Dissociation Behavior of Poly(fumaric acid) and Poly(maleic acid). 1. Potentiometric Titration and Intrinsic Viscosity

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ABSTRACT: Potentiometric titration at different concentrations of added salt and intrinsic viscosity at different degrees of dissociation were measured to study the dissociation behavior of the stereoisomeric polyacids poly(fumaric acid) and poly(maleic acid), both of which have the same molecular formula with a carboxyl group at every carbon in the main chain. The titration curves show that poly(fumaric acid) exhibits apparently two-step dissociation and poly(maleic acid) exhibits it more clearly. From analysis of the titration curves it is found that the intrinsic dissociation constants are the same for both polyacids and almost independent of the concentration of added salt or the type of the counterion. It also reveals a remarkable difference in the dissociation behavior between the regions $\alpha < 0.5$ and $\alpha > 0.5$, where α is the degree of dissociation; that is, at $\alpha > 0.5$ the electrostatic free energy increases more steeply with α and depends more significantly on the charge density, the configuration of the polyacid, and the type of the counterion than at $\alpha < 0.5$. Intrinsic viscosity of each polyacid in aqueous salt solution increases with increase of α, attains a maximum near $\alpha = 0.5$, and decreases gradually beyond it. Such a complicated dissociation behavior of both polyacids is discussed in terms of the electrostatic interaction between the ionized groups existing closer to each other in comparison with that of poly(acrylic acid).

Introduction

The dissociation behavior of vinylic poly(carboxylic acids) such as poly(acrylic acid) (PAA) or poly(methacrylic acid) having a carboxyl group at every second carbon in the main chain has been extensively studied experimentally by various kinds of measurements.[1,2] These results have been analyzed theoretically by use of a rodlike model having cylindrical symmetry with the smeared charge density[3,4] or by a line charge model such as the limiting law proposed by Manning.[5] That is, potentiometric titration behavior of these polyacids has successfully been interpreted quantitatively by the electrostatic potential of a polyion as a function of both the smeared charge density on the surface of a polyion assumed as a rod, related to the degree of dissociation, α, and the concentration of added salt, C_s, in the medium.[6,7] Recently with a sample of PAA having a high molecular weight with a narrow molecular weight distribution,[8] studies on the conformational properties such as intrinsic viscosity[9] or the particle scattering factor obtained by light scattering[10,11] have also made a great progress in elucidating the nature of the long-range electrostatic interaction within a polyelectrolyte chain, at least in the region of C_s higher than 0.01 N, in terms of the same concept as the excluded volume effect for nonionic polymers.

On the other hand, poly(carboxylic acids) having higher charge densities than these vinylic polyacids, such as poly(fumaric acid) (PFA) and poly(maleic acid) (PMA), represented by the same molecular formula which have a carboxyl group on every carbon atom along the main chain, are of considerable interest in relation to the effect of charge density on the solution properties of polyelectrolytes. It can be reasonably expected for them to show some characteristic features in their dissociation behavior different from vinylic polyacids due to the stronger Coulombic interaction, especially at the shorter distance. Very few works on them, however, have been done yet, since the preparation of both polymers is not so easy owing to the existence of the two bulky substituents at both ends of a double bond in their monomers.

In 1963 Lang et al.[12] succeeded in preparing PMA by hydrolysis of poly(maleic anhydride) obtained from radiation polymerization. They also reported that the titration curves of PMA with several kinds of bases always have clear inflection points near the middle of the neutralization as if it had two kinds of carboxyl groups with differnt dissociation constants in an equal amount. Sakurada et al.[13] observed that the titration curve of PMA is almost the same as that of PFA prepared from poly(diethyl fumarate) and the reduced viscosities of dilute solutions of both polymers exhibit maxima around $\alpha = 0.35$. Their report, however, did not include detailed discussion on them. Subsequently, Muto et al.[14] carried out another measurement of potentiometric titration of PMA using various kinds of cations as counterions. They found that at $\alpha < 0.5$ the value of the apparent dissociation constant, pK_a, defined later, becomes slightly larger as the size of the cation becomes smaller while the tendency is reversed at $\alpha > 0.5$. Moreover, Barone et al.[15] reported the striking observations that even four-step dissociation appears in the titration of PMA at lower C_s or in the absence of salt and that the reduced viscosity at higher C_s does not depend on α. They discussed such peculiar behavior of PMA from the view point of the ditacticity of PMA, presumed to be a more complicated configuration than that of PAA.

On the alternating copolymers of maleic acid, since the preliminary report by Ferry et al.,[16] more extensive works have been done, for example, by Strauss et al.[17] and by Sugai et al.[18] These copolymers should have the same charge density as the common vinylic polyacids if the charges were smeared uniformly over the whole chain, but actually they always exhibit two-step dissociation. The reason is that their actual intercharge distances are not even and thus the carboxyl groups in the maleic acid unit always exist as a definite pair separated from the others. The emphasis of these studies, however, has been chiefly laid on the hydrophobic effect of alkyl groups in the alternative monomer unit, which causes in some cases abnormal behavior at lower α both in the potentiometric

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titration curve and in the intrinsic viscosity.[17,18] Such abnormalities found during the course of dissociation of the alternating copolymers of maleic acid are usually referred to as the transition from a compact globule to an extended coil and are ascribed to the change in the balance between the hydrophilic and the hydrophobic interaction within a copolymer chain.

On the other hand, regarding PFA, Otsu et al.[19] carried out the extensive works on the radical polymerization of diesters of fumaric acid. They found that the fumarates with more bulky substituents can be polymerized at higher yields and that poly(di-*tert*-butyl fumarate) thus prepared can be converted to PFA by pyrolysis around 200 °C. Recently we have succeeded independently in polymerizing di(trimethylsilyl) fumarate with a radical initiator and in preparing PFA by acid hydrolysis therefrom as reported in the previous paper,[20] which includes the preliminary results on the titration behavior of PFA different either from that of PAA or from that of PMA; that is, PFA also has a two-step dissociation but not one as clear as PMA.

It may be natural to ask why these polyacids, PFA and PMA, dissociate apparently in two steps irrespective of the same molecular formula as poly(carboxymethylene), $-(CH(COOH))-$. There is no definite reason for them to form a pair of carboxyl groups in the same way as the alternating copolymers of maleic acid whereas the monomers from which PFA and PMA were prepared are sure to have a pair of carboxyl groups which have the trans configuration for fumaric acid and the cis configuration for maleic acid, respectively. Thus as a first step to elucidate the dissociation behavior characteristic of PFA and PMA, this paper aims to present more detailed results on their dissociation behavior obtained from the measurements of potentiometric titration and intrinsic viscosity in quantitative comparison with those of PAA. Further analysis of their titration behavior in terms of the electrostatic short-range interaction will be presented in a succeeding paper.[21]

