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Dissociation Behavior of Poly(itaconic acid) by Potentiometric Titration and Intrinsic Viscosity

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ABSTRACT: The potentiometric titration and intrinsic viscosity were measured under various conditions to study the dissociation behavior of poly(itaconic acid) (PIA), a polyelectrolyte with the same average charge density as poly(fumaric acid) (PFA) and poly(maleic acid) (PMA) but with a different arrangement of the carboxyl groups. The titration curves showed that PIA exhibits an apparent two-step dissociation similar to PFA and PMA. The analysis revealed that the intrinsic dissociation constant of PIA is smaller than that of PFA and PMA and that the electrostatic free energy of PIA at degree of dissociation $\alpha < 0.5$ is larger than that of PFA and PMA, but at $\alpha > 0.5$, the value of PIA lies between those of PFA and PMA. The intrinsic viscosity increased with increasing α, attained a maximum near $\alpha = 0.5$, and then decreased steeply. The dissociation behavior of PIA was discussed in terms of the discrete charge model including effects of the short-range electrostatic interaction and the difference in the dissociation behavior between α- and β-COOH. The calculated titration curve was in quantitative agreement with the observed one. It was concluded that the difference in the local distribution of charges, rather than overall charge density on a polymer chain, plays a dominant role in the dissociation behavior of polyacids with high charge density.

Introduction

Polyelectrolyte solutions are known to have a number of properties different from those of both nonpolymeric electrolytes and nonionic polymers. The properties characteristic of polyelectrolyte solutions have been accounted for by the strong electrostatic potential produced by a large number of charges on a polymer chain.[1,2]

Among the solution behavior of the polyelectrolytes, the potentiometric titration is closely related to the electrostatic interaction between a dissociating proton and ionized groups on a polymer chain. On the other hand, the intrinsic viscosity, which expresses the average dimension of a macromolecule, is related to the electrostatic interaction between ionized groups on a polymer chain. These properties depend on the charge density and charge distribution on a polymer chain.

We have reported previously that poly(fumaric acid), PFA, and its stereoisomer, poly(maleic acid), PMA, both of which have charge densities exactly twice as high as that of poly(acrylic acid), PAA, and poly(methacrylic acid), PMeA, dissociate in two steps due to short-range electrostatic interaction from the neighboring ionized groups. Also PMA shows a clearer two-step dissociation than PFA because of the configurational difference between them.[3,4] Moreover, the rod model with a smeared charge density was found to be unable to interpret the results of these polyacids, in marked contrast to the ordinary poly(vinylic carboxylic acids) which have been analyzed successfully by the smeared charge model.[5-8] In the subsequent paper, we reported on a theoretical study of the apparent two-step dissociation of PFA and PMA and on the difference in the dissociation behavior between them resulting from the local configurational difference, by using a discrete charge model including short-range interactions.[9] That is, the difference in the local charge distribution on a polymer chain strongly affects its dissociation behavior.

Muto carried out a potentiometric titration of poly(itaconic acid), PIA, a polyelectrolyte that has the same average charge density as PFA and PMA, but its carboxyl groups are located differently from those of PFA and PMA, using various kinds of cations as counterions.[10] He analyzed the data in terms of two empirical pK values and found that at degree of dissociation $\alpha < 0.5$, the apparent pK value, pK_a, defined later, becomes slightly larger as the size of the cation becomes smaller, whereas the tendency is reversed at $\alpha > 0.5$, in agreement with the results for ordinary poly(carboxylic acids). But he did not discuss further the physical meaning of two pKs or the changes in pK_a mentioned above. Here, it will be particularly important to compare the effect of the charge distribution along the polyelectrolyte chain on the titration behavior of PIA with that of other polyelectrolytes reported previously. The charge distribution of PIA may be compared either with that of PAA and PMeA because they have the same charge interval along the main chain or with that of PFA and PMA because they have the same overall charge density. Also comparison can be made between PAA having α-COOH and poly(vinylacetic acid), PVAc, having β-COOH as a reference material for PIA which has both COOH's. Actually, α- and β-COOH of PIA are essentially distinguishable from each other in contrast to COOH's of PFA and PMA, although the difference in pK between α- and β-COOH was proved to be slight. In addition to the difference in the relative position, the higher rotational freedom of α-COOH as compared to that of β-COOH may affect its dissociation behavior. What we are interested in is to clarify the effect of the difference in location and distribution of the charges on a polyelectrolyte chain on the dissociation behavior.

