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Dissociation Behavior of Poly(maleic acid): Potentiometric Titrations, Viscometry, Pulsed Field Gradient NMR, and Model Calculations

J. de Groot, G. J. M. Koper,* M. Borkovec,† and J. de Bleijser

Leiden Institute of Chemistry, Gorlaeus Laboratories, University of Leiden, P.O. Box 9502,
NL-2300 RA Leiden, The Netherlands

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ABSTRACT: Potentiometric titrations, pulsed field gradient NMR, and viscometry of poly(maleic acid) have been carried out in different salt solutions of varying ionic strength. The shape of the titration curve depends strongly on the type of cation used, especially beyond $\alpha = 0.5$. Above 5 times excess salt concentration, the potentiometric titration curves can be fit satisfactorily to an equation derived on the basis of a random Ising model, using three free parameters: the intrinsic dissociation constant K_0 and two excess free energies ϵ_r and ϵ_m describing the nearest-neighbor interaction across a racemic and mesomeric bond, respectively. The stereochemistry of PMA is modeled using an additional parameter P_r, which is the probability of racemic propagation during synthesis. This parameter was determined by ^{13}C NMR. The results compare favorably with those obtained for other poly(carboxylic acid)s. Except for a gradual expansion of the polymer coil upon charging, no conformational changes are observed by PFG-NMR and viscometry. Rather, attractive intermolecular interactions appear to play a role at high degrees of dissociation.

Introduction

Poly(acrylic acid) (PAA) can, in many aspects, be considered as the archetypal polyelectrolyte because its potentiometric titration behavior can be successfully described by an infinite rod model with a smeared charge density.[1,2] Its viscometric behavior, which shows a monotonically increasing specific viscosity with degree of dissociation, is in accordance with this picture where a gradual expansion of the coil with charge density accounts for the increase in the viscosity through the Flory−Fox equation.[3,4] Other models are successful in describing the behavior of this polyelectrolyte as well, such as the line charge model of Manning[5] or the discrete charge models based on the statistical mechanical Ising model.[6,7]

Within the family of poly(carboxylic acid)s, PAA can certainly not be considered as the archetypal molecule. In particular, poly(maleic acid) (PMA) distinguishes itself by a rather pronounced two-step potentiometric behavior.[8] Poly(fumaric acid) (PFA), the stereoisomer of PMA, also shows two-step titration behavior albeit less pronounced than that of PMA. In addition, PFA shows a clear maximum in the intrinsic viscosity at 50% dissociation and it has been suggested that PMA behaves likewise.[8]

It has been recognized long ago that interactions between neighboring pairs of charged sites are responsible for the apparent two-step titration behavior.[7] From such an analysis it follows immediately that, to avoid the formation of energetically unfavorable pairs, the 50% protonation state of linear polymers is stabilized, sometimes over 1 or more pH units. In the case of poly(propylenimine) dendrimers, for which each protonation site has three nearest neighbors, the same mechanism leads to an intermediate plateau at $^2/_3$ degree of protonation.[9,10] For weak interactions, a mean field or Bragg−Williams approximation[6] of the Ising model suffices to obtain an adequate description of the titration behavior, as has been demonstrated for PAA,[7] but it requires full statistical mechanical evaluation to obtain quantitative agreement in the case of stronger interaction, such as in the case of poly(vinylamine).[11] A systematic treatment of the application of Ising models to the iteration behavior of homologous series of oligomers and the associated polymers[12] may require the inclusion of higher order interactions, such as triplet interactions in the case of poly(ethylene imine).[13]

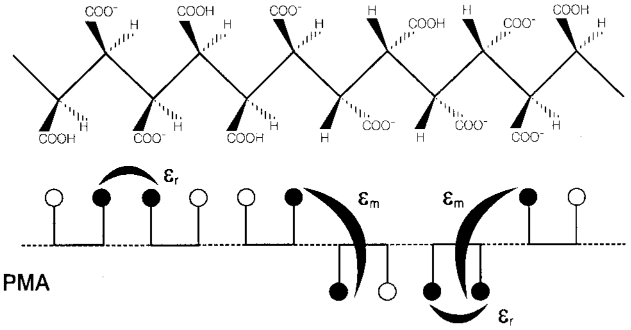

Figure 1. Effect of the stereochemical configuration on the electrostatic interactions inside a partially charged PMA chain. In the projection of the chain, the solid lines in the backbone refer to the bond in maleic acid monomer and it is therefore always racemic. The broken lines refer to the bonds formed between maleic acid monomers during synthesis and they can therefore be racemic or mesomeric. The black and white dots refer to charged (COO$^-$) and uncharged (COOH) carboxylates, respectively.