Experimental Section

1. Preparation of PFA and PMA. The method of preparation of PFA was reported previously.[20] Di(trimethylsilyl) fumarate monomer, synthesized by the reaction of fumaric acid in dry THF containing an excess amount of triethylamine with chlorotrimethylsilane added dropwise at −70 °C under an argon atmosphere, was polymerized in an ampule sealed under high vacuum by initiation of α,α'-azobis(isobutyronitrile). Poly(di(trimethylsilyl)fumarate) was then hydrolyzed in THF solution under argon at its boiling point (66 °C) for 2 h with a small amount of HCl added as a catalyst. After the addition of an amount of NaOH aqueous solution, the sodium salt of PFA was precipitated in excess methanol. The yield of PFA was 27%. The quantitative analysis was not done on the number of $-COOH$ per repeating unit in the PFA sample thus prepared, but its chemical composition was confirmed by the ^1H NMR spectrum, which has no peak at all characteristic of the trimethylsilyl ester group as repoted in detail previously.[20]

PMA was prepared in the similar way as reported by Lang et al.[12] The maleic anhydride in 50% acetic anhydride solution sealed in an ampule under vacuum was polymerized at room temperature by irradiation of ^{60}Co γ-ray at Nagoya University, Nagoya, Japan, with the dose rate of 3.5×10^4 rad/h for 17.5 h. Thus the total dose irradiated during polymerization was 0.61 Mrad. Poly(maleic anhydride) thus prepared was precipitated in excess benzene, collected by filtration, and dried in vacuo after it was washed with fresh benzene repeatedly. It was converted to PMA by keeping its aqueous solution with HCl at 0 °C for a week. The hydrolyzed mixture was dialyzed and then passed through a mixed bed of the ion-exchanged resins. The yield of PMA was 32%. The complete conversion of poly(maleic anhydride) to PMA was confirmed qualitatively by infrared spectroscopy using a KBr pellet in a Jasco A-3 infrared spectrophotometer. As shown in Figure 1, the characteristic bands at 1850 and 1780 cm^{-1} for the stretching vibration of the anhydrous carbonyl group disappeared completely. As judged from the titration equivalence of the PMA sample dried carefully, the degree of hydrolysis of PMA was 96 ± 4%.

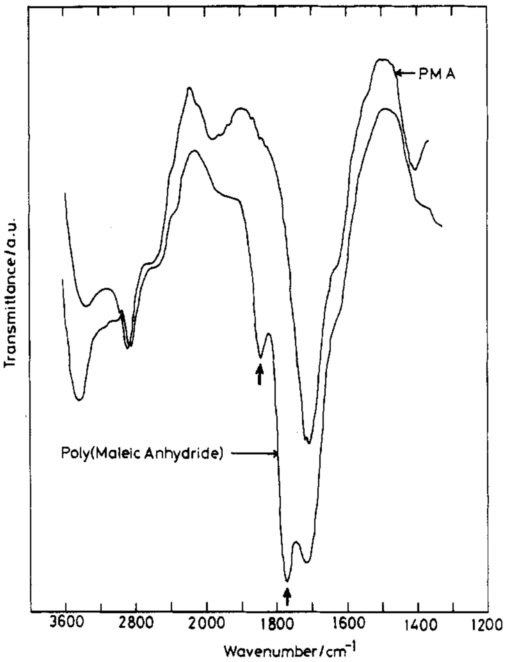

Figure 1. Infrared spectra of poly(maleic anhydride) and PMA. Arrows indicate characteristic bands for stretching vibration of anhydrous carbonyl.

The number-average molecular weight, M_n, of the corresponding methyl esters, poly(dimethyl fumarate) and poly(dimethyl maleate), was determined by a vapor-pressure osmometer type 117 of the Corona Electric Co. in benzene at 60 °C. The methylation of both polyacids was carried out at room temperature with diazomethane. With the determined values of their M_n's, those of PFA and PMA are estimated to be 6.6×10^3 and 1.7×10^4, respectively.

In addition to PFA and PMA, PAA was used in the potentiometric titration measurements as a typical vinylic poly(carboxylic acid) for comparison. The sample of PAA was commercially available as Aron A-20 of Toagosei Chemical Industries Co., Ltd., whose nominal molecular weight is 4.0×10^4.

2. Potentiometric Titration and Intrinsic Viscosity. Potentiometric titration was done in the same way as reported previously,[20] using a digital pH meter Model 225 of Iwaki Glass Co. with a glass electrode IW051, under an atmosphere of argon at room temperature, 25 ± 1 °C. The solutions for the measurements were prepared by adding a definite amount of salt to the solution passed through a mixed bed of ion-exchanged resins. The added salts used here were monovalent alkali metal chlorides, such as LiCl, NaCl, KCl, and CsCl. Their concentrations, C_s, ranged from 0.005 to 0.1 N and the polymer concentrations, C_p, were from 0.01 to 0.05 N. The data analysis was the same as reported previously.[20] The degree of dissociation, α, was determined from the end point of the titration after correcting for the amounts of free H^+ and OH^-. Within the experimental errors, the dependence of the titration curve on C_p was found to be negligible. The solutions of PFA and PMA sometimes become turbid in the presence of the salt at the region of higher α and at lower α. In order to confirm the reversibility of the titration in such a turbid solution, the back-titration with HCl was carried out in some cases, starting from the turbid solution having been completely neutralized with NaOH. Each titration was confirmed to be almost completely reversible even in such a turbid solution as shown in Figure 2, for example. In addition the reproducibility of the titration was confirmed for most cases over the whole range of α, which may be additional support for the accuracy in the present study.

The viscosity of the dilute solutions of PFA and PMA was measured by a modified Ubbelohde-type viscometer at 25 °C in

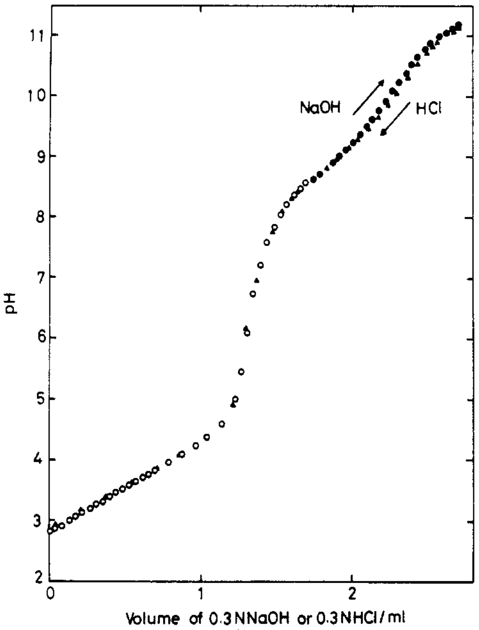

Figure 2. Titration curve of PMA at C_p = 0.020 N in 0.100 N NaCl with 0.300 N NaOH (○) and the back-titration curve of the same solution with 0.300 N HCl (△) after complete neutralization. Filled symbols indicate turbid solutions.