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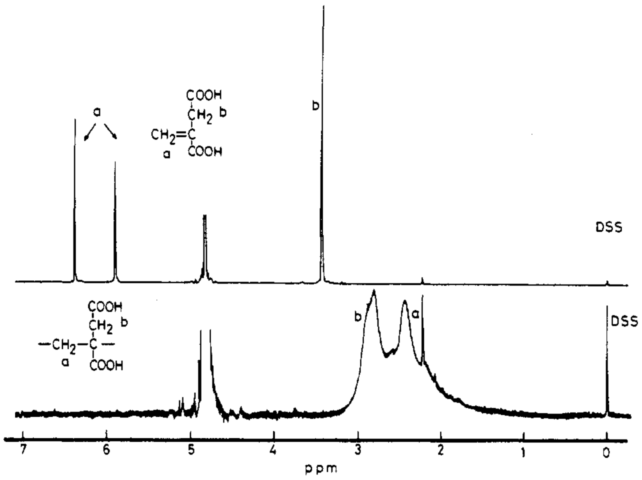

Figure 1. 270-MHz ^{1}H NMR spectra of PIA in 4.0 g/100 mL of D_2O solution and the monomer in D_2O solution, at 25 °C with sodium 3-(trimethylsilyl)propanesulfonate as an internal standard.

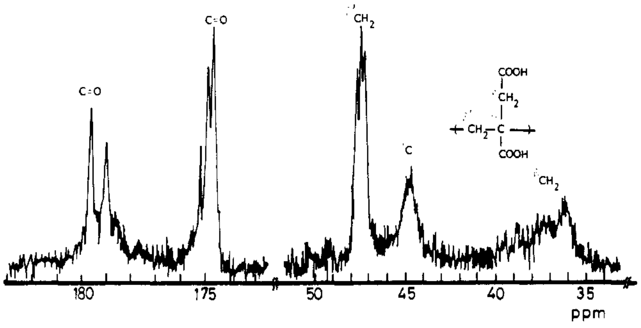

Figure 2. ^{13}C NMR spectrum of PIA.

The purpose of this paper is to present the details of the dissociation behavior of PIA, by measuring the potentiometric titration and intrinsic viscosity at various α. In addition, by comparing the dissociation behavior of other polyacids, such as PFA, PMA, and PAA, the characteristic dissociation behavior of polyelectrolytes with high charge density is analyzed on the basis of the discrete charge model reported previously, from the viewpoint of the difference in local distribution of the ionized groups.

Experimental Section

1. Materials. PIA was prepared by the procedure of Marvel and Shepherd.[11] Itaconic acid monomer was twice recrystallized from water before use. Thirty grams of the monomer was polymerized in 70 mL of a 0.5 N HCl aqueous solution with 0.15 g of potassium peroxysulfate as an initiator at 60 °C for 3 days under vacuum. The reaction mixture was repeatedly dialyzed against water, passed through a mixed bed of ion-exchange resins, and finally freeze-dried. The polymer was obtained in 10% yield. The chemical structure of PIA was confirmed with ^{1}H and ^{13}C NMR spectra as shown in Figures 1 and 2, respectively, where the peaks of $CH_2=$ in the monomer disappeared completely. The solutions of PIA for the measurements were prepared by passing them again through a mixed bed of ion-exchange resins and adding a required amount of NaCl to them just before measurement. The concentrations of PIA, C_p, were usually 4.32–8.63 mN for titration and the initial C_p for viscometry was 0.344–1.0 g/dL, depending on α, and the concentrations of NaCl, C_s, were 0.0050–0.10 N for titration and 0.10 N for viscometry. The titration was carried out with carbonate-free NaOH containing NaCl as a titrant.

