

Temperature Dependence of Viscosities and Potentiometric Titration Behavior of Aqueous Poly(acrylic acid) and Poly(methacrylic acid) Solutions

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ABSTRACT: The viscosities of poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) have been measured in aqueous 0.25 M NaCl solutions at 5, 15, 25, 35, and 45°C as a function of various degrees of neutralization. The potentiometric titration data for these polycarboxylic acids in water at 5, 25, and 45°C are also reported. Both results indicate that the compact conformation of PMA at low degree of dissociation is more stabilized at lower temperatures. The origin of the hydrophobic interaction has been discussed and it has been suggested that any change of water structure around hydrophobic groups is not required to account for the pH-induced conformational transition of PMA.

KEY WORDS Viscosity / Potentiometric Titration / Poly(acrylic acid) / Poly(methacrylic acid) / Aqueous Solution / Conformational Transition / Hydrophobic Interaction

Some synthetic polyelectrolytes, such as poly(methacrylic acid) (PMA), in aqueous solutions undergo a pH-induced conformational transition from a compact coil to an extended coil form at relatively low degrees of ionization, α . Such an anomalous behavior was at first described in the study of viscosity and pH of PMA solution by Katchalsky¹ and then has attracted the attention of many researchers because of a resemblance to the well-known globular-to-coil transition of proteins.

Katchalsky has attributed the resistance to the chain expansion as being due to van der Waals attraction and especially hydrogen bonding between various parts of the PMA molecules. Arnold² showed that the solution viscosity and pK of poly(acrylic acid) (PAA)

increase monotonously with the increase in α , and stated that the reason of the different behavior of two polycarboxylic acid remains obscure, although it could be connected with the greater flexibility of the PAA molecule as compared with that of PMA.

Anufrieva *et al.*³ have explained the stabilization of the compact coil form of PMA from the point of view of the structural change of water around methyl group on PMA molecule, *i.e.*, hydrophobic interaction. This idea has been supported by the studies of solubilization of hydrophobic molecules⁴ and calorimetry.⁵ This appears, at present, to be a most popular interpretation for the conformational transition of PMA and the other polycarboxylic acids.

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Yamashita and Kwak,⁶ however, have concluded from their precise heat capacity measurements that there is no evidence of the hydrophobic interactions in the conformational transition behavior of PMA. Recently, on the basis of the fluorescence studies, Bednář *et al.*⁷ suggested the importance of intramolecular hydrogen bonds between the ionized and unionized carboxyl groups, in addition to the hydrophobic interactions. Thus, the exact nature of the conformational transition is still poorly understood. The hydrophobic interactions through the intermediary of the water-structural change would be very sensitive to temperature or pressure. In the present study we measured the temperature dependence of viscosities and potentiometric titrations of aqueous PAA and PMA solutions.

EXPERIMENTAL

Materials

Purified methacrylic acid was dissolved in water and polymerized with hydrogen peroxide as an initiator in a nitrogen atmosphere. Concentration of monomer was about 20 wt%, that of peroxide 0.6 wt%, the polymerization temperature was 90°C, and the reaction time was about 2 hours. The gel-like solution was diluted with water and then PMA was precipitated by the addition of concentrated HCl solution. The polymer obtained was again dissolved in distilled water and purified by dialysis. The molecular weight was estimated to be 7.4×10^5 from the intrinsic viscosity of Na-type polymer in 2 M NaNO₃ solution at 25°C.⁸

Commercial product of 25% aqueous PAA solution was diluted with very dilute HCl solution and purified by dialysis against distilled water. The molecular weight was 2.4×10^5 from the viscosity measurements of the polymer with degree of neutralization of 0.4 in 0.5 M NaBr solution at 25°C.⁹

The concentrations of the polyacids in aqueous stock solutions were determined by

conductometric titrations with a carbonate-free 0.1 M NaOH solution.

Viscosity Measurements

By adding a calculated amount of 0.5 M NaOH solution to the stock solution, we obtained solutions of PAA or PMA with various degrees of neutralization; $\alpha' = 0, 0.1, 0.2, 0.3$, and 0.8 . The viscosities of these polymer solutions containing 0.25 M NaCl were measured by using Ostwald-type dilution viscometers at 5, 15, 25, 35, and 45°C. The viscosities of unionized PMA in 0.002 M HCl solutions were also measured at 5, 25, and 45°C. Flow times of water in three viscometers used were 250–300 s at 25°C and a kinetic energy correction could be neglected. The temperature of the thermostat bath was maintained within 0.02°C using a thermister temperature controller constructed in our laboratory.