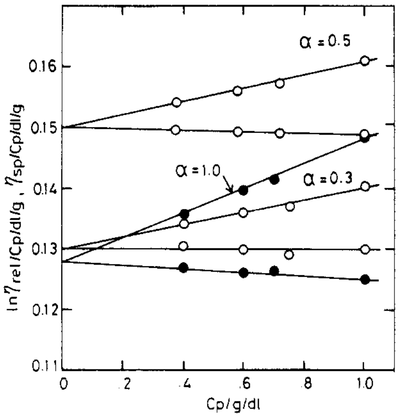

Figure 3. Intrinsic viscosities of PFA at α = 0.3, 0.5, and 1.0, respectively, in 0.05 N NaCl aqueous solution. Filled circles indicate turbid solutions.

NaCl aqueous solution at C_s = 0.05 N and then the intrinsic viscosity $[\eta]$ was determined from the intercept extrapolated at $C_p = 0$ in both plots of η_{sp}/C_p vs. C_p and of $\log \eta_{rel}/C_p$ vs. C_p as shown in Figure 3, where η_{sp} and η_{rel} are specific and relative viscosities, respectively. The shear-rate dependence of $[\eta]$ was confirmed to be negligible in this study.

Results

In general, the pH of the polyelectrolyte solution is described by

$$\mathrm{pH} = \mathrm{p}K_0 - \log\,[(1-\alpha)/\alpha] + 0.4343(\mathrm{d}G_{el}/\mathrm{d}\alpha)/RT \quad (1)$$

where $\mathrm{p}K_0$ is an intrinsic dissociation constant of an ionized group in the polyelectrolyte, $(\mathrm{d}G_{el}/\mathrm{d}\alpha)$, the electrostatic Gibbs free energy change per unit degree of dissociation as a function of α, R, the gas constant, and T, the absolute temperature. The apparent dissociation constant $\mathrm{p}K_a$, is usually defined by

$$\mathrm{p}K_a = \mathrm{pH} + \log\,[(1-\alpha)/\alpha] \quad (2)$$

which is experimentally measurable. It becomes a so-called dissociation constant under the conditions where the effect of G_{el} is negligible, as in a low molecular weight acid. Combining eq 2 with eq 1 leads to

$$\mathrm{p}K_a = \mathrm{p}K_0 + 0.4343(\mathrm{d}G_{el}/\mathrm{d}\alpha)/RT \quad (3)$$

Some examples of the plots of $\mathrm{p}K_a$ vs. α for PFA, PMA, and PAA at different C_s's of NaCl are shown in Figure 4, where the data in the turbid solutions are denoted by filled symbols. The appearance of turbidity in solutions at higher α depends on various factors such as C_p or the configuration of the polyacid. Above all, the most important factor seems to be C_s, since addition of the salt significantly promotes turbidity of the solution. Comparison with the usual vinylic poly(carboxylic acids), such as PAA, shows that it is strange that the solutions of PFA and PMA become turbid *at higher α even in such a dilute salt solution as C_s = 0.1 N*!

There are some features noticed in these titration curves. First of all, remarkable is the existence of two modes in the dissociation behavior of PFA and PMA separated near the middle point of neutralization as reported in previous works.[12-15] That is, the $\mathrm{p}K_a$ of PMA increases at lower α in a similar way to that of PAA, rises steeply near α = 0.5, and then increases gradually again at higher α in contrast

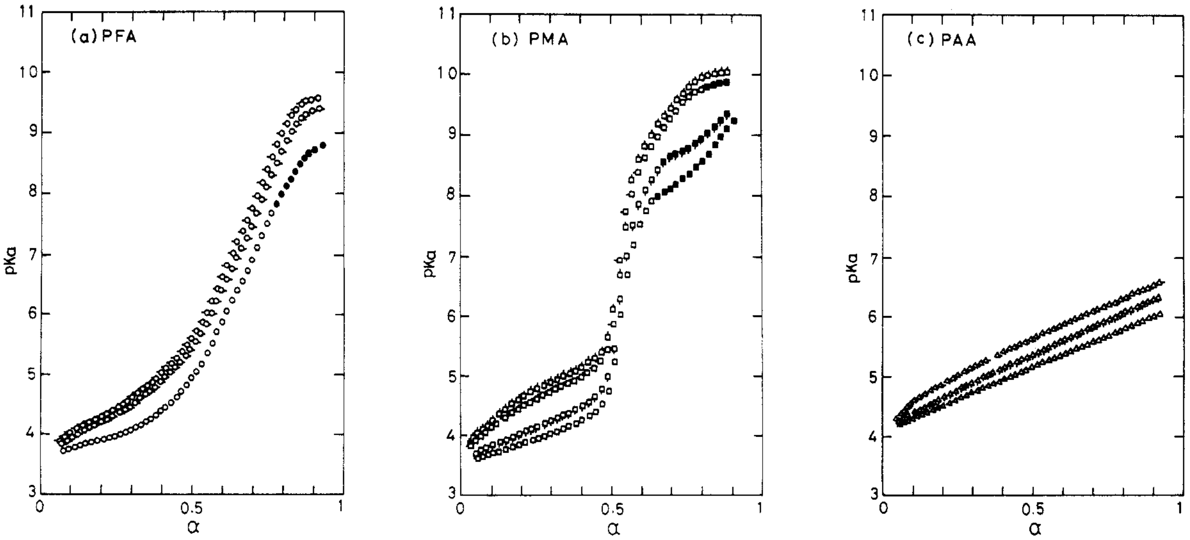

Figure 4. Apparent dissociation constant in NaCl solution: (a) PFA at C_p = 0.011 N, (-○) PFA at C_s = 0.014 N, (○-) PFA at C_s = 0.028 N, (○) PFA at C_s = 0.100 N; (b) PMA at C_p = 0.045 N, (□) PMA at C_s = 0.005 N, (-□) PMA at C_s = 0.010 N, (□) PMA at C_s = 0.050 N, (□) PMA at C_s = 0.100 N; (c) PAA at C_p = 0.010 N, (△-) PAA at C_s = 0.024 N, (△) PAA at C_s = 0.052 N, (△) PAA at C_s = 0.100 N. Filled symbols indicate turbid solutions.

Table I
Intrinsic Dissociation Constants

acid	counterion	C_s/(mol/L)	pK_0 (av)
PFA	Na^+	0.100	3.45
		0.027	3.60 (3.50 ± 0.07)
		0.014	3.45
PMA	Na^+	0.100	3.40
		0.050	3.50 (3.50 ± 0.06)
		0.010	3.55
		0.005	3.55
	Li^+	0.100	3.45
	K^+	0.100	3.55
	Cs^+	0.100	3.45
PAA	Na^+	0.100	4.10
		0.050	4.10 (4.13 ± 0.04)
		0.024	4.18
propionic acid			4.87[a]
succinic acid			4.51[b]

[a] From ref 24. [b] Estimated value from pK_{01} in ref 24 by eq 8.

to the nearly constant increase in that of PAA over the whole range of α. As C_s becomes higher, the apparent two-step dissociation of PMA becomes clearer. Such a behavior of PMA suggests the presence of two kinds of ionized groups having different dissociation constants, as will be discussed later. It is difficult to judge whether the apparent separation point is exactly at $\alpha = 0.5$, because some errors are inevitably included in determining the end point of each titration, which is not always as clear as that of PAA, especially at lower C_s. Summarizing all the data in the present experiments, however, it seems reasonable to assume it just at $\alpha = 0.5$. The values of pK_a of PFA in Figure 4 are calculated from the data presented in a previous paper,[20] where it has already been pointed out that PFA dissociates in two steps like PMA but less clearly and behaves as a whole in an intermediate manner between PMA and PAA. This is in disagreement with the observation of Sakurada et al.,[13] who reported that the titration curves are almost the same for both polyacids. However we have no reason for the discrepancy.