2. Measurements. The 270-MHz ^{1}H NMR and 67.80-MHz ^{13}C NMR spectra were run at room temperature on a FT NMR spectrometer of JEOL type GX-270. Recording conditions for ^{13}C NMR were as follows; 3.4-μs pulse width, 16K points, 4500 scans, relaxation delay of 30 s between pulses, deuterated acetone including 30 wt % H_2O as a solvent, and polymer concentration of 12 wt %. The chemical shifts were determined by assigning 29.8 ppm to the methyl group of deuterated acetone. The assignment of the peaks of PIA followed the paper of Horata et al.[12]

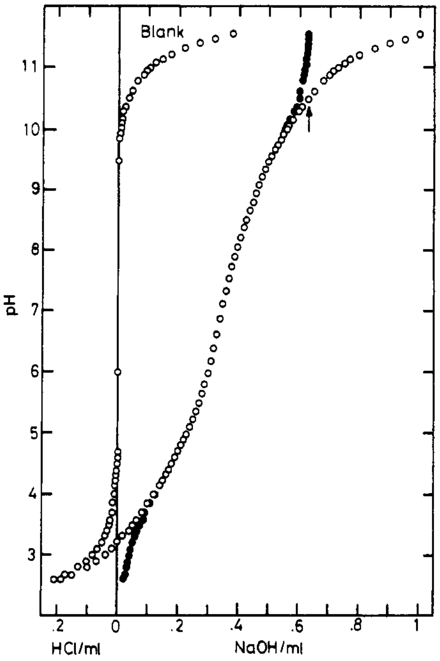

Figure 3. Potentiometric titration of PIA (C_p = 0.008 63 N) in NaCl (C_s = 0.10 N).

The potentiometric titation was carried out with an Orion Research EA-920 ion analyzer with a Ross-pH complex glass electrode Model 8102. Other experimental procedures of the potentiometric titration and viscometry were the same as those of the previous works,[3,4,13] where the experimental conditions were given in detail. An example of the potentiometric titration of PIA with HCl and NaOH at C_p = 8.63 mN and C_s = 0.10 N is shown in Figure 3. The end point is not clear enough to be determined in the original titration curve as in the cases of PFA and PMA.[3,4] By substracting the contribution of free OH^-, however, the end point of titration could be determined clearly, as shown with an arrow in the same figure.

Results

The negative logarithm of the apparent dissociation constant, pK_a, defined by

$$pK_a = pH + \log [(1 - \alpha)/\alpha] \tag{1}$$

is not constant but usually increases with α for polyelectrolytes. The pK_a can be expressed by a sum of two terms[4] as

$$pK_a = pK_0 + (0.4343/RT)(dG_{el}/d\alpha) \tag{2}$$

where K_0 is the intrinsic dissociation constant independent of α, R the gas constant, T the absolute temperature, and G_{el} the electrostatic Gibbs free energy of dissociation of 1 mol of protons. The plots of pK_a versus α at different C_s's are shown in Figure 4. Evidently, PIA appears to dissociate in two steps analogously to PFA and PMA, reported previously.[3,4] It is noted that different from the titrations of PFA and PMA, the solution of PIA does not become turbid even at higher α.[4,13]

The application of eq 2 to Figure 4 gives the value of pK_0 as 4.0. It is uncertain whether pK_0 depends on C_s or not, because the pK_a values have some experimental uncertainties. This value of pK_0 of PIA seems to be slightly smaller than that of PAA but much larger than those of PFA and PMA, as summarized in Table I. The differ-

