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Sodium Ion Activity and Electrical Conductivity of Poly(maleic acid) and Poly(isobutylene-*alt*-maleic acid) in Aqueous Salt-Free Solution

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ABSTRACT: The sodium ion activity and electrical conductivity of poly(maleic acid) (PMA) and an alternating copolymer of isobutylene with maleic acid (PIM) in aqueous salt-free solution were measured at 25 °C as a function of the degree of dissociation (α) and polymer concentration (C_p). These results were compared with those of poly(acrylic acid) (PAA) to investigate the effect of charge density and distribution of charged groups in a polyelectrolyte chain on the counterion binding. The activity coefficients of sodium ions of PMA and PIM increased above $\alpha = 0.6$ at low C_p, whereas those of PAA decreased gradually with α at all C_p's. Correspondingly, the electrical conductances of PMA and PIM increased steeply above $\alpha = 0.5$ at low C_p, whereas those of PAA increased slightly above $\alpha = 0.5$ at all C_p's. The values of the activity coefficient of Na^+ in PMA under salt-free conditions deviated from those predicted by the theories of Manning and Katchalsky–Lifson. The same tendency was observed in PIM for higher α regions. These deviations became remarkable with increasing α or decreasing C_p. These results suggest that the bound sodium ions are fairly labile for $\alpha > 0.5$ in dilute, salt-free solutions of PMA and PIM. This means that, in these cases, condensed counterions may be more or less replaced by dissociated protons in the neighborhood of a polyion, corresponding to the polyion phase.

Introduction

Many studies on the electrostatic interaction of a polyion with counterions and co-ions have so far been carried out with various measurements, including activity coefficient[1-6] and electrical conductivity.[7-10] As a result, counterion activity coefficients are significantly lower in polyelectrolyte solutions than those in simple salt solutions of comparable concentration, interpreted by the concept of ion binding. The higher the charge density of the polyelectrolyte becomes, the greater the counterion–polyion interaction is, and, consequently, the lower the activity coefficient of the counterion is. Even at infinite dilution, the activity coefficients of counterions and the osmotic coefficients of the solution are, as well-known, usually very low.

The analysis of distribution of small ions around a polyion and related solution properties can be roughly classified into two methodologies. One is the application of the Poisson–Boltzmann equation to an infinite cylinder with a smeared charge density developed by Lifson and Katchalsky.[11] The other is Manning's counterion condensation theory[12,13] originally introduced by Oosawa's two-phase model,[14,15] in which the thermodynamic and transport properties of the small ions around a linear polyion in solution are given as limiting laws for an infinite line charge. Manning's theory predicts that the activity coefficient of the univalent counterion γ_+ is expressed as

$$\gamma_+ = e^{-0.5\xi} \qquad (1)$$

for the charge density parameter $\xi < 1.0$ and as

$$\gamma_+ = \xi^{-1}e^{-0.5} \qquad (2)$$

for $\xi > 1.0$. In eqs 1 and 2, ξ is given by

$$\xi = e^2/DkTb \qquad (3)$$

where e, D, k, T, and b are the elementary electric charge, dielectric constant of the solvent, Boltzmann constant, absolute temperature, and average axial spacing between charged groups on the polyion, respectively. The counterion condensation theory as well as the two-phase model could be regarded as a limit of the Poisson–Boltzmann theory. The interaction of polyion with a small ion has so far been expressed by both theories.

Previous studies on potentiometric titration of poly(maleic acid) (PMA), an alternating copolymer of isobutylene with maleic acid (PIM), and other maleic acid copolymers revealed that they dissociated apparently in two steps by the strong short-range electrostatic interaction.[16-22] In addition, their intrinsic viscosity decreased in the region of degree of dissociation $\alpha > 0.5$ with α.[16,17,19] Furthermore, the solution of PMA produced a precipitation at high α even at a dilute salt concentration, $C_s <$ 0.1 N NaCl.[16] The appearance of precipitation and the decrease of intrinsic viscosity in the region of $\alpha > 0.5$ are closely related to the strong electrostatic interaction between a polyion with a high charge density and surrounding small ions. Therefore, it is of importance to examine the influence of the charge density and distribution of charged groups on the small ions, to clarify the solution behavior of PMA and PIM, in comparison with that of poly(acrylic acid) (PAA).

The present study presents the details of the activity coefficients of sodium ions and the electrical conductances of PMA and PIM in aqueous salt-free solution at various polymer concentrations (C_p) and degrees of dissociation (α) and compares these results with those predicted from the theories.