To explain the difference between PMA and PFA, one has to take into account their difference in stereochemistry.[14] There are two types of bonds in the polymer chain and their occurrence depends on the configuration of the monomers and on their propagation during polymerization. For PMA (see Figure 1), the odd bond originating from the monomer is necessarily racemic and the even one can be either racemic, with probability P_r, or mesomeric. This probability was determined by

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* Corresponding author.

† Department of Chemistry, Clarkson University, Potsdam, New York 13699-5814.

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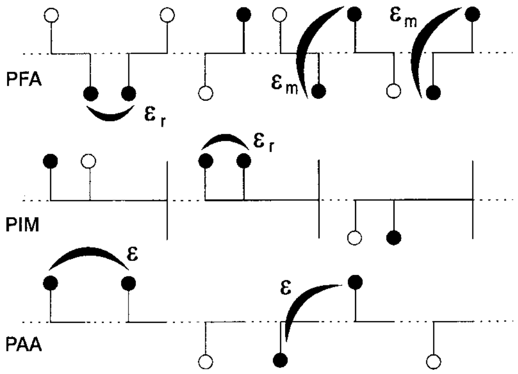

Figure 2. Projections of partially charged PFA, PIM, and PAA with the electrostatic interactions that occur inside these molecules. The projections are identical to that shown in Figure 1. In the projection of the chain the solid lines in the backbone refer to the monomer units and are in PFA always mesomeric. The broken lines refer to the bonds formed between monomer units and can be racemic or mesomeric in PFA. The black and white dots refer to charged and uncharged carboxylates, respectively.

^{13}C NMR spectroscopy.[15] In PFA (see Figure 2), every odd bond originating from the monomer is mesomeric and the even bond is mesomeric with a probability of ±0.5 determined by Wang et al.[16] The two types of bonds imply different distances between nearest neighbor sites, and hence there is a difference in interaction strength. Therefore, a difference in abundance of these bond types will have consequences for the titration behavior. Kawaguchi et al.[14] have tried to take this difference explicitly into account in their Ising model treatment of the titration behavior of PMA and PFA. However, the regularity introduced by calculating the titration behavior for chains with the typical configuration probably led to the unsatisfactory result they obtained. Here, this analysis is repeated with the important modification of accounting explicitly for the randomness in the distribution of racemic and mesomeric bonds in the chains.

Conformational changes in polymers can also lead to deviant titration behavior such as is the case with poly(L-glutamic acid), which undergoes a helix−coil transition upon charging,[17] or with poly(methacrylate).[18,19] Usually, conformational transitions just influence the intrinsic viscosity strongly and the effect on the titration behavior is limited.

In the following section the appropriate Ising model is outlined that accounts for the random distribution of racemic and mesomeric bonds and that is used to fit the experimental titration data. Subsequently, the results obtained with potentiometric titration and viscometry of PMA in the presence of various salts are reported. The model is shown to be successful in describing the experimental titration data and the obtained values are discussed in conjunction with those obtained from the experimental data of Kitano et al. on PMA, PFA, PAA, and poly(maleic acid-*co*-isobutene) (PIM).[8,20] The interactions across the mesomeric bonds are found to be equivalent, but the interaction strengths across the racemic bonds differ. It is hypothesized that, in the case of PMA, local charge stabilization over longer stretches of racemic bonds, due to proton sharing between adjacent carboxylic groups, effectively reduces the interaction strength.

From the intrinsic viscosity versus degree of dissociation for PMA it was verified that, just like for PFA,[8] a maximum is found at 50% dissociation. Since this cannot be attributed to a conformational transition, it is hypothesized that attractive intermolecular interactions play a role here and that ultimately precipitation occurs. Nevertheless, the measured titration curves did not show a significant dependence on polymer concentration.