Potentiometric Titrations

The pH measurements were made using an Orion Model 801A ion meter equipped with a Denkikagaku MG511 glass electrode and a Horiba 2535A calomel electrode connected by a saturated KNO₃-agar salt bridge. The titrations were carried out with carbonate-free 0.1 M NaOH solution under nitrogen atmosphere at 5, 25, and 45°C. The polyacid concentrations were 4.653 and 4.372×10^{-3} monomol dm⁻³ for PAA and PMA, respectively.

RESULTS AND DISCUSSION

Potentiometric Titration

The pH-titration results were expressed in terms of the dependence of an apparent dissociation constant pK_a on the degree of dissociation α , where $pK_a = \text{pH} + \log[(1-\alpha)/\alpha]$. The results for PAA and PMA solutions at three temperatures are given in Figures 1 and 2, respectively. It is evident that the pK_a values for PAA increase monotonously with the

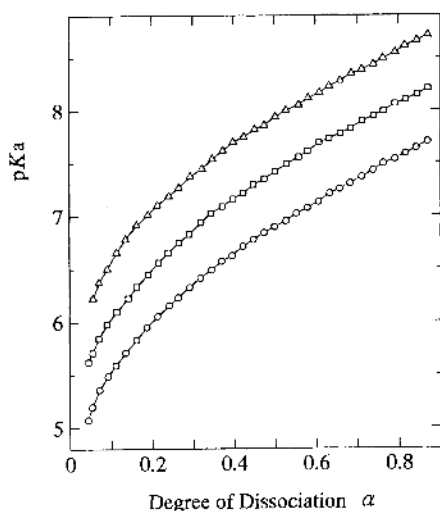


Figure 1. Modified pH-titration curves of poly(acrylic acid) in aqueous solution. \circ , 5°C; \square , 25°C; \triangle , 45°C. For clarity, the ordinate scale for the data at 25 and 45°C has been displaced by 0.5 and 1.0 pK_a unit, respectively.

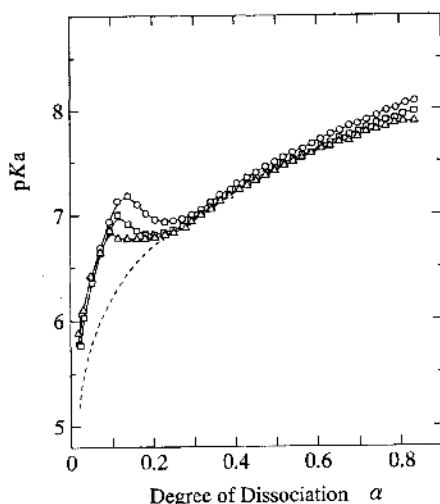


Figure 2. Modified pH-titration curves of poly(methacrylic acid) in aqueous solution. \circ , 5°C; \square , 25°C; \triangle , 45°C. The broken line represents the hypothetical titration curve of the extended coil form at 25°C.

increase in α , while the pK_a curves for PMA pass through a maximum at low dissociation, dependent on the temperature. The anomalous pK_a behavior observed for PMA at $\alpha=0-0.3$ has been well-known and in general interpreted

in terms of the transition from a compact coil at low pH to an extended coil form at higher degrees of dissociation of polyacid. As the temperature is decreased, the transition becomes more pronounced and the onset of the transition shifts to higher α .

The titration behavior of PMA differs markedly from that of PAA not only in the existence of the conformational transition but also in the acid strength. The difference between pK_a values of PAA and PMA at very low degrees of dissociation is as much as 1 pH unit, that is, the acid strength of PMA is about ten times smaller than that of PAA. This is a clear contrast to the case of corresponding low molecular carboxylic acids: $pK_a=4.876$ and 4.860 for propionic and isobutyric acids, respectively.¹⁰ There seems no satisfactory theory to interpret the difference in acid strength of these polycarboxylic acids. It is, however, interesting to note that a more pronounced conformational transition has been observed for polycarboxylic acids having lower acid strength as can be seen from the comparison of the pH titration behavior of poly(methacrylic acid) with poly(ethacrylic acid),¹¹ maleic acid-styrene with maleic acid- α -methylstyrene copolymers,¹² or copolymers of maleic acid and various alkylvinylethers.¹³

The standard free energy change ΔG_t° for the transition is given by

$$\Delta G_t^\circ = 2.303RT \int_0^1 (pK_a - pK_a') d\alpha$$

where pK_a' is the hypothetical value for the extended coil form without the transition. According to the procedure of Leyte and Mandel,¹⁴ the pK_a' values were estimated by extrapolation of the curve for dissociated extended form at higher pH region to the lower α region with the aid of the Henderson-Hasselbalch plot. The pK_a' values at 25°C are illustrated in Figure 2 as a broken line.