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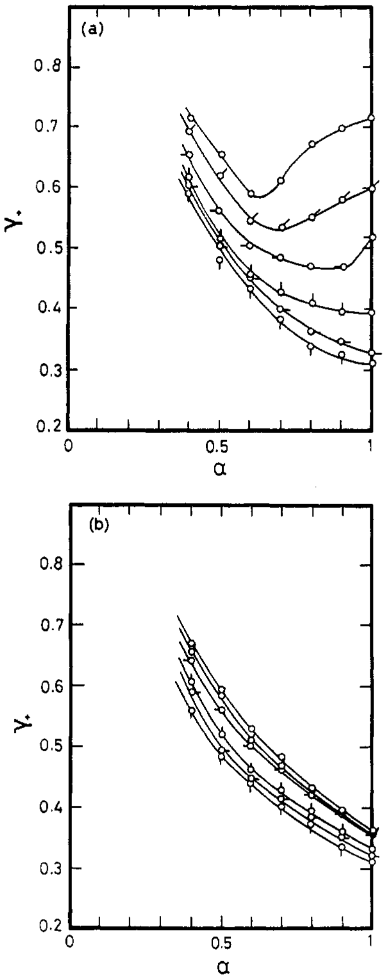

Figure 1. Plots of the activity coefficients of sodium ions γ_+ against α at various C_p's for (a) PMA and (b) PAA: (○) C_p = 2.4 mN, (♂) 6.0 mN, (-○) 9.6 mN, (ȯ) 24 mN, (○-) 30 mN, and (♀) 60 mN.

Materials and Methods

The samples of PMA, PIM, and PAA were the same as used in the previous paper.[16,17]

The electromotive force (EMF) was measured using an Orion Research EA-920 Ionanalyzer in conjunction with an Orion sodium ion selective glass electrode 96-11 and an Orion single-junction reference electrode (with a filling solution of lithium trichloroacetate saturated with AgCl) under an argon atmosphere. All measurements were carried out in a stirred solution thermostated at 25.0 ± 0.1 °C. The output of the EMF was recorded automatically by using an Ohkura desk-top recorder. The time needed for each run was approximately 60 min. Calibration curves were determined both before and after each measurement on the polyelectrolyte solutions. Electrode slopes were Nernstian between 0.2 and 100 mN NaCl, within an error of 2%, and were never found to differ more than 1 mV/decade between the two calibrations. Numerical values of the activity coefficients of the standardized NaCl and NaOH solutions were the ones in the data book calculated by the extended Debye–Hückel equation. The C_p ranged from 2.4 to 60 mN.

The electrical conductivity was measured with a Toa Electronics conductivity meter CM-40S connected with a conductivity cell CGT-511 under an argon atmosphere. The frequency was 80 Hz below 2 mS and 3 kHz above it. The errors of the observed conductances due to the change in frequency were less than 0.5% for a salt solution with a conductance of 2 mS. The cell was calibrated by using standard KCl and NaCl solutions. All measurements were carried out in slowly stirred solutions thermostated at 25.0 ± 0.1 °C. The time needed for each run was about 1 h. C_p ranged from 0.5 to 80 mN.

The solutions for measurements were prepared by passing through a mixed bed of ion-exchange resins and bubbling by argon gas for 15 min just before use. The concentration was determined by potentiometric titration as reported in the previous paper.[16,17]