The quantitative comparison of dissociation behavior among the polyacids must become clearer if the values of two parameters in eq 3, pK_0 and G_{el}, are determined in Figure 4. pK_0 can be estimated by extrapolation of pK_a to $\alpha = 0$ from the data at $\alpha > 0.05$ because the uncertainty of the calculated value of log $[(1 - \alpha)/\alpha]$ is larger in nature at both extreme regions of $\alpha < 0.05$ and of $\alpha > 0.95$. The values of pK_0 thus determined are summarized in Table I. It is found that the pK_0 of PMA is almost independent of C_s and even of the type of the cation, as will be shown later, and that it is the same as that of PFA but smaller than that of PAA, which is in good agreement with the one reported by Nagasawa et al.[6,7] To evaluate the effect of the electrostatic interaction during the dissociation, we can separate the term ΔpK from pK_a as

$$\Delta pK = pK_a - pK_0 = 0.4343(dG_{el}/d\alpha)/RT \qquad (4)$$

The typical plots of ΔpK vs. α at $C_s = 0.100$ N for these polyacids are shown in Figure 5. Alternatively, from the numerical integration of the value of ΔpK, the difference in the electrostatic Gibbs free energy between 0 and α necessary to carry a proton from a polyion to infinity, ΔG_{el}, is determined as follows:

$$\Delta G_{el}(\alpha) = \int_0^{\alpha} (dG_{el}/d\alpha)\, d\alpha = 2.303RT \int_0^{\alpha} \Delta pK\, d\alpha \qquad (5)$$

although ΔG_{el} is not used in the present study. At $\alpha < 0.5$ there is little difference among the polyacids in the electrostatic term such as ΔpK in Figure 5. But the difference in ΔpK becomes significant at $\alpha > 0.5$; that is, ΔpK of PMA increases steeply at $\alpha > 0.5$ and that of PFA also increases similarly but not so steeply, while that of PAA continues increasing at the same rate as at $\alpha < 0.5$. To compare the dissociation behavior more precisely between the regions of $\alpha < 0.5$ and $\alpha > 0.5$, the dependence of ΔpK on C_s for the typical α is shown in Figure 6, where the data are obtained by interpolation in Figure 5. This figure shows the significantly large difference in ΔpK at $\alpha = 0.8$ in contrast to the very small difference at $\alpha = 0.4$.

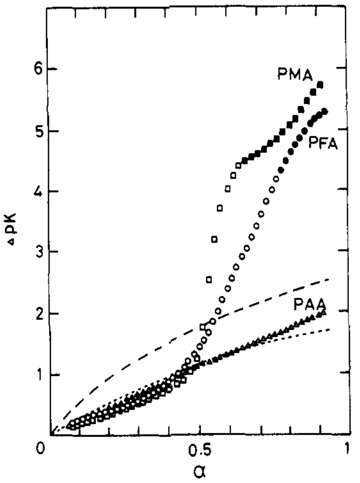

Figure 5. Dependence of ΔpK on α at $C_s = 0.100$ N for the same data as in Figure 4. (○) PFA; (□) PMA; (△) PAA. Filled symbols indicate turbid solutions. Broken and dotted lines are calculated curves for PFA or PMA, and for PAA, respectively, using the model with the parameters given in the text.

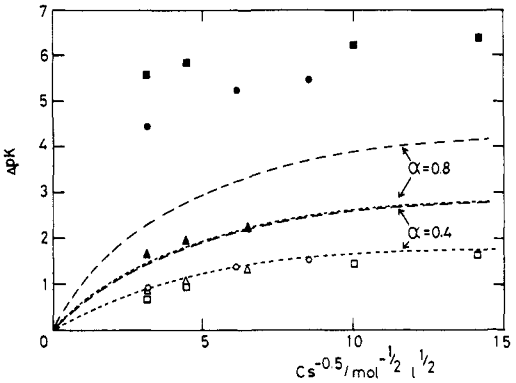

Figure 6. Dependence of ΔpK on C_s for interpolated data at $\alpha = 0.4$ (open) and $\alpha = 0.8$ (filled) in the same plots as in Figure 5. Symbols and lines are the same as in Figure 5.

Figure 7 shows the dependence of the pK_a of PMA on the type of cation at $C_s = 0.100$ N. There is some tendency in the appearance of a clear end point in the titration curve on the type of the cation. That is, the smallest cation Li^+ gives the clearest end point among them and it becomes less clear as the size of cation becomes larger, while the end point also becomes clearer as C_s becomes larger, as already noted in Figure 4. The data in the turbid solutions are also denoted by the filled circles. In addition to the peculiar formation of turbid solution at higher α, as mentioned before, the larger cations, K^+ and Cs^+, also yield a turbid solution at lower α with a C_s even as high as 0.1 N although not described in detail here. Such phenomena are known commonly as phase separation or salting out of the polyelectrolyte solution caused by adding more salt to it. However, the straightforward comparison of the turbid regions for different counterions may be misleading in Figure 7, since the C_p's are not the same even at the same C_s. The liability for the solution to become turbid is very sensitive not only to C_s and the type of the cation

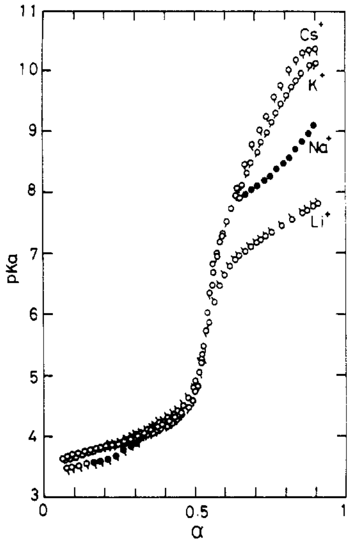

Figure 7. Dependence of apparent dissociation constant of PMA at C_s = 0.100 N on type of cation: (ò) Li^+ at C_p = 0.021 N; (○) Na^+ at C_p = 0.045 N; (ρ) K^+ at C_p = 0.021 N; (Q) Cs^+ at C_p = 0.033 N. Filled circles indicate turbid solutions.

but also to C_p, the configuration, and the molecular weight of the polyelectrolytes as mentioned before. Although a more careful study will be needed on the appearance of turbidity in the solutions of these polyacids, it is presumed that a turbid solution is more likely to appear as C_s, C_p, or the size of the cation becomes larger.