The values of ΔG_t° obtained by graphical integration are 670, 600, and 540 J mol⁻¹ at 5,

25, and 45°C, respectively. The error in the ΔG_i° estimation is considered to be about 10%. The ΔG_i° values estimated in this study are comparable with those found in the literature: 740 J mol⁻¹¹⁵ at 5°C, 710 J mol⁻¹¹⁶ at 11°C, 720 J mol⁻¹¹⁶ at 18°C, 585,¹¹ 770,¹⁴ and 720 J mol⁻¹¹⁶ at 25°C, 630 J mol⁻¹¹⁶ at 32°C, 610 J mol⁻¹¹⁶ at 39°C, 690 J mol⁻¹¹⁷ at 45°C, 640 J mol⁻¹¹⁵ at 50°C, and 510 J mol⁻¹¹¹ at 80°C.

Some scatter of the values among the literature and this study may be in part attributed to the differences of concentrations of polymer or added electrolytes and/or to somewhat different tacticity of the PMA samples used by various authors. Schafer *et al.*¹⁶ have clearly indicated that the increase in ionic strength reduces the ΔG_i° values. The tacticity is one of the decisive factors in determining the conformational transition behavior. A marked irreversible titration curve can be observed for isotactic PMA, but not for syndiotactic PMA.^{18,19} It is apparent that isotactic PMA is a weaker acid and exhibits a more pronounced conformational transition than syndiotactic or atactic PMA,^{20,21} the latter was used in the present work.

In spite of the scatter in ΔG_i° values, it is evident that the ΔG_i° values decrease with the increase in temperature. The larger ΔG_i° and higher α of the onset of transition at lower temperature indicate that the compact form of PMA at low ionization region is more stabilized with the decrease in temperature.

Viscosity

Because of the polyelectrolyte nature of the samples studied, the intrinsic viscosity $[\eta]$ is in general obtained only in the presence of low molecular weight electrolytes. In this study 0.25 M NaCl aqueous solution was used as a solvent, where the reduced viscosity η_{sp}/C_p can be represented by the well-known relation: $\eta_{sp}/C_p = [\eta] + k'[\eta]^2 C_p$, where k' is Huggins constant and C_p is polymer concentration. The typical examples are shown in Figures 3 and 4

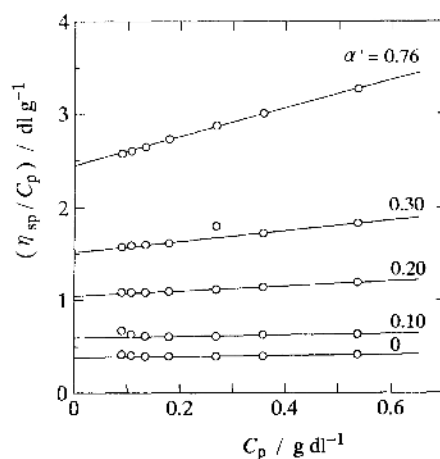


Figure 3. Reduced viscosities of poly(acrylic acid) in 0.25 M NaCl aqueous solutions of various degrees of neutralization α' at 25°C.

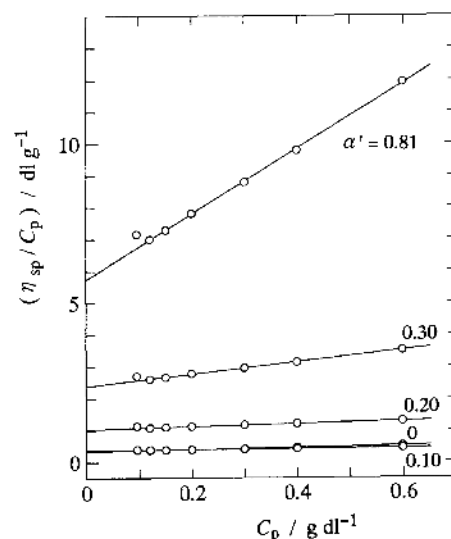


Figure 4. Reduced viscosities of poly(methacrylic acid) in 0.25 M NaCl aqueous solutions of various degrees of neutralization α' at 25°C.