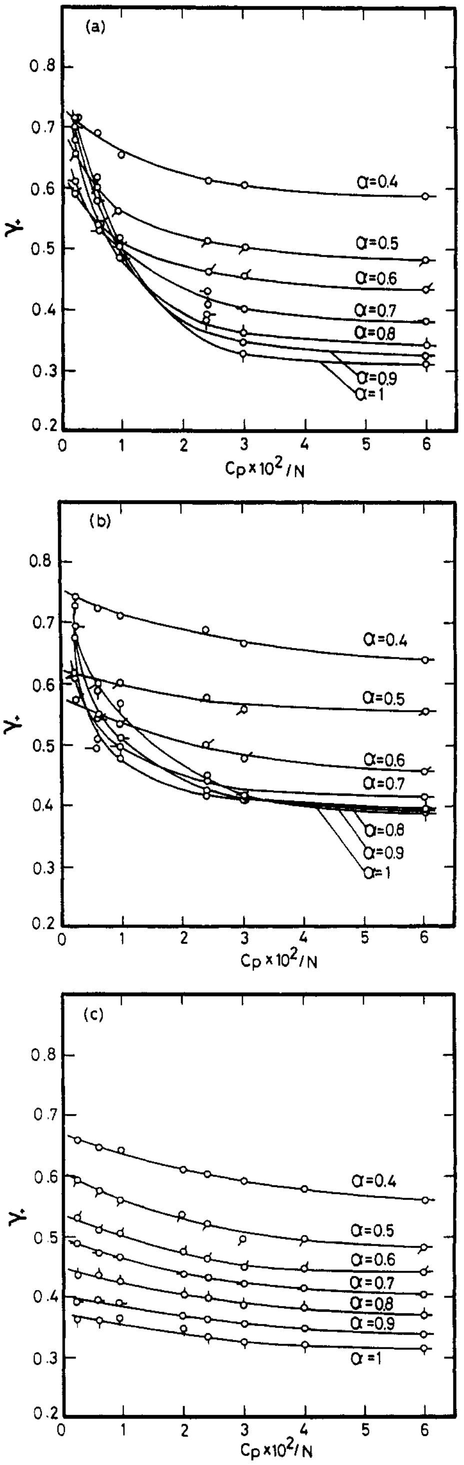

Figure 2. C_p dependence of γ_+ at various α's for (a) PMA, (b) PIM, and (c) PAA: (○) α = 0.4, (ρ) 0.5, (♂) 0.6, (-○) 0.7, (ȯ) 0.8, (○-) 0.9, and (♀) 1.0.

Results and Discussion

Plots of activity coefficients of sodium ions γ_+ in aqueous salt-free solutions of PMA and PAA for various C_p's against α are shown in Figure 1. Strictly speaking, the degree of dissociation should be replaced by the degree of neutralization, but the difference between both quantities seems very small except for $\alpha < 0.1$. In marked contrast to the monotonical decrease in γ_+ of PAA with increasing α at

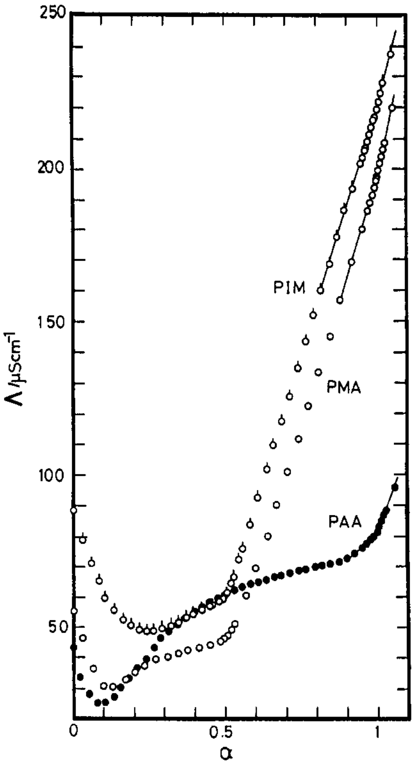

Figure 3. Conductometric titration curves of PMA (○), PIM (ό), and PAA (●) at C_p at C_p = 2.0 mN.

all C_p's, γ_+ of PMA at low C_p increases with α above α = 0.6. At high C_p, γ_+ of PMA decreases with α. In addition, this figure shows that the minimum point of γ_+ of PMA shifts toward higher α as C_p increases. As mentioned in the Introduction, it has been widely accepted that the higher the charge density of the polyelectrolyte becomes, the lower the activity coefficient should be. Therefore, it is very unusual that the activity coefficients of PMA increase with increasing charge density above α = 0.5. Maeda[23] reported that the counterion activity coefficients of poly(*S*-carboxyethyl-L-cysteine), which shows a β-coil conformational transition and an aggregation with neutralization, increase with increasing charge density in the transition region. PMA at high charge density, however, does not seem to produce any conformational transition. The α-dependences of γ_+ for PIM at various C_p's were similar to those for PMA, as shown later. The C_p dependences of activity coefficients of PMA, PIM, and PAA for various α's are shown in Figure 2. Whereas the γ_+ of PAA decreases gradually with C_p at all α's, the γ_+ of PMA and PIM at $\alpha > 0.6$ increases steeply with decreasing C_p. In addition, the γ_+ of PMA and PIM is higher than that of PAA of comparable charge density at all C_p's. Therefore, from the measurements of the activity coefficients in salt-free solutions, it is concluded that PAA with a uniform charge distribution attracts more strongly the counterion than PIM with the same average charge density as PAA but with a pairwise array of two carboxyl groups, and PMA with a charge density twice as high as PAA, in contrast to our simple expectation.

