If there exist only two kinds of species, COOH and COO^-, this plot should become linear. We reported previously that this plot is linear for PAA but not for PIM.[6] It is noted here that both PFA and PMA show a break point at $a = 0.5$ (i.e., $\bar{A}(\nu(C=O)) - \bar{A}(\nu_a(COO^-))$ of PFA and PMA decreases gradually with a at $a < 0.5$ and decreases more steeply at $a > 0.5$) and that PMA shows a more definite break point than PFA. This manner similar to that of PIM should be due to the existence of hydrogen-bonded species, in addition to free COOH and COO^-. The difference between them is closely ascribed to the difference in the type and the extent of hydrogen bonding between PFA and PMA, as will be discussed later.

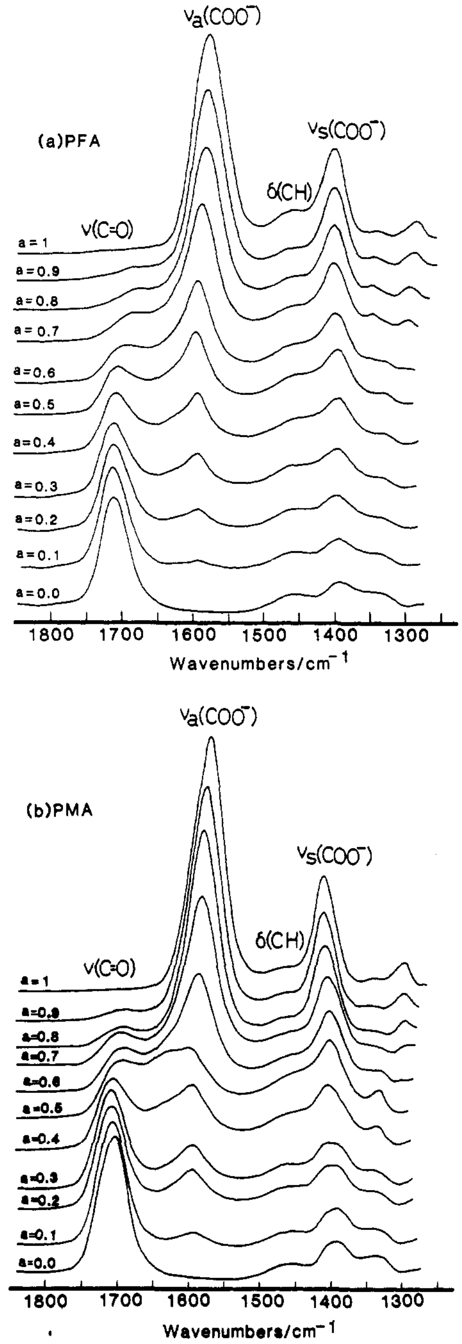

Figure 2. IR spectra at various a in salt-free solution; (a) PFA, $C_p = 0.439$ N, $d = 29.8$ μm; (b) PMA, $C_p = 0.477$ N, $d = 56.0$ μm.

The difference in frequency between the asymmetric and symmetric carboxylate vibration, $\Delta\nu$, is shown in Figure 5, where, at $a < 0.5$, $\Delta\nu$ of PFA and PMA is constant, keeping the value by 30–36 cm^{-1} higher than that of PAA, and drops gradually above $a = 0.5$. This manner is also similar to that of PIM and due to the existence of hydrogen-bonded species. Therefore, we concluded that the carboxyl groups of both PFA and PMA form ionic hydrogen bondings during neutralization and that the extent and type of hydrogen bonding of PFA are different from those of PMA. We will discuss the reason for this.

Discussion

The starting materials of PFA and PMA used here were bis(trimethylsilyl) fumarate in the trans configuration and