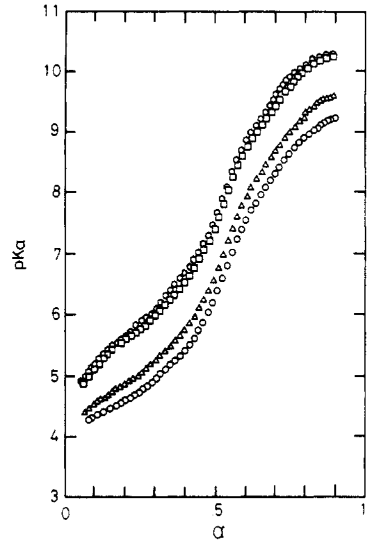

Figure 4. Plot of pK_a of PIA (C_p = 0.008 63 N) against α in NaCl solutions at C_s = 0.0050 N, 0.0010 N, 0.050 N, and 0.10 N from top to bottom, respectively.

Table I
Negative Logarithm of Intrinsic Dissociation Constants

acid	N	pK_0	pK_{01}
PIA	1	4.0	3.7
PFA[a]	2	3.5	3.2
PMA[a]	2	3.5	3.2
PAA[a]	0	4.1	
propionic acid[b]	0	4.87	
succinic acid[c]	1	4.19	
propane-1,2,3-tricarboxylic acid[d]	2	3.48	
butane-1,2,3,4-tetracarboxylic acid[c]	2	3.40	

[a] From ref 4. [b] From ref 14. [c] From ref 15. [d] From ref 16.

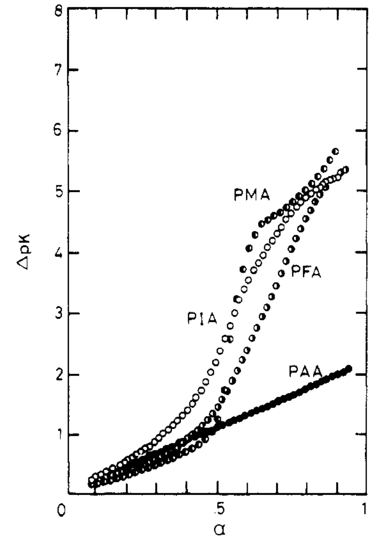

Figure 5. Plot of ΔpK versus α at C_s = 0.10 N NaCl for PIA (○), PFA (◑),[4] PMA (◐),[4] and PAA (●).[4]

ences in pK_0 for these polyacids are due mainly to the inductive effects of the nearest-neighbor carboxyl groups,[17] which will be discussed later in comparison with those of the low-molecular-weight organic acids.

The electrostatic part of pK_a, represented by ΔpK, written as[4,9,13]

$$\Delta pK = pK_a - pK_0 = 0.4343/RT(\mathrm{d}G_{el}/\mathrm{d}\alpha) \qquad (3)$$

is plotted against α for C_s = 0.10 N in Figure 5, where the data of the other polyacids are also reproduced for comparison to the literature values. The value of ΔpK of PIA in the region of $\alpha < 0.5$ is the largest in these polyacids, and at $\alpha > 0.5$, the value lies between PFA and PMA.

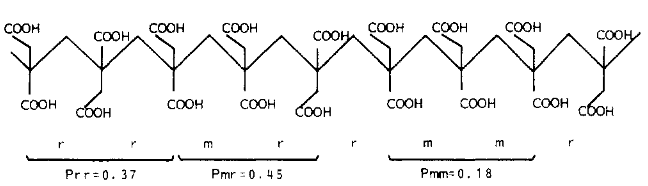

Figure 6. Most probable configuration of PIA.