Theoretical Section

In this section the appropriate Ising model for poly(carboxylic acid) chain molecules is outlined and a recursion method is derived to fit the model to experimental data. The result is the average degree of dissociation of a single linear chain of N ionizable sites as a function of pH that can be calculated provided the free energy of formation of all protonation states with respect to the fully protonated chain is known.[12] To model this free energy, we define for each site the state variable ζ_i that has the value of 0 when the site is protonated and 1 if it is deprotonated and hence charged.[21] All possible protonation states are described by the set $\{\zeta_1\zeta_2...\zeta_N\}$. Because long-range interactions are expected to be screened by the excess salt,[22] the expansion of the formation free energy

$$F(\zeta_1\zeta_2...\zeta_N) = \sum_{k=1}^{N}\mu_k\zeta_k + \sum_{k=1}^{N}E_{k,k+1}\zeta_k\zeta_{k+1} + ... \qquad (1)$$

is expected to converge rapidly.[12] In this expression μ_k is the chemical potential of site k when charged while the others are protonated. When all sites are assumed to be equivalent with site affinity pK_0, then $\mu_k = (kT \ln 10)\text{p}K_0$, where kT represents thermal energy. Here, we shall only take into account nearest-neighbor pair interactions and the expansion in eq 1 is truncated after the second term. Justification for neglecting the longer ranged electrostatic interaction is found in the magnitude of the nearest-neighbor interaction, which appears not to be of electrostatic nature only. In the particular case of the poly(carboxylic acid)s described in this work, there are two possible types of bonds between the protonation sites, racemic and mesomeric (see Figure 1), and these give rise to two different nearest-neighbor interaction energies, i.e.

$$E_{k,k+1} = \delta_k E_r + (1 - \delta_k)E_m \qquad (2)$$

where the variable δ_k equals 1 when the sites k and $k + 1$ are connected by a racemic bond and it equals 0 when the sites are connected by a mesomeric bond. In what follows, rather than the pair energies themselves, the associated shifts on the pH scale are used, i.e., $\epsilon_r = E_r/(kT \ln 10)$ and $\epsilon_m = E_m/(kT \ln 10)$.

The degree of dissociation

$$\alpha = \frac{1}{N}\sum_{k=1}^{N}\langle\zeta_k\rangle \qquad (3)$$

is calculated from the grand canonical partition function

$$\Xi_N = \sum_{\zeta_1\zeta_2...\zeta_N} \exp[-\beta\mu\sum_{k=1}^{N}\zeta_k - \beta F(\zeta_1\zeta_2...\zeta_N)] \qquad (4)$$

with μ the proton chemical potential, such that pH = $\mu/(kT \ln 10)$ and $\beta = 1/kT$, as

$$\alpha = -\frac{1}{N}\frac{\partial \ln \Xi_N}{\partial \mu} \qquad (5)$$

For a fit to the experimental data, eq 5 has to be evaluated very many times and therefore it is essential to have a computationally efficient procedure. Evaluating Ξ_N by direct summation is a problem of the order 2^N, which becomes prohibitive already at quite modest values for N. To evaluate the grand partition function Ξ_N and its derivative, we use a transfer matrix technique.[23,24] This technique utilizes the fact that the site variables ζ_i are two-valued and that one may write

$$\Xi_n = \tilde{\Xi}_n(0) - \tilde{\Xi}_n(1) \qquad (6)$$

where $\tilde{\Xi}_n(\zeta)$ is the partition function for n sites with the nth site in state ζ.

Now adding a new site results in

$$\tilde{\Xi}_{n+1}(0) = \tilde{\Xi}_n(0) + \tilde{\Xi}_n(1) = \Xi_n$$

$$\tilde{\Xi}_{n+1}(1) = z\tilde{\Xi}_n(0) + zu_{n,n+1}\tilde{\Xi}_n(1) \qquad (7)$$

where $u_{\mathrm{kl}} = \exp(-\beta E_{\mathrm{kl}})$ and $\log z = \mathrm{pH} - \mathrm{p}K_0$. The average number of charged sites, ν_n, can be expressed in terms of two auxiliary variables that obey the following recursion relations

$$a_{n+1} \equiv \frac{\tilde{\Xi}_{n+1}(1)}{\tilde{\Xi}_{n+1}(0)} = z\frac{1 + a_n u_{n,n+1}}{1 + a_n} \qquad a_1 = z$$

$$b_{n+1} = 1 + \frac{a_n b_n (u_{n,n+1} - 1)}{(1 + a_n)(1 + a_n u_{n,n+1})} \qquad b_1 = 1 \qquad (8)$$

as

$$\nu_{n+1} = \nu_n + \frac{a_{n+1} b_{n+1}}{1 + a_{n+1}} \qquad \nu_1 = \frac{z}{1 + z} \qquad (9)$$