Some examples of the electrical conductometric titration curves of PMA, PIM, and PAA at C_p = 2.0 mN are shown in Figure 3. Remarkable is the existence of two modes in the conductance change with α of PMA and PIM separated near α = 0.5, like a potentiometric titration reported previously.[16,17] That is, the conductance of PMA and PIM increases gradually below α = 0.5, in a way similar to that of PAA, and then increases steeply above it, in contrast to the slight, single-mode increase in that of PAA over the whole range of α. This fact may be closely related to the presence of two kinds of ionized groups having different dissociation constants as reported in the previous papers,[16,17] suggesting that PMA and PIM below C_p = 10 mN and above α = 0.5 do not so strongly interact with sodium ions, in agreement with the results of activity coefficients. It is known that the steep increase in the conductance above α = 0.5 also appeared in the low molecular weight monomers: fumaric acid and maleic acid. In Figure 3, the first decrease in the conductance at low α is due to disappearance of free H+ ions, as well-known

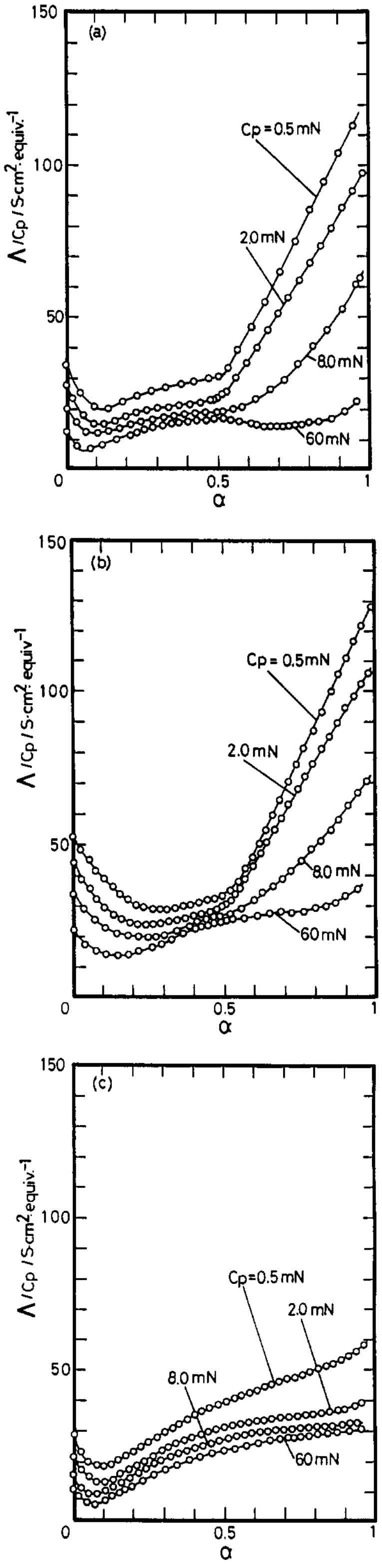

Figure 4. Conductometric titration curves reduced for C_p at various C_p's: (a) PMA, (b) PIM, and (c) PAA.