for PAA and PMA solutions at 25°C, respectively. In most cases the above linear relation holds and $[\eta]$ values were estimated by the extrapolation to $C_p = 0$. We observed that the reduced viscosity increases slightly with decreasing concentration at low C_p for both PAA and PMA with very low degree of neutralization α' . It has been shown that in the

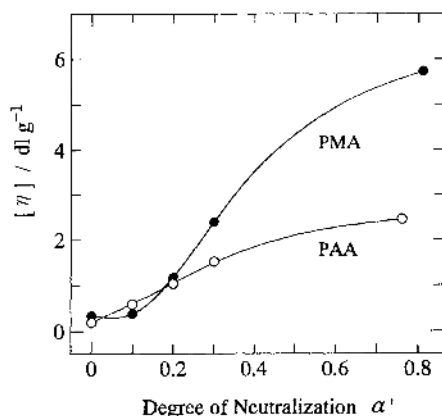


Figure 5. Intrinsic viscosities of poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) as a function of degree of neutralization α' at 25°C.

presence of added electrolytes the degree of ionization of unneutralized PMA increases very steeply at lower polymer concentrations.²² Such a self-ionization effect results in the increase in viscosity of polyacids even in the presence of large amounts of added electrolytes. In this case a linear extrapolation procedure was employed from the points at higher concentrations.

The dependences of $[\eta]$ on α' at 25°C are shown in Figure 5 for PAA and PMA solutions. The intrinsic viscosity of PAA increases monotonously with increasing neutralization because of the increase in electrostatic repulsion between charges on polymer chains. As has been well known, on the other hand, for PMA in low α' region the polymer coil expands only little up to a critical degree of ionization. This anomalous viscosity behavior can be considered as one of the evidences of the compact-to-extended coil transition of PMA.

The temperature dependences of $[\eta]$ estimated for PAA and PMA are shown in Figures 6 and 7, respectively. With increasing temperature the $[\eta]$ value of PAA with various α' increases monotonously or passes through a broad maximum between 15 and 35°C, whereas $[\eta]$ decreases for PMA with $\alpha' = 0$, varies little

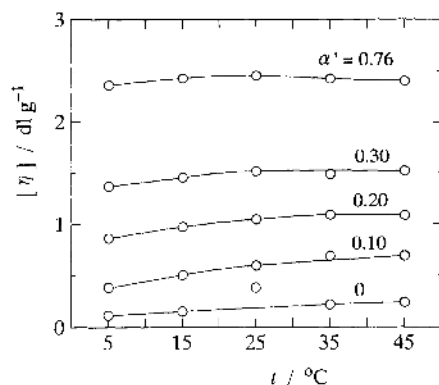


Figure 6. Temperature dependences of the intrinsic viscosities of poly(acrylic acid) of various degrees of neutralization α' .

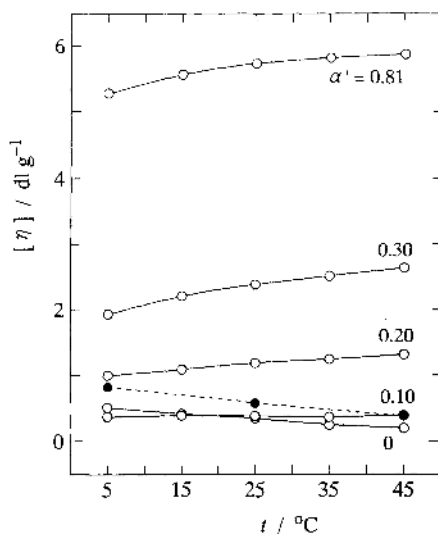


Figure 7. Temperature dependences of the intrinsic viscosities of poly(methacrylic acid) of various degrees of neutralization α' . The filled circles represent the intrinsic viscosities of undissociated poly(methacrylic acid) in 0.002 M HCl solution.

for $\alpha' = 0.1$, and increases in a similar manner to PAA for the larger α' samples. In Figure 7 are also included the $[\eta]$ values determined in 0.002 M HCl solution at 5, 25, and 45°C, where PMA can be considered to be in an undissociated state. It has already been known that the temperature dependence of $[\eta]$ for the unneutralized PMA is negative.²³ The conver-