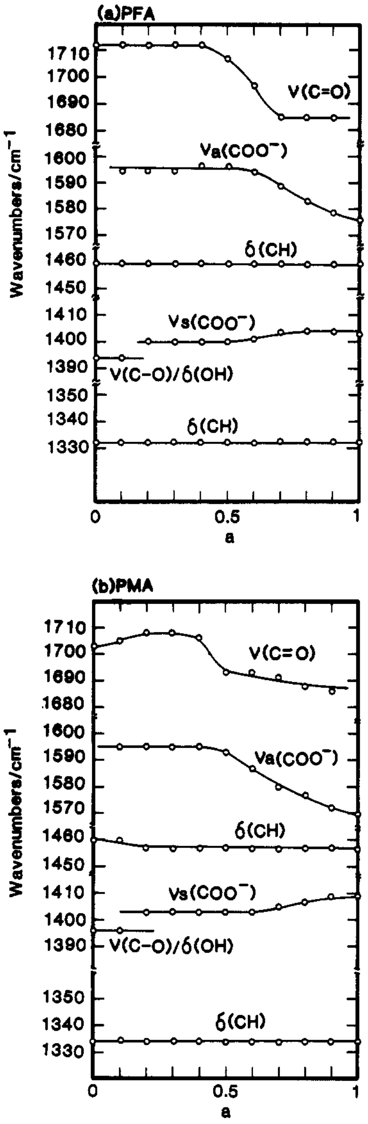

Figure 3. Plots of characteristic absorption frequencies against a: (a) PFA and (b) PMA. ν and δ represent stretching and bending, respectively.

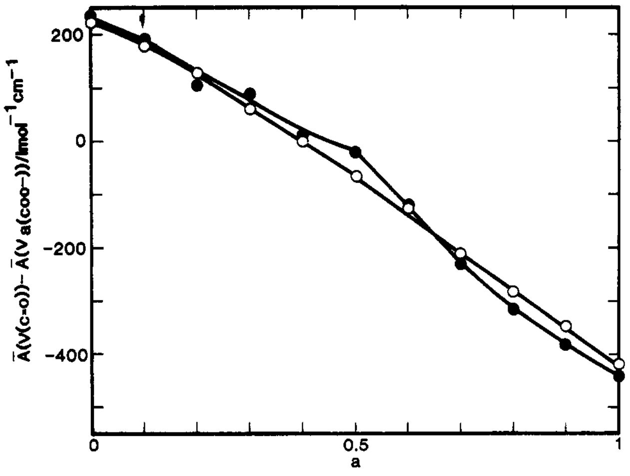

Figure 4. Plots of $\bar{A}(\nu(C{=}O)) - \bar{A}(\nu_a(COO^-))$ against a: PFA (○) and PMA (●).

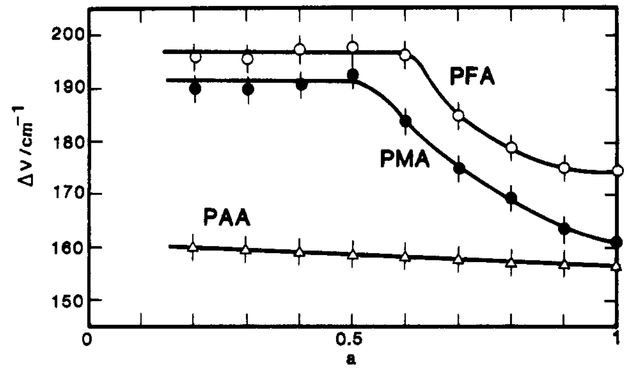

Figure 5. Plots of $\Delta\nu$ against a: PFA (○), PMA (●), and PAA (△).[6]

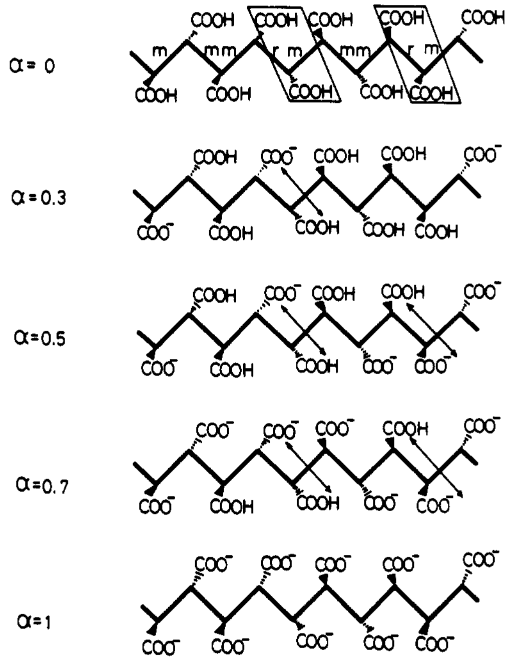

Figure 6. Most probable configuration and schematic process of dissociation for PFA at $m = 0.75$ and $r = 0.25$, where m and r represent the fractions of meso and racemic diads, respectively.