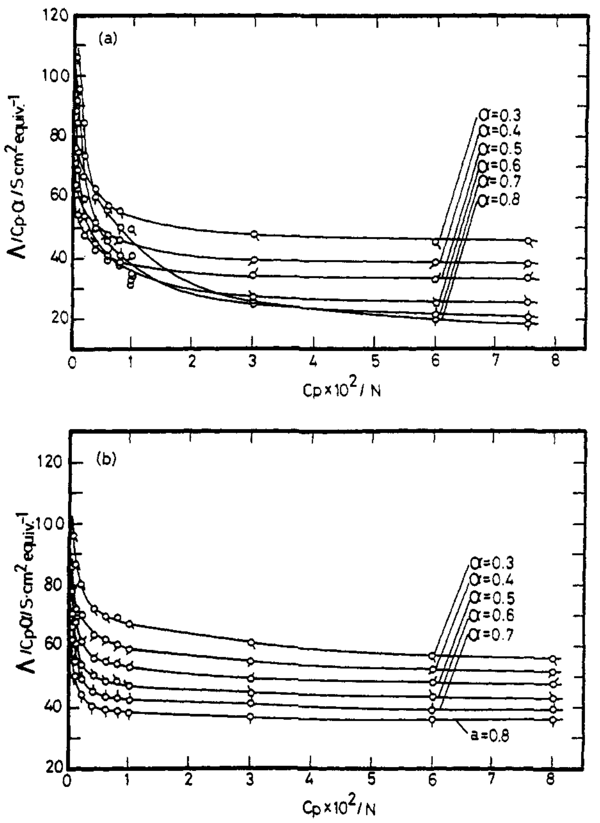

Figure 5. C_p dependence of conductance reduced for $C_p\alpha$ at various α's: (a) PMA and (b) PAA.

in the low molecular weight organic weak acids. That is, at low α, the conductance is higher for substances with a higher intrinsic dissociation constant.

Generally, a conductance of a weak polyelectrolyte in a salt-free solution is defined by the equation

$$\Lambda = C_p\alpha(\lambda_p + \lambda'_c) \qquad (4)$$

where λ_p and λ'_c are the equivalent conductivities of the polyion and counterion, respectively. The conductometric titration curves reduced for C_p at various C_p's are shown in Figure 4. Whereas the conductances of PAA increase gradually with α at all C_p's, those of PMA and PIM at low C_p show an inflection point at $\alpha = 0.5$ as mentioned above and the inflection point seems to shift toward higher α as C_p increases. At higher C_p, the conductometric titration curves of PIM become identical to those of PAA. It is also noted here that conductance of PMA at $C_p = 60$ mN shows a maximum at $\alpha = 0.5$. This may be due to the contribution from the polyion of PMA since the conductivity of the polyion may be a function of the square of the charge density and the degree of ion binding if a PMA molecule assumes a compact form. Evidently, the conformation of a PMA molecule is not a compact one, but it is certain that a PMA molecule bears the maximum charge at $\alpha = 0.5$, as confirmed by the results of the intrinsic viscosity.[16,17] The C_p dependences of conductance reduced for $C_p\alpha$ at various α's are shown in Figure 5. Whereas the $\Lambda/C_p\alpha$ of PAA decreases monotonically with C_p at all α's, that of PMA in the region of $\alpha > 0.6$ increases steeply with decreasing C_p. This result is qualitatively consistent with the results of activity coefficients. That is, the results of both the activity coefficients and the conductances of PMA and PIM suggest that at low C_p the polyion with maleic acid units does not bind the counterions so strongly.

The comparison of the activity coefficients in the present paper with the values predicted by the theories of Katchalsky–Lifson and of Manning is shown in Figure 6. This figure shows that the activity coefficient of PAA can be well explained by Katchalsky–Lifson's theory rather than Manning's. Both theories, however, cannot express the increase in the activity coefficients of PIM at $\alpha > 0.5$ and the activity coefficients of PMA at all.

To evaluate the contribution of only the polyion to the total conductivity, eq 4 was rewritten to the equation

$$\alpha\lambda_p = \Lambda/C_p - \alpha\gamma_+\lambda_c \qquad (5)$$

where λ_c is the equivalent conductivity of the sodium ion in a low molecular weight electrolyte solution of comparable concentration. In eq 5, γ_+, is introduced so as to evaluate the actual counterion concentration effective to the conductance as freely mobile ions, and the experimentally observed values of γ_+ are used to keep the self-