From Figure 7, indicating the effect of the type of cation on the pK_a of PMA at C_s = 0.100 N, it is found that for any type of cation studied here PMA always dissociates in two steps, but there are some differences in the plots of pK_a vs. α. Especially at $\alpha > 0.5$ is the dependence of pK_a on the type of the counterion more significant than at $\alpha < 0.5$. That is, as the size of the cation becomes larger, the pK_a at higher α is surely larger in the order $Li^+ < Na^+ < K^+ < Cs^+$, in agreement with the observation on PAA by Gregor et al.[22] On the other hand, with an increase in the size of the cation, it becomes smaller at lower α, although the difference in pK_a is much less than at higher α. The tendency is reversed for α slightly higher than 0.5. Such a dependence of pK_a on the size of the cation has already been reported by Muto et al.[14] It is not clear why the reversal of the tendency occurs at such a region of α. The values of pK_0 determined in Figure 7 are also shown in Table I, where pK_0 is regarded as almost independent of the type of the cation. The dependence of ΔpK on the type of the cation is not given here because the plot is the same as Figure 7 except for the position of zero in the ordinate as long as pK_0 is the same. Thus it is presumed from this figure that ΔpK depends significantly on the type of the cation, especially at higher α; that is, as the size of the cation becomes larger, ΔpK at higher α increases more steeply. It is noted that at lower α the tendency of ΔpK is reversed, despite the slight difference among them.

Figure 8 shows the results of viscometry as plots of the $[\eta]$ of PFA and PMA vs. α at C_s = 0.050 N NaCl, respectively. At lower α, the $[\eta]$ of PFA increase with α, attains a maximum near α = 0.5, and appears to decrease beyond it. In connection of the appearance of a maximum in the plot of $[\eta]$ vs. α, it should be noted that the solution of PFA at C_s = 0.050 N NaCl begins to be turbid near α = 0.7. This value of α = 0.5, at the maximum point of $[\eta]$, differs slightly from the results of Sakurada et al.,[13] who reported it at α = 0.35. In Figure 8 the tendency of $[\eta]$ in the turbid solution is tentatively denoted by a broken line. The behavior of $[\eta]$ of PMA is supposed to be similar to that of PFA, but the liability for PMA solution to become turbid was so strong that $[\eta]$ could not be measured at $\alpha > 0.5$. Since the molecular weights of both polymers are not the same, it cannot be judged in Figure 8 whether there should be any difference in the tendency of $[\eta]$ for both polyacids. The difference in the precipitation phenomena between them may be, to a great extent, attributed to the difference in the molecular weight as well, since the phase equilibrium of the polymer solution is known to depend significantly on the molecular weight of the polymer.[23]

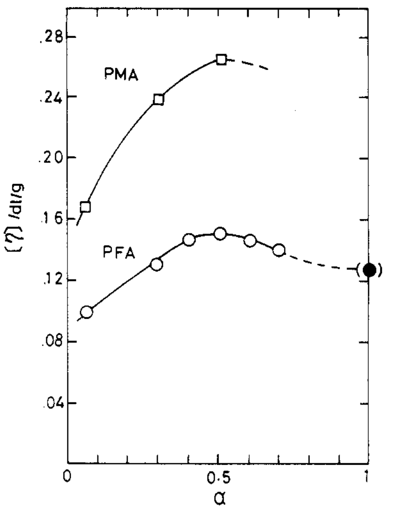

Figure 8. Dependence of $[\eta]$ of PFA and PMA on α in 0.050 N NaCl at 25 °C. Broken lines indicate only the expected tendencies.

Discussion

As for the electrostatic interaction in the polyelectrolyte solution in the presence of salt, there exist three types of pairwise electrostatic interactions: (1) between small ions from both polyelectrolytes and added salts, (2) between a small ion and a charge on a polyion, and (3) between charges on the same polyion or on different polyions. The potentiometric titration is closely related to the electrostatic interaction between a proton and an ionized group on a polyion in case 2. The electrostatic interaction can be transmitted to the longer distance in such a functional form as the direct Coulombic or the screening Debye–Hückel potentials. However it is the electrostatic *short-range interaction* which has a primary effect on the dissociation behavior of the polyacid. Therefore in the analysis of the potentiometric titration, it is essential to know the local arrangement of the ionized groups even if any model is adopted.

Although the configurations of PFA and PMA have not yet been known, we can expect that there should exist some difference in them, since the preparation methods of PFA and PMA were quite different as mentioned in the Experimental Section; that is, PFA may retain the trans configuration in the original monomer unit and PMA may retain the configuration as close to the cis configuration as possible during the acid hydrolysis of poly(maleic anhydride) under relatively mild conditions. Therefore it is reasonable to conclude that the difference in the titration behavior between PFA and PMA is attributable to the configurational difference between both polyacids. To confirm this conclusion, the exact configurations, that is, the ditacticities of both polyacids as suggested by Barone et al.,[15] will have to be determined directly by spectroscopic methods such as NMR or IR.

The potentiometric titration of the polyacid is analyzed quantitatively in terms of eq 3 including two parameters, pK_0 and G_{el}. Since pK_0 is the intrinsic dissociation constant for –COOH to start dissociating from the unionized polyacid without charges, it should remain constant in nature. Actually, however, it may be alterable to some extent, depending upon the surroundings, for example, the group of the substituents in the neighbors, and the local dielectric constant, through the standard chemical potential. In Table I the values of $\mathrm{p}K_0$ for PFA and PMA are regarded as the same value, 3.5 ± 0.1, independent of C_s and the type of the counterion within the experimental errors, which are smaller than that of PAA, 4.1 ± 0.1. This difference in $\mathrm{p}K_0$ between the polyacids having different charge densities may be attributed to the following factors: the binding energy of a proton to a polyacid owing to the anisotropy of charge density resulting from the adjacent substituent groups, the possibility of intramolecular hydrogen bonding contributing to the entropic change on the dissociation of PFA and PMA, and the hydration of the polyacids since PFA and PMA are considered to be more hydrophilic than PAA. Referring to the values of $\mathrm{p}K_0$ of the analogous low molecular weight organic acids listed in the same table,[24] the difference in $\mathrm{p}K_0$ between PFA or PMA and PAA can be reasonably understood; that is, the presence of the carboxyl groups in the neighbors is likely to reduce the value of $\mathrm{p}K_0$. In view of the nearly identical values of $\mathrm{p}K_0$ for PFA and PMA, it is concluded that the configuration of –COOH in the polyelectrolyte chain having an even higher charge density affects little the value of $\mathrm{p}K_0$, in agreement with the results of stereoregular PAA and poly(methacrylic acid) reported previously.[6,7] We cannot estimate the extent of the effect of the hydrogen bonding on $\mathrm{p}K_0$, which will have to be confirmed by spectroscopic methods.