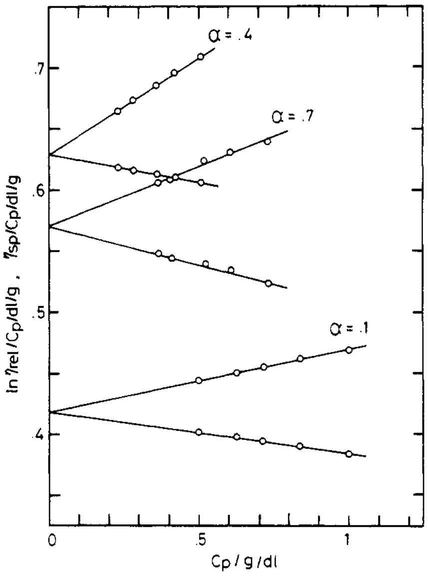

Figure 7. Viscosity–concentration profiles of PIA at α = 0.1, 0.4, and 0.7 in C_s = 0.10 N NaCl aqueous solution.

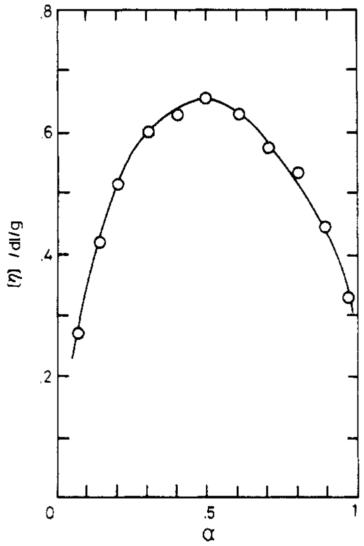

Figure 8. Dependence of [η] of PIA on α at C_s = 0.10 N NaCl.

From the ^{13}C NMR spectrum of PIA shown in Figure 2, the triad tacticities were determined as P_{mm} = 0.18, P_{mr} = 0.45, and P_{rr} = 0.37. The typical local configuration of PIA is shown in Figure 6, taking into account the triad tacticities.

The intrinsic viscosity, [η], was determined from plots of both η_{sp}/C_p versus C_p and ln η_{rel}/C_p versus C_p, as shown in Figure 7, where η_{sp} and η_{rel} are specific and relative viscosities, respectively. Figure 8 shows the results of viscometry as a plot of [η] versus α at C_s = 0.10 N. At lower α, [η] of PIA increases with α, attains a maximum near α = 0.5, and in turn decreases steeply. It should be noted here that the value of $[\eta]$ at $\alpha = 0$ is nearly the same as that at $\alpha = 1.0$. The decrease in $[\eta]$ observed at higher α seems to be characteristic of the polyelectrolytes with high charge density.[4,13,18,19]

Discussion

One of the most interesting results in the present investigation is the effect of the difference in the local charge distribution on the dissociation behavior of polyelectrolytes. Compared with the dissociation behavior of PAA, we may conclude that the presence of carboxymethyl groups in PIA suppresses the dissociation of α-COOH in a similar manner as PFA and PMA. As shown in Figure 5, the electrostatic Gibbs free energy of PIA in the region $\alpha < 0.5$ is much larger than that of PFA and PMA. This seems to be closely related to a weaker interaction between β-COOH and adjacent α-COOH, compared with that between two α-COOH's in PFA or PMA. On the other hand, in the region $\alpha > 0.5$, PIA shows an intermediate one between PFA and PMA. Since at least in the region of $\alpha > 0.5$ the ionized groups will separate from each other as far as possible, the local distribution of the charges of PIA may be intermediate between those of PFA and PMA.

The two carboxyl groups of PFA and PMA in close proximity are equivalent in the polymer structure, that is, both are bonded to the main chain, and their pK's should be equal if the electrostatic interaction between them is absent. On the other hand, the two carboxyl groups of PIA are bonded differently, one to the main chain and the other to the side chain. This difference may lead to the dissociation of β-COOH first because the internal motion of β-COOH is less restricted and the effect of the electric potential of the polyion is weaker than for α-COOH. In addition, the effect of the decrease in the dielectric constant of the neighboring medium resulting in an enhancement of the electrostatic interaction is reduced for β-COOH because its average position is located outside of the main chain. Therefore, β-COOH behaves more freely from the constraints of the neighboring α-COOH and other β-COOH's in the process of dissociation. This is why the curve of pK_a shows a rather symmetrical S shape, in contrast with that of PFA or PMA.