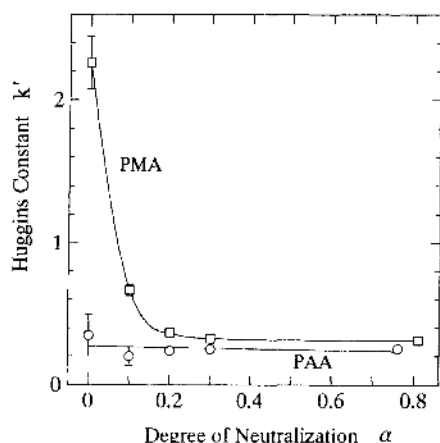


Figure 8. Huggins constants k' of poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) as a function of degree of neutralization α' at 25°C.

sion of sign of the temperature dependence of viscosity accompanying neutralization of polyacids has been also found for hyaluronic acid.²⁴ On the other hand, Sugai and Ohno²⁵ have found the reverse effect for maleic acid–styrene copolymer; the temperature coefficient is positive for the compact form at lower α' and negative for the expanded coiled form at higher α' . The most striking aspect of the present results is that the intrinsic viscosities of PMA at low temperatures decrease with the increase in neutralization up to $\alpha'=0.1$. Such an abnormal behavior may be closely related to the origin of the stability of the compact form.

In Figure 8 are illustrated the Huggins constant k' determined at 25°C for PAA and PMA with various degrees of neutralization. The k' values for all PAA samples and for PMA with $\alpha' > 0.2$ are actually identical to that expected for neutral polymer–good solvent systems: $k' = 0.2$ – 0.3 .²⁶ The marked contrast between PAA and PMA is apparent at low ionizations. Extraordinarily high k' values at $\alpha'=0$ were also observed at the other temperatures, but we could not find an unambiguous regularity on the temperature dependence because some uncertainties in the estimation of concentration dependence of

η_{sp}/C_p and $[\eta]$ may increase for low α' samples due to self-ionization of the weak polyacid. The values of k' estimated for unionized PMA ($\alpha'=0$) in 0.002 M HCl solution are 0.53, 0.54, and 0.64 at 5, 25, and 45°C, respectively. Strange to say, these values are much smaller than those for unneutralized PMA ($\alpha'=0$) but coincide with the k' value for θ -condition,²⁶ which is known to be 0.002 M HCl at 30°C for PMA.²⁷

Conformational Transition of PMA

In general, the conformational transition of PMA has been interpreted in terms of the competition between electrostatic repulsion between charges on the polymer chain and some attractive interactions such as hydrogen bond between carboxyl or carboxylate groups, van der Waals or hydrophobic interactions between methyl groups. The hydrogen bonding interactions have been proposed by Katchalsky in his explorative study.¹ Since no transition can be observed for PAA, Mandel and co-workers^{14,15,28} have suggested that the van der Waals forces due to the methyl groups are important.

Since Kauzmann²⁹ offered a new concept “hydrophobic bond” to explain the stability of native proteins, much attention has been directed towards assessing the importance of the interactions between hydrophobic molecules or groups in water. This approach has also been used to describe the anomalous solution properties of poly(methacrylic acid). Considering the fact that no conformational transition is observed for PAA which differs from PMA only by nonexistence of α -methyl group, it appears to be rather natural to attribute the origin of the transition to the hydrophobic interactions between methyl groups. The conformational transition of copolymers of maleic acid and various hydrophobic co-monomers has also been investigated extensively (see, *e.g.*, ref 6, 17, and 30 and references therein). These studies have clarified that the least hydrophobic ethylene

copolymer does not bring about any conformational transition and that in general the more hydrophobic the co-monomers the more pronounced is the conformational transition. Therefore, it has been widely accepted that the compact form of polycarboxylic acids is stabilized by the intramolecular hydrophobic interactions of apolar groups on the polymer chain.