On the other hand, the electrostatic term in $\mathrm{p}K_a$, related to $\Delta\mathrm{p}K$ by eq 4 or ΔG_{el} by eq 5, is a parameter concerning the tendency of a proton liable to dissociate from the ionized polyacid chain with charges. Thus it is natural for $\Delta\mathrm{p}K$ to depend significantly on both α and C_s, since the dissociation is the electrostatic process for a proton to move away against the attraction of the other $-\mathrm{COO}^-$ groups that have already dissociated. In addition to the plot of $\Delta\mathrm{p}K$ vs. α at constant C_s in Figure 5, the plot of $\Delta\mathrm{p}K$ vs. $C_s^{-1/2}$ at constant α in Figure 6 is also suitable for a quantitative comparison, which represents just the effect of C_s and the charge density on the electrostatic free energy change during titration. From the structural point of view, the dependence of the electrostatic term, $\Delta\mathrm{p}K$, on α is considered as follows: At $\alpha < 0.5$, the probability of the presence of the dissociated $-\mathrm{COO}^-$ groups in the neighbors of the –COOH groups in question is not so large that the electrostatic free energy change, $\mathrm{d}G_{el}$, of the dissociation should depend little on either the charge density or the configuration of –COOH. On the other hand, at $\alpha > 0.5$, where more than half of the carboxyl groups in the neighbors have already been dissociated, a proton on PMA is the most difficult to dissociate, probably owing to the more compact configuration of –COOH in PMA than in PFA, whereas a proton on PAA is the least affected by increasing the charge density since it has originally only half the amount of –COOH groups possessed by PFA or PMA. Therefore, the difference in $\Delta\mathrm{p}K$ at $\alpha > 0.5$ between PFA and PMA, as stated repeatedly, is surely due to their configurational difference. Such an effect of the chain configuration of the polyelectrolytes on their titration behavior was fully discussed by Nagasawa et al.,[6,7] who found a fairly large difference in the titration curves of PAA or poly(methacrylic acid) having different tacticities, especially at higher α. In addition, G_{el} for PFA and PMA may possibly contain some amount of contribution of the hydrogen bonding which is supposed to form between the carboxyl groups closer to each other,[14] so that during the titration the amount of hydrogen bonding may also vary to affect the value of $\mathrm{p}K_a$.[25]

There may arise another question of how the results will be altered if the abscissa in Figure 5 is represented by the scale of the charge density instead of α. The charge density at only a half degree of dissociation for PMA or PFA should correspond to that at complete dissociation for PAA. Further discussion on the effect of the charge density on the dissociation of polyacids will be done in the latter part of this paper, where we must recalculate not only α but also $\mathrm{p}K_a$, which is a function of α.

If G_{el} is the free energy only from the electrostatic interaction, it can be related to the electrostatic potential, ψ, on the surface of the polyelectrolyte by

$$\mathrm{d}G_{el}/\mathrm{d}\alpha = N_A e\psi \tag{6}$$

where N_A is the Avogadro constant and e is the elementary electric charge. With the assumption of the local conformation of the polyelectrolyte as a rod, the surface electrostatic potential, ψ, of a rod with the smeared charge density was determined by direct solution of the Poisson–Boltzmann equation by use of a computer.[3,4] This method was successfully applied to the potentiometric titration of PAA and poly(methacrylic acid) by Nagasawa et al.[3,6,7] and Sugai et al.[4] The calculated values according to the method by Kotin et al.[3] are compared with the present titration data in Figures 5 and 6 where it is assumed that the apparent radius of a rod is 0.55 nm, the intercharge distances at $\alpha = 1$ are 0.125 nm for PFA or PMA and 0.251 nm for PAA, and the dielectric constant is 78.54. The data on PAA can be fitted well to the curves calculated in terms of such a rod model with the smeared charge density in these figures, as already reported by Nagasawa et al.[6,7] On the other hand, the data on PFA and PMA cannot be explained at all by such a model. In addition to the fact that such a simple model does not explain two-step dissociation for PFA or PMA over the whole range of α, their data points lie far below the calculated lines even at $\alpha < 0.5$. If the calculated values were to be fitted to the titration data at $\alpha < 0.5$, we should have assumed that the radius of a rod was the unreasonable value of larger than 2 nm. Although PFA and PMA should have been considered more suitable to a rod model with the smeared charge density in view of both their stiffer chains and their higher charge densities than PAA, the reverse proves to be the case in the present study. The reason is not clear why the titration curves of PFA and PMA at lower α do not agree at all with the calculation in Figures 5 and 6. Probably the dissociation behavior characteristic of PFA and PMA may be ascribed to a stronger short-range interaction other than their higher charge densities, which cannot be incorporated in the rod model with smeared charges.

So far all the carboxyl groups on PFA and PMA were considered to have the same $\mathrm{p}K_0$ since the molecular formulas of both polyacids are the same as that of poly(carboxymethylene) except for the configurational difference. The occurrence of the steep increase in $\Delta\mathrm{p}K$ near $\alpha = 0.5$ suggests that it becomes more difficult for a proton to dissociate against the attractive force of the dissociated groups in its neighbors, primarily, the nearest neighbors that are supposed to have been dissociated at $\alpha > 0.5$. It is reasonable to presume that there may exist a considerable difference in the free energy change between the regions of $\alpha > 0.5$ and $\alpha < 0.5$. Thus we might select another approach to analyze the present titration data of PFA and PMA in terms of the two different K_0's. This

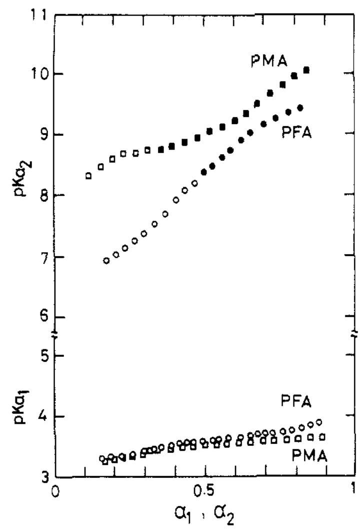

Figure 9. pK_{a1} and pK_{a2} of PFA and PMA at C_s = 0.100 N NaCl for the same data as in Figure 5. Symbols are the same as in Figure 5.

Table II
First and Second Intrinsic Dissociation Constants

acid	from eq 7 pK_{01}	 pK_{02}	from eq 10 pK_{01}	 pK_{02}
PFA[a]	3.20	6.2[b]	3.20	6.1[b]
PMA[a]	3.20	7.9[b]	3.20	8.1[b]
PAA[a]	4.13			
succinic acid	4.21[c]	5.64[c]		
fumaric acid	3.02[c]	4.38[c]		
maleic acid	1.92[c]	6.23[c]		

[a] Average values for Na^+ as a counterion. [b] Including larger errors in comparison with pK_{01}. [c] From ref 24.

is the case if the dissociation constant K_{01} is assigned to one of the –COOH groups on every second carbon atom along the main chain and another K_{02} to the remaining –COOH groups. This corresponds to the assumption that there is another K_0 at higher α which includes the increase in G_{el} around α = 0.5 in itself. If K_{01} is larger than K_{02}, then a proton of –COOH having K_{01} is easier to dissociate than that having K_{02}, although some effect of G_{el} may actually be present.