The strength of the acidity of a poly(vinylic carboxylic acid) is well-known to result from both the intrinsic dissociation constant and the electrostatic interaction from the ionized groups. We will consider separately these two effects to compare with the other polyelectrolytes and the corresponding low-molecular-weight organic acids. The value of pK_0 is mainly influenced by the inductive effect or the electron-withdrawing effect of the other carboxyl groups, the dielectric constant of the solvent, and the conformation of the polyelectrolyte. Judging from the value of pK_0 of PIA, which is larger than that of PFA and PMA in Table I, the difference in pK_0 may result mainly from the difference in the number of neighboring carboxyl groups. Since the inductive effect through the chain steeply decreases with increasing distance, the number of carbon atoms between two carboxyl groups is of importance.[20] This number is at least two. In PAA, every carboxyl group is separated by three carbon atoms from the next carboxyl groups, but in PIA, PFA, and PMA, there exists a pair of carboxyl groups separated by two carbon atoms. Therefore, we introduce the number N of carboxyl groups that are separated by two carbon atoms from a particular carboxyl group in a polymer structure. The value of N is 2 for PFA and PMA, 1 for PIA, and 0 for PAA. Then we estimate the inductive effect in terms of N, by applying the following expression predicting a proportionality between the difference in pK_0 and N

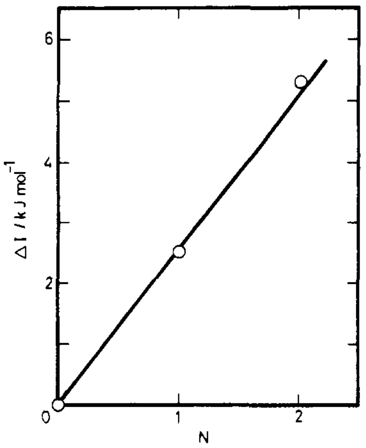

Figure 9. Plot of the inductive effect of COOH ΔI against N. The solid line results from the model compounds corresponding to PIA, PFA, and PMA.

$$\Delta I = \Delta G_0^{\,0} - \Delta G_0^{\,N} = kN \tag{4}$$

where $\Delta G_0{}^N$ is the Gibbs free energy change for 1 mol of dissociating protons when a polyelectrolyte chain is uncharged and is calculated from p$K_0{}^N$ by $\Delta G_0{}^N = 2.303RT\mathrm{p}K_0{}^N$. The values of p$K_0$ of PAA and propionic acid are taken as references for a polyelectrolyte and a low-molecular-weight organic acid, respectively. In accordance with the above expression, a plot of ΔI against N is found to be linear, as shown in Figure 9, where the thick solid line is calculated from the low-molecular-weight carboxylic acids in Table I. This figure shows that ΔI of a polyelectrolyte is essentially the same as that of the low-molecular-weight acids, and from the slope of this plot, ΔI per COOH is found to be about 2.6 kJ mol^{-1}. Considering the additivity and short-range nature of the inductive effect, the linearity as well as the same relationship for both polyacids and low-molecular-weight acids in Figure 9 is reasonably acceptable.