maleic anhydride in the cis configuration, respectively. For PFA, any two successive diads are formed through two different mechanisms with different tactic probabilities, one for the addition mode and the other for the chain-end rotation. Thus, the propagation step in α,β-disubstituted monomers generates two pseudoasymmetric centers. Taking into consideration the fact that dialkyl fumarates can polymerize by free-radical polymerization, but the cis isomers, dialkyl maleates, can polymerize only with difficulty, the rate of rotation around the C–C backbone in the chain end is much slower than that of propagation. Therefore, it seems reasonable to assume that the chain of PFA retains the monomer configuration with a large extent. If one assumes that the cis and trans addition modes in polymerization proceed with the same probability, the extent of meso and racemic diads should be 0.75 and 0.25, respectively. Recently, Ando et al. reported that the extents of meso and racemic diads for poly(diisopropyl fumarate) are 0.78 and 0.22, respectively, by means of ^{13}C NMR.[8] Therefore, we assumed the most probable configuration of PFA, as shown in Figure 6, where meso and racemic diads were assumed to be in a ratio of 0.75 to 0.25, respectively. It is noted here that PFA has 50% pairs of carboxyl groups which can form hydrogen bonding. The distance between the trans carboxyl groups in the original monomer of PFA is about 0.49 nm, so that the hydrogen bonding between them can be formed with difficulty. In UV spectra of PFA, the increase in absorption at $\lambda = 220$ nm is not as clear as those of PMA and PIM. This implies that PFA has less hydrogen-bonding pairs than PMA and PIM. This is one reason why UV spectra of PFA show intermediate behavior between those of PAA

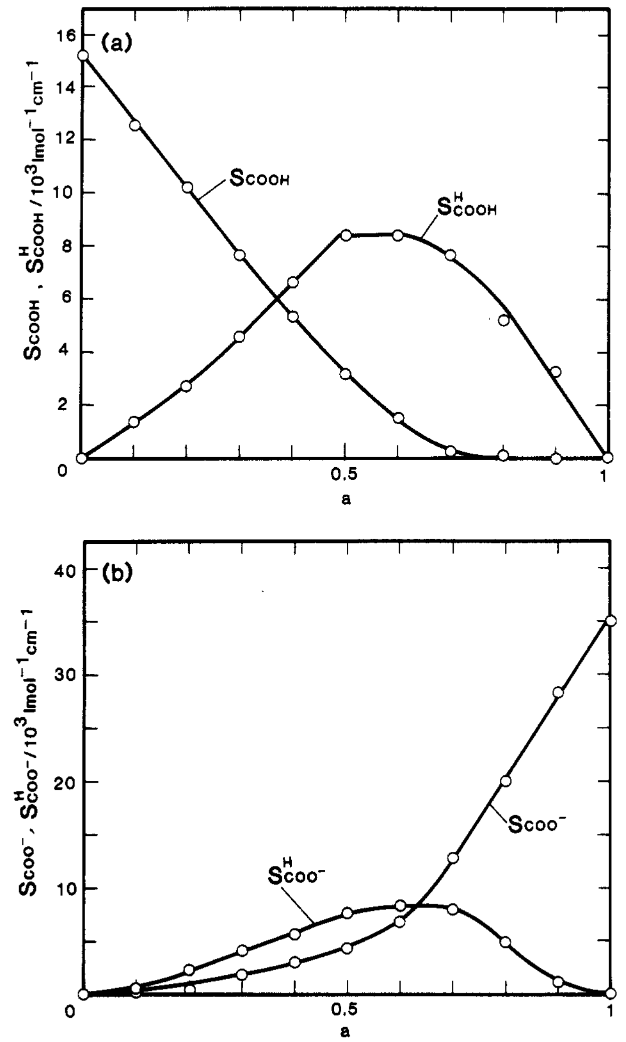

Figure 7. Plots of the areas of separated bands of PFA against a: (a) S_{COOH}, S^H_{COOH}; (b) S_{COO^-}, $S^H_{COO^-}$.

and PMA or PIM and are qualitatively consistent with those of the potentiometric titration reported previously.[1]