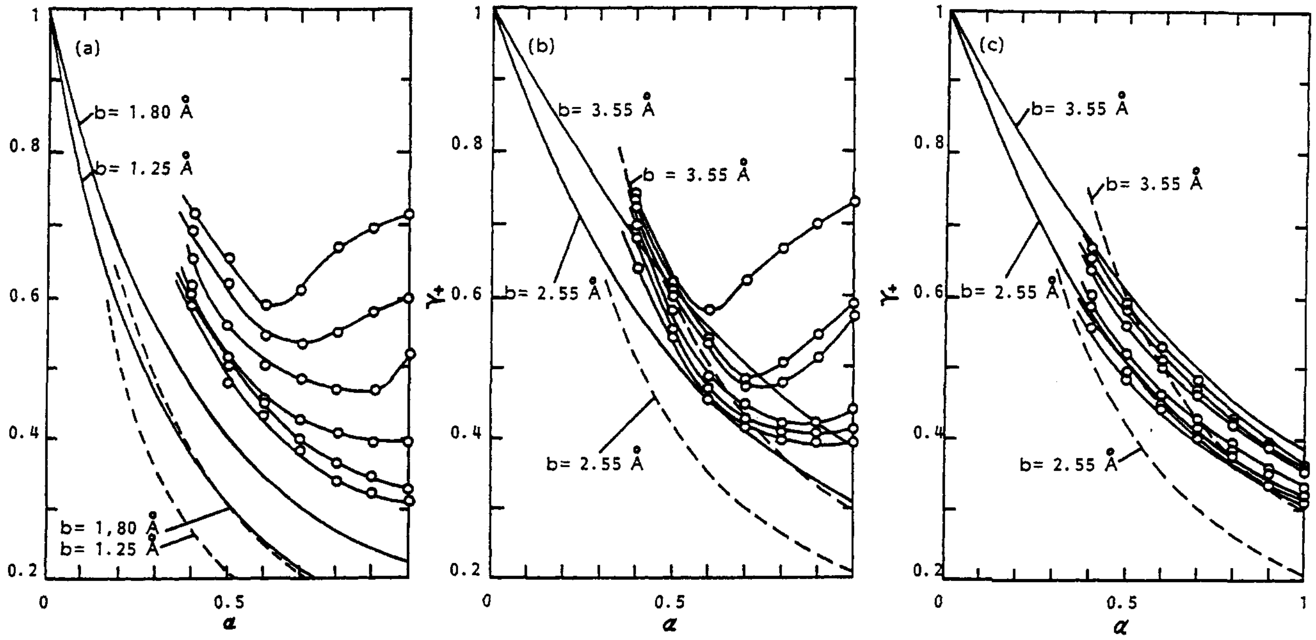

Figure 6. Comparison of observed γ_+'s with theoretical curves. The solid and broken lines represent the curves calculated by theories of Katchalsky–Lifson for $C_p = 2.4$ mN and Manning, respectively, where b is the average distance between charged groups.

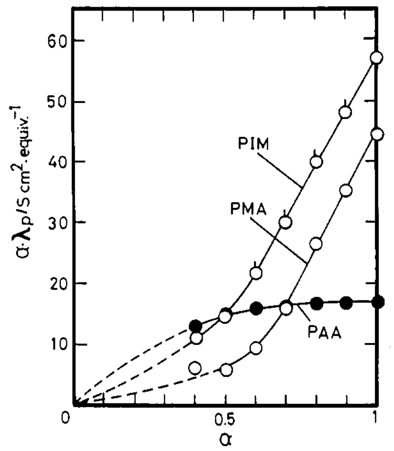

Figure 7. Plots of $\alpha\lambda_p$ vs α of PMA (○), PIM (ȯ), and PAA (●).

consistency between the observed activities and conductances. The plot of $\alpha\lambda_p$ at C_p = 6 mN as a function of α is shown in Figure 7, where the $\alpha\lambda_p$ of PMA and PIM increases steeply with increasing α, contrary to that of PAA which increases gradually. This fact indicates that the steep increase in the total conductance of PMA and PIM at $\alpha > 0.5$ is due to the contribution of the polyion.

The reason for the unusually high values of γ_+ and conductances obtained in the present study is not well understood. One of the possible reasons is that, for $\alpha > 0.5$, a part of the counterions, e.g., Na$^+$, is not strongly bound to the polyion, while the same amounts of the protons in the pair of COOH to be dissociated as a second step remain undissociated. Another one is that a part of the counterions is replaced by dissociated protons in the vicinity of the polyion, as is the case of the strong polyacids such as poly(styrenesulfonic acid), where dissociated protons are condensed in the acidic form. In any case, the high values of γ_+ as well as the sharp rise of the conductance are due mainly to the release of the counterions, and the contribution of dissociated protons seems very small. Also the theoretical assumption of an infinite rod model to account for the ion condensation seems not well satisfied as C_p is lowered. In addition, an infinite rod model is rather inappropriate for analyzing the conductivity of polyelectrolyte solutions, because the overall conformation of a polyion is an important factor in the process of the motion of a polyion in solution under an external field.[24] Further study should be needed to clarify the origin of the unusually high fraction of counterions in the solvent phase in the solutions of PMA and PIM.

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Registry No. PMA (homopolymer), 26099-09-2; PIM (copolymer), 135639-46-2; Na, 7440-23-5.