It is clear that the rod model with a smeared charge was not applicable to the electrostatic Gibbs free energy of PIA at any α or of PFA and PMA as reported previously.[4] Therefore, the discrete charge model including the short-range interaction and the difference in the location of carboxyl groups should be applied to express the dissociation behavior of PIA. We now have determined the probability of the local configuration of PIA as shown in Figure 6, assuming the main chain as a trans-planar zigzag conformation. Such a complicated configuration, however, leads to rather complicated calculations because of the irregularity of the interaction parameter. If we assume that only the electrostatic interaction from neighboring carboxyl groups contributes to the dissociation behavior of the polyelectrolytes, however, $\Delta\mathrm{p}K_{\mathrm{short}}$ can be approximately rewritten as

$$\Delta\mathrm{p}K_{\mathrm{short}} = \sum_{i=\mathrm{m,r}} P_i \Delta\mathrm{p}K_{\mathrm{short}\,i} \tag{5}$$

where P_i expresses the probability of the diad tacticity, P_m or P_r. In addition to the configuration, the conformation of the β-COOH on the side chain must be considered. The calculation was carried out for two extreme conformations: trans and gauche against the carboxyl group on the main chain. A detailed procedure of the calculations has already been shown in previous papers.[9,13] The one-dimensional Ising model with the second-nearest-neighbor interaction is applied to the calculation in

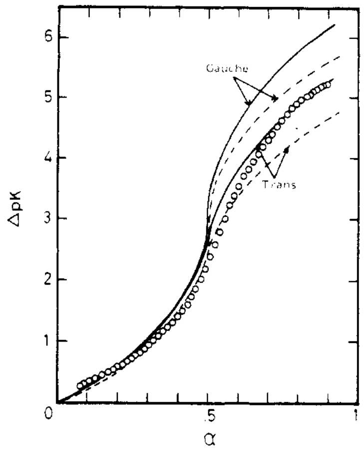

Figure 10. Comparison of calculation based on an Ising model with the experimental ΔpK (O) of PIA in Figure 5, where the dielectric constant and local salt concentration are assumed to be 22 and 1.0 N, respectively. Solid and broken lines represent ΔpK and ΔpK_{short}, respectively, for the gauche and trans conformations of COOH of the side chain with respect to the main chain.

the same way as in the previous paper, using a matrix method. A comparison of the model calculation with the experimental data is shown in Figure 10, where we assume the dielectric constant, D, around the ionized groups and the local salt concentration C_s^* as 22 and 1.0 N,[9] respectively. From this figure, the model calculation for the trans conformation is found to be in quantitative agreement with the experimental data.

The conformation of a flexible polymer chain in dilute solution is usually understood in terms of the short-range and long-range interactions, known as the two-parameter theory.[21] If the electrostatic long-range interaction plays a dominant role in $[\eta]$ of a flexible polyelectrolyte chain, $[\eta]$ may increase monotonically with increasing α.[22] On the other hand, C_s in the vicinity of the polyelectrolyte chain seems to increase with increasing α. As a result, the electrostatic interaction decreases. However, we do not know any explicit functional form of $[\eta]$ in terms of α or any definite reason why $[\eta]$ of PIA in Figure 8 is nearly symmetrical with respect to $\alpha = 0.5$, despite no possibility of any conformational transition at such a high α. Such a strange dependence of $[\eta]$ on α is found commonly in the other maleic acid polymers such as PFA and PMA or the alternating copolymers of maleic acid with isobutylene,[13] alkyl vinyl ether,[18] or styrene.[19] The latter two were proved to cause a conformational transition from the compact form to the expanded coil.

There have been two interpretations of the decrease in $[\eta]$ at $\alpha > 0.5$: hydrogen bonding between COO^- and COOH in neighboring carboxyl groups[18,19] and the local salt concentration being higher than the bulk value at $\alpha > 0.5$.[8,9] A hydrogen bond may be formed between COOH on the main chain and COO^- on the side chain in an intermediate region of α. This possibility seems, however, inappropriate for the reason of the decrease in $[\eta]$, because it does not affect very much the flexibility of the main chain and because the hydrogen bond between two unionized carboxyl groups may be equally probable for $\alpha < 0.5$. At present, the main reason for the decrease in $[\eta]$ at $\alpha > 0.5$ may be the high salt concentration in the polymer domain due to the strong electrostatic potential.

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