As shown in Figure 3a, ν(C=O) of un-ionized carboxyl groups gradually shifts to a lower wavenumber by 30 cm^{-1} above a = 0.5, and ν_a(COO$^-$) of ionized carboxyl groups shifts to a lower wavenumber by 24 cm^{-1} above a = 0.5. These shifts are qualitatively consistent with those in the spectra of PIM reported in the previous paper, and we carried out peak separation to analyze the extent of hydrogen bonding as in the same procedure. The frequencies of free COOH, free COO$^-$, hydrogen-bonded COOH, and hydrogen-bonded COO$^-$ were assumed to be 1712, 1579, 1669, and 1599 cm^{-1}, respectively, independent of a. Each absorbance was assumed to be represented by a Gauss–Lorentz function. The spectra of PFA could be completely represented by only four species over a whole range of a. The dependences of the areas of separated bands, S, on a were shown in Figure 7, where S_{COOH}, S^H_{COOH}, S_{COO^-}, and $S^H_{COO^-}$ represent the areas of free COOH, hydrogen-bonded COOH, free COO$^-$, and hydrogen-bonded COO$^-$, respectively. The areas of hydrogen-bonded species, S^H_{COOH} and S_{COO^-}, increase with a below a = 0.5, retain a constant value up to a = 0.7, and then decrease with a. It is noted here that there exist free COO$^-$ at $a < 0.5$ and free COOH at $a > 0.5$. It is also of interest to compare these with the results on PIM, where S^H_{COOH} and $S^H_{COO^-}$ of PIM attain maxima at a = 0.5 and show symmetrical shapes around each maximum point. In addition, neither free COO$^-$ exists below a = 0.5 nor free COOH exists above a = 0.5. This means that all ionized COO$^-$'s are immediately hydrogen-bonded below a = 0.5 and that, above a = 0.5, the COO$^-$·····HOOC pair is destroyed by the neutralization. In contrast, PFA does not show symmetrical shapes about a = 0.5. This is due to the possible coexistence of both the carboxyl groups which can form hydrogen bonding and the carboxyl groups which cannot form hydrogen bonding as shown in Figure 6. The linear increase in S^H_{COOH} and $S^H_{COO^-}$ with a below a = 0.5 and the constancy of hydrogen-bonded species up to a = 0.75 may be explained as follows: first, the carboxyl groups which can form hydrogen bonding and those which cannot form hydrogen bonding dissociate with the same probability below a = 0.5. Second, the carboxyl groups which do not form hydrogen bonding dissociate, and finally hydrogen-bonded carboxyl groups dissociate. The dissociation process for PFA was shown in Figure 6. There remains a question as to why PFA dissociates apparently in two steps at α = 0.5, not at 0.75, because, if only hydrogen bonding strongly affects the dissociation process, apparent two-step dissociation must occur at α = 0.75. In fact, two-step dissociation at α = 0.5 of PFA is less clear than that of PMA and PIM.[1] This suggests that the increase in ΔpK at α = 0.5 results from the strong electrostatic interaction from neighboring ionized groups, rather than hydrogen bonding, since at α = 0.75 the electrostatic interaction from the neighboring charges is too strong to show a further clear two-step dissociation at this α. This is one reason why PFA shows the ambiguous two-step dissociation at α = 0.5. That is, dissociation behavior of PFA can be interpreted by the balance between Coulombic interaction at α = 0.5 and hydrogen bonding at α = 0.75.

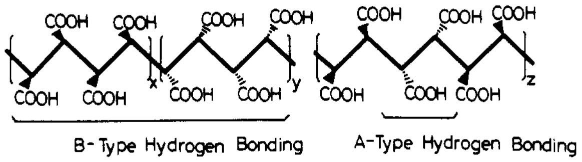

Figure 8. Type of hydrogen bonding for PMA.