If the first dissociation process with K_{01} occurs independently of the second one with K_{02}, that is, the ratio K_{01}/K_{02} is much larger than 1, we can separate each dissociation process to calculate the degree of dissociation, α_i, (i = 1 or 2), and the apparent dissociation constant, pK_{ai} is recalculated at each region in the same way as eq 2 and 3. Thus

$$pK_{ai} = pH + \log[(1-\alpha_i)/\alpha_i] = pK_{0i} + 0.4343(dG_{eli}/d\alpha_i)/RT \qquad (i = 1, 2) \quad (7)$$

which is plotted in Figure 9 where pK_{0i} is obtained by extrapolation to α_i = 0 in the same way as in Figure 4. It should be noted that the following numerical relationship holds between pK_0 and pK_{01} for the first dissociation process:

$$pK_{01} = pK_0 - \log 2 \quad (8)$$

The value of pK_{01} of PFA experimentally determined by eq 7 still remains the same as that of PMA, as shown in Table II, which is in good agreement with the one calculated from eq 8 using pK_0 in Table I. However, it becomes different from that of PAA more significantly than the corresponding value in Table I. It is noted that the pK_{02} of PFA is considerably smaller than that of PMA although the data for the second dissociation process are more scattered, probably because of the uncertainty of the end point in the turbid solution.

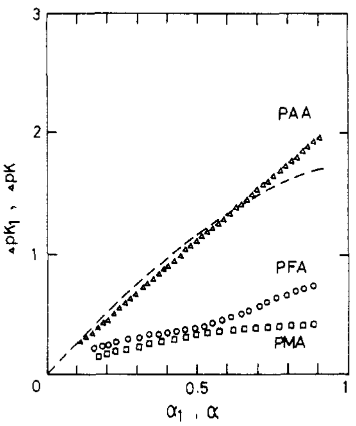

Figure 10. Dependence of ΔpK_1 of PFA and PMA on α_1, and of ΔpK of PAA on α for the same data as in Figure 5. Symbols and line are the same as in Figure 5.

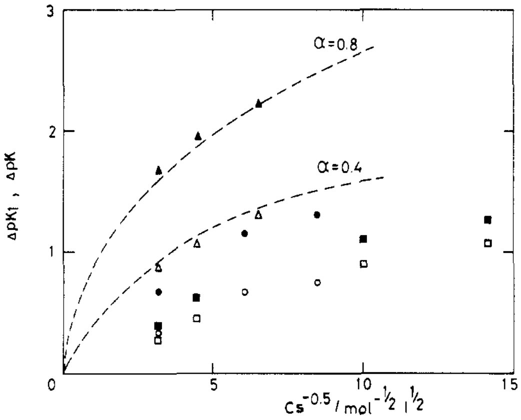

Figure 11. Dependence of ΔpK_1 of PFA and PMA, and of ΔpK of PAA, on C_s for interpolated data at α_1 and α = 0.4, and at α_1 and α = 0.8, respectively, in the same plots as in Figure 10. Symbols and lines are the same as in Figure 5.

The electrostatic term in pK_{ai}, ΔpK_i, for each dissociation process can be determined in the same way as before. In particular we are much concerned with the comparison of ΔpK_1 of PFA or PMA with ΔpK of PAA, because during the first dissociation process of PFA and PMA the overall charge densities of both polyacids should be the same as that of PAA. Some typical plots are shown in Figures 10 and 11, where the calculated curves are also presented, using the same model as in Figures 5 and 6 with the same parameters except for the line charge density for PFA or PMA which is equal to that for PAA in these figures. It is clear that, when one corrects for the charge density and neglects the second dissociation, the first dissociation behavior of PFA is nearly the same as that of PMA but unexpectedly differs from that of PAA, in contrast with Figures 5 and 6 where the overall charge density of PMA or PFA at α is not the same but twice as large as that of PAA at the same α. This discrepancy between both groups of polyacids in Figures 10 and 11 has not been explained yet, but one of the reasonable causes for it may be some contribution of hydrogen bonding whose formation may be possible for PFA or PMA[14] but not for PAA[26], since G_{el} could contain the free energy change due to the formation of hydrogen bonding[25] or the conformational transition,[27] as mentioned before. Moreover, from the fact that ΔG_{el2} for PMA, though not shown here, is larger than that for PFA while the ΔG_{el1} of both polyacids are nearly the same, it is presumed that the arrangement of –COOH of PMA is more compact than that of PFA, since the second dissociation should be affected more significantly by the electrostatic short-range interaction in the neighbors than the first one. This may be helpful to determine the configurations of both polyacids.

If K_{01}/K_{02} is not exceedingly larger than 1, we must take into account the effect of the other dissociation on each dissociation process. Dubin et al.[28] proposed the following analytical expression instead of eq 7 to analyze the titration data of maleic acid copolymers:

$$\mathrm{pH} + \log\,[(1 - \alpha')/(2\alpha') + \{((1 - \alpha')/(2\alpha'))^2 + (K_{02}/K_{01})((2 - \alpha')/\alpha')\}^{1/2}] = \mathrm{p}K_{01} + 0.4343(\mathrm{d}G_{\mathrm{el}}/\mathrm{d}\alpha')/RT \quad (9)$$

where they assumed that the copolymers have two kinds of –COOH with different intrinsic dissociation constants, K_{01} and K_{02}, and the degree of dissociation, α', varies from 0 to 2. It can be used for that case where the first and the second dissociation processes are interrelated. Assuming that K_{02} is somewhat smaller than K_{01}, we can rewrite eq 9 as follows:[29,30]

$$\mathrm{pH} + \log\,[(1 - \alpha')/\alpha'] + \log\,[1 + \alpha'(K_{02}/K_{01})\{(2 - \alpha')/(1 - \alpha')^2\}] = \mathrm{p}K_{01} + 0.4343(\mathrm{d}G_{\mathrm{el}}/\mathrm{d}\alpha')/RT \quad \text{for } 0 < \alpha' < 1 \quad (10a)$$

and

$$\mathrm{pH} + \log\,[(2 - \alpha')/(\alpha' - 1)] = \mathrm{p}K_{02} + 0.4343(\mathrm{d}G_{\mathrm{el}}/\mathrm{d}\alpha')/RT \quad \text{for } 1 < \alpha' < 2 \quad (10b)$$

We are concerned here with only the values of $\mathrm{p}K_{01}$ and $\mathrm{p}K_{02}$. Their values determined by eq 10 are shown in Table II, where they are in good agreement with those determined by eq 7.