However, some experimental results on the conformational transition are in conflict with the explanation based on the hydrophobic interactions. For example, the calorimetric study revealed that the transition to the extended form of PMA is accompanied by an increase in enthalpy and a slight increase in entropy.¹⁷ As has been pointed out by Mandel *et al.*,¹⁵ this is exactly the opposite of the expectation based on the hydrophobic bond theory by Kauzmann. He has considered that the hydrophobic interaction is resulted from the melting of so-called iceberg³¹ around non-polar groups in water that is accompanied by positive enthalpy and entropy changes. In other words, the hydrophobic interaction originates essentially from the anomalously large entropy loss accompanying dissolution of nonpolar substances in water. Thus, Kauzmann has explained the very low solubility of hydrocarbons or inert gases in water in terms of this unfavorable entropy effect. It has been often said, therefore, that the hydrophobic interaction is "entropy driven" and, hence, becomes more efficient with increasing temperature. On the contrary, the present study on the temperature dependence of the potentiometric titration behavior and viscosity clearly shows that the conformational transition of PMA is stabilized at lower temperatures. Consequently, it is concluded that the compact form of PMA can not be attributable to the hydrophobic interactions.

In this connection it is relevant to note that the hydrophobic bond theory has been criticized by Shinoda³² on the basis of the analysis of the solubility of hydrocarbons in

water over a wide range of temperature. He concluded that the slight solubility of nonpolar solutes in water is mainly the effect of a large positive enthalpy of mixing, not the entropy effect and the solubility of nonpolar molecules in water must be increased by the iceberg formation. Ramadan *et al.*³³ reached the same conclusion from the study of thermodynamic transfer function of argon from cyclohexane to water and to hydrazine. From this point of view, recently Privalov and Gill³⁴ have interpreted the unfolding of the compact structure of protein at low temperature, *i.e.*, cold denaturation. He wrote that "the stabilization of the compact state of a protein, usually attributed to hydrophobic interaction, is primarily due to van der Waals interactions between the protein nonpolar groups, and the contribution of water solvation by these group, in spite of the widely held opinion, actually destabilizes the compact state."

The modification of water structure like iceberg formation would be accompanied by an adequate change in various partial molar quantities, especially partial molar heat capacity. Precise measurements of the partial molar volumes and heat capacities at 25°C by Yamashita and Kwak,⁶ however, revealed that these partial molar quantities of PMA vary monotonously with ionization, just like PAA. That is, the conformational transition of PMA does not accompanied by any significant change of partial molar quantities, although obvious transitions in partial molar volume and heat capacity can be observed for copoly-(maleic acid-styrene). This situation remains unaltered in the partial molar volume behavior at lower or higher temperatures.³⁵ These results indicate that the conformational transition of PMA can not be ascribed to the interactions through the intermediary of structural change of water around hydrophobic groups.

It is well known that the aqueous PMA solution exhibits a LCST (lower critical solution temperature) type phase diagram³⁶ and gelation takes place for the concentrated

aqueous solution with increasing temperature.³⁷ These phenomena are often observed for aqueous solutions of solutes consisting of weak polar group and adequately hydrophobic group, and the hydrophilic-hydrophobic balance is generally a dominant factor determining the LCST.³⁸ Such a solubility behavior may influence the temperature dependence of solution viscosity. That is, with increasing temperature the decreased solubility of unionized PMA in water may bring about the reduction of the solution viscosity as is illustrated in Figure 7. The abnormally large Huggins constant k' found for slightly dissociated PMA described in Figure 8 may indicate that significant intermolecular interactions can take place even in these dilute solutions due to decreased solute-solvent interactions.^{26,39}

Wright and coworkers^{19,21} have suggested that the importance of the effect of ionic hydrogen bond formation on the conformations of partly ionized poly(methacrylic acid). This hydrogen bond results from essentially geometrical restriction of polymer chain and therefore such a hydrogen bond formation can not expected for more flexible PAA. From the computations of energies of accessible dyad, furthermore, they have shown that the conformational transition behavior of PMA can be explained by consideration of the rotational states of methyl and methylene groups rather than by intramolecular attractions such as hydrophobic interactions or hydrogen bonding.⁴⁰ The importance of geometrical constraints has also been revealed by the conformational studies for various maleic acid copolymers.^{12,13}

The interpretation of the origin of the conformational transition of PMA in terms of the local geometry of the polymer chain seemed to us at present the most reasonable. In addition, ionic hydrogen bonding may contribute to the stabilization of the compact form. The decrease in the intrinsic viscosity of PMA accompanying ionization during the initial

stage of neutralization at lower temperatures (Figure 7) can be interpreted in terms of such strong attractive force only. The hydrogen bond interaction becomes to be weakened as the temperature is increased. This may also explain the anomalous pK_a change at lower temperatures, *i.e.*, the pK_a values in the transition region decrease (acid strength increases) with increasing ionization in competition with the increase in electrostatic repulsion (Figure 2).

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