On the other hand, since PMA was synthesized from the anhydride structure of maleic acid which retains the configuration of two carboxyl groups in the monomer, two carboxyl groups in the original monomer units of PMA can form hydrogen bonding, like PIM. However, two addition modes, cis and trans addition, in polymerization make a more complex configuration as shown in Figure 8, where the A-type is hydrogen bonding with a definite pair like PFA and PIM while the B-type is hydrogen bonding which can be formed between four equivalent carboxyl groups resonating each other. They should be spectroscopically distinguished from each other since the resonance structure strongly affects the frequency of the carboxyl groups. One example of possible resonance structures of B-type hydrogen bonding at a = 0.5 is shown in Figure 9. Although the ionized groups will separate locally from each other as far as possible, all resonance states cannot be distinguished energetically from each other, because of the existence of electrostatic interaction from neighboring ionized groups. This resonance structure suggests that the four states, free COOH, free COO$^-$, hydrogen-bonded COOH, and hydrogen-bonded COO$^-$, can exist simultaneously by way of pairing the hydrogen bondings. The spring constant of the stretching vibration band of C=O is well-known to be influenced by the resonance effect. That is, the stretching vibration frequency of C=O in COOH is higher than that in COO$^-$ due to the resonance effect of COO$^-$, which leads to the decrease

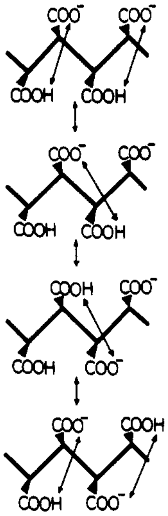

Figure 9. Some resonance structures of B-type hydrogen bonding at $\alpha = 0.5$.

of the spring constant. Hydrogen bonding also gives rise to the decrease in the spring constant of C=O in COOH and to the increase in that of COO^-. As reported in the previous paper, $\nu(C{=}O)$ and $\nu_a(COO^-)$ of PIM shift by 50 cm^{-1} to a lower wavenumber and by 27 cm^{-1} to a higher wavenumber, respectively. In contrast, $\nu(C{=}O)$ of PMA shifts by 25 cm^{-1} and $\nu_a(COO^-)$ shifts by 25 cm^{-1} as shown in Figure 3. The small shift for $\nu(C{=}O)$ of PMA is ascribed to the resonance structure as shown in Figure 9 because the spring constant of B-type hydrogen-bonded COOH is little affected by the resonance among the four equivalent carboxyl groups, compared with A-type hydrogen-bonded COOH in a definite paired COOH·····$^-$OOC.

Although we also tried the peak separation of the IR spectra of PMA, no resolution could be made by only four species including free COOH, free COO^-, hydrogen-bonded COOH, and hydrogen-bonded COO^- with any frequency assumed. A-type and B-type hydrogen bonding, in addition to free COOH and COO^- must be taken into account, leading to difficulty in calculation. If addition in polymerization proceeds with the same probability of the cis and trans modes, the type of hydrogen bonding of PMA is only B-type. At this stage, however, the peak separation could not be achieved over the complete range of a.

Finally, we must describe a reason why hydrogen bonding can form only between cis β-COOH's and not between γ-COOH's. It has been well-known that the distance, the angle, the less free-rotation, and the relative position between the donor and the acceptor are of importance in order to form the strong hydrogen bonding. Generally speaking, the distance which can form hydrogen bonding needs to be about 0.4 nm. If only so, even carboxyl groups in PAA and PMeA can form hydrogen bonding. We examined the ability of hydrogen bonding to form by using the molecular model for partial structures for PAA and PMA or PIM. It is reasonable to assume that when COOH and nearest-neighbor COO^- lie on the same plane, the strongest hydrogen bonding can be formed. In PIM and PMA, if one tries to move COOH and COO^- on the same plane with the fixed backbone, H of COOH and O^- of COO^- can come to the shortest distance. This is a very favorable structure for formation of hydrogen bonding. On the other hand, in PAA the hydrogen atom of COOH cannot approach O^- in COO^- on the same plane. This is the main reason why hydrogen bonding can be formed only between cis β-COOH's.

Conclusions

1. About 50% of the carboxyl groups of PFA can form intramolecular hydrogen bonding. The two-step dissociation of PFA is due to the effect of the simple electrostatic interaction at $\alpha = 0.5$ and the hydrogen bonding at $\alpha = 0.75$.
2. The carboxyl groups of PMA can form intramolecular hydrogen bonding among the four equivalent carboxyl groups which resonate each other. The two-step dissociation of PMA at $\alpha = 0.5$ is due to the effect of both the hydrogen bonding and simple electrostatic interaction.
3. The difference in titration curves between PFA and PMA is due to the different extent and type of the hydrogen bondings produced from their configurational difference, in addition to simple electrostatic interaction.

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