There may still arise a question, as discussed above, whether it is reasonable to apply these equations, eq 7–10, to the present data on PFA and PMA whose –COOH groups are indistinguishable from one another along the main chain, in contrast to those in the alternating copolymers of maleic acid where they make a definite pair at every unit of maleic acid separated from the others. If their dissociation behavior can be interpreted in terms of the model in which the –COOH groups are not distinguished, such a model will be more preferred in the present study. The apparent two-step dissociation of PFA and PMA should result from a strong short-range interaction. Along this line, using the linear Ising model, we will analyze $\Delta\mathrm{p}K$ in the titration behavior of PFA and PMA in a succeeding paper.[21]

The repulsive force between the charges on the same polyion through the ionic atmosphere of added salts, regarded as the case (3) at the beginning of the discussion, causes the expansion of a polyelectrolyte chain. Such an interaction affects little the local conformation of a polyelectrolyte chain whose apparent stiffness has proved to be kept almost constant during the course of the dissociation from the small-angle X-ray scattering measured by Muroga et al.[31] Thus it should be considered as a kind of the long-range interaction in a similar way as the so-called excluded volume effect of a nonionic polymer chain.[9-11] The intrinsic viscosity $[\eta]$ of the polyelectrolyte can also be related to the mean square end-to-end distance $\langle R^2 \rangle$, for example, by the well-known Flory–Fox equation[23,32,33]

$$[\eta] = \Phi\langle R^2 \rangle^{3/2}/M \quad (11)$$

where Φ is the so-called Flory constant slightly dependent on the excluded volume effect and M is the molecular weight of the polymer. Roughly speaking, if Φ is assumed to be kept constant in the present study where $[\eta]$ was measured for the same polymer as a function of α, the change of $[\eta]$ must be directly related to the dimensional change of a polymer chain. From such a point of view the expansion process of PFA and PMA chains observed by $[\eta]$ in Figure 8 with increasing α seems to be strange in contrast with the common polyacids such as PAA,[32] whose $[\eta]$ increases monotonously with α due to the electrostatic long-range interacton, that is, the Coulombic repulsion between the ionic groups within a chain. If such a conformational transition were to occur as is the case of poly(methacrylic acid) at lower α from a compact globule to a random coil due to the balance of the hydrophobic and the electrostatic effects,[34] some abnormal behavior of $\mathrm{p}K_{\mathrm{a}}$ as well as $[\eta]$ might appear during the course of dissociation. It seems reasonable, however, to assume that the increase in $[\eta]$ of PFA and PMA at $\alpha < 0.5$ is attributable to the electrostatic repulsion in the same way as that of PAA, while at $\alpha > 0.5$ any effect reduces $[\eta]$ and their chain dimensions until PMA and PFA are precipitated out of the solutions. Although we have not yet found any cause for the contraction of the chain dimension and the appearance of the turbidity in their solutions at higher α, it might be imagined that PFA and PMA at higher α have such high charge densities that the stronger electrostatic potential in the neighbors of the polyion could attract the small ions in larger quantities whose apparent local concentrations in the neighbors of polyacid chains are exceedingly higher than those in the medium. Therefore one reasonable conjecture on this abnormal behavior might be the occurrence of a kind of phenomena called "local salting out" in the solution of PFA or PMA at higher charge densities in the presence of added salt even if the bulk C_{s} is not high enough to precipitate the polymer. In addition, the hydrogen bonding may also affect the behavior of $[\eta]$. In any event we will have to examine the interaction between small ions and the ionized groups of PFA and PMA as a function of α directly by measuring the other thermodynamic quantities such as the activity coefficients and the mobilities of the small ions or the binding of the counterions to a polyion with spectroscopic methods.

Conclusions

The following conclusions were made from the detailed analysis of the measurements of potentiometric titration and intrinsic viscosity of the stereoisomeric polyacids, PFA and PMA, which have charge densities twice as high as vinylic poly(carboxylic acids) such as PAA:

1. PFA and PMA appear to dissociate in two steps.
2. PMA exhibits two-step dissociation more clearly than PFA due to the possible configurational difference between them.
3. The solutions of PFA and PMA become turbid at higher α in the presence of salts as well as at lower α.
4. The type of the alkali metal cation has some effect on the titration curves of PMA, more significantly at the region of $\alpha > 0.5$ than at $\alpha < 0.5$.
5. The values of $\mathrm{p}K_0$ of PFA and PMA are almost the same but smaller than that of PAA, in agreement with those of the analogous low molecular weight organic acids.
6. $\Delta\mathrm{p}K$ related to the free energy change during the dissociation depends significantly both on the configuration and on the charge density of the polyacid at $\alpha > 0.5$ while it depends little on them at $\alpha < 0.5$.
7. The rod model with the smeared charge density proves to be inapplicable to the dissociation behavior of PFA and PMA not only in the steep increase in $\Delta\mathrm{p}K$ around $\alpha = 0.5$ but also at the region of $\alpha < 0.5$ where PFA and PMA are expected to have the same overall charge density as PAA.

8. [η] of PFA possibly as well as PMA increases with α at lower α, attains a maximum near $\alpha = 0.5$ and then decreases beyond it, and finally the solution becomes turbid.

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Polymer Probe Dynamics

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ABSTRACT: A quaternary polymer solution system consisting of polystyrene (PS), poly(methyl methacrylate) (PMMA), toluene (TOL), and α-chloronaphthalene (CNA) has been selected to study the structure (size) and dynamics [translational (and internal) motions] of both the polymer pseudonetwork and the probe. In this work, a trace amount of poly(methyl methacrylate) with $M_w = 5.7 \times 10^6$ and $M_w/M_n \sim 1.2$ was used as the "optically labeled" chain (probe) diffusing in the polystyrene ($M_w = 2.0 \times 10^7$, $M_w/M_n \sim 1.8$) pseudonetwork. The pseudonetwork was formed by dissolving PS in an isorefractive mixed solvent (MS) of TOL and CNA. At 38 °C and with a volume fraction $\phi_{CNA} = 0.72$ in the mixed solvent, PS (with preferential adsorption) was refractive index matched. The absolute scattered intensity of the refractive index matched polymer solution (PS/MS) was comparable to the scattering power of the mixed solvent. Static and dynamic light scattering measurements were used to characterize the probe (PMMA) and the polymer (PS) pseudonetwork separately. By changing the MS composition, we could characterize the structure and the dynamics of PS in the mixed solvent in semidilute solutions. Thus, we were able to determine independently static and dynamic properties of the polymer matrix, such as the correlation length (L, or mesh size) and the cooperative diffusion coefficient (D_c). Properties of the isorefractive polymer (PS) matrix were obtained by interpolation. The structure (size), dynamics, and interaction of the PMMA probe could then be investigated in detail in the well-characterized PS/MS isorefractive matrix. In particular, photocount autocorrelation function measurements of the PMMA probe in the PS/MS matrix showed the presence of at least two dominant characteristic modes even at small scattering angles for R_g(PMMA) $\gg L$(PS). The slow mode could be identified with the translational motion of the center of mass of the PMMA probe chain while we suggest that the fast mode might be related to a coupling of PMMA motions with the cooperative motion of the PS/MS matrix.

I. Introduction

Entanglement of polymer coils in semidilute solutions is responsible for the pseudogel behavior. Dynamic light scattering of semidilute polymer solutions has shown the existence of a fast relaxation mode expressed in terms of the so-called cooperative diffusion coefficient.[1] Although observation of a very slow mode has been reported by several groups,[2] its nature remains unclear.[3-5] The very slow mode (denoted $D_{V\text{-slow}}$) was interpreted as the self-diffusion of a single polymer chain reptating through the entangled polymer coils.[2] However, the magnitude of $D_{V\text{-slow}}$ appeared to be too small when compared with the self-diffusion coefficient (D_s) obtained by other techniques such as forced Rayleigh scattering.[6] A clustering of polymer chains (rather than a single polymer chain) diffusing through the entangled polymer coils was then proposed

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