From these variables, the degree of dissociation is calculated to be

$$\alpha_n = \frac{\nu_n}{n} \qquad (10)$$

where the subscript n labels the sites. The iteration process is readily programmed on a computer and results in a very efficient algorithm. The bonds in the poly(carboxylic acid) chains are either racemic or mesomeric, and this is taken into account by drawing at random interaction parameters from the appropriate probability distribution.

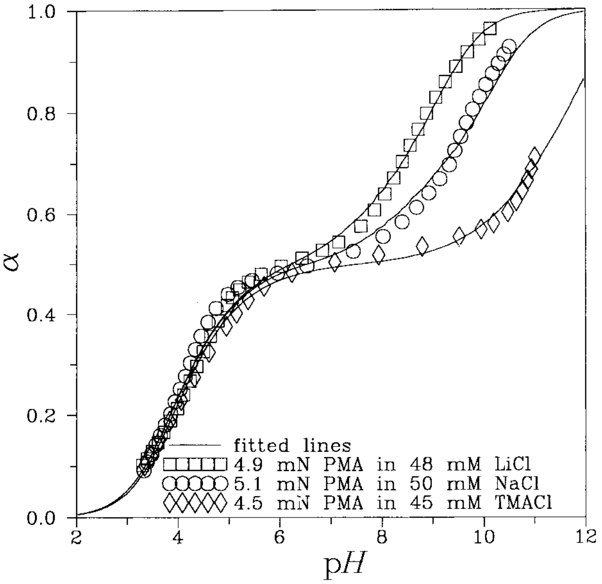

Figure 3. Potentiometric titration curves of poly(maleic acid) (PMA) plotted as the degree of dissociation α versus pH for LiCl, NaCl, and tetramethylammonium chloride (TMACl). The ionic strength is ca. 50 mM, and the concentration of ionizable groups, ca. 5 mN. Solid lines are best fits with the random Ising model with parameters given in Table 1.

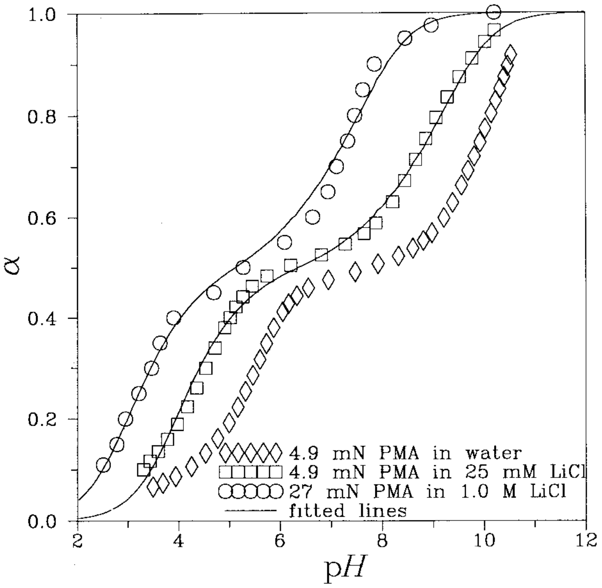

Figure 4. Potentiometric titration curves of poly(maleic acid) (PMA) plotted as the degree of dissociation α versus pH for LiCl at various ionic strengths and concentrations of ionizable groups. Solid lines are best fits with the random Ising model with parameters given in Table 1.

Methods

Synthesis of PMA ($M_w = 17600 \pm 300$ g) by γ irradiation of maleic anhydride was based on the method of Lang et al.[25] and is described in a previous paper.[15]

The potentiometric titrations of PMA were performed with a Radiometer Vit 90 video titrator equipped with a Radiometer GK240IC combined glass/reference electrode, calibrated with buffer solutions of pH 4 and 7 (Titrisol, Merck). PMA samples of 20 mL were prepared in a concentration range from no added salt up to 1 M of added salt. Salts used were purified LiCl (p.a.), NaCl (p.a.), and tetramethylammonium chloride (TMACl, p.a.), the first two obtained from Merck and the last from Fluka. For each of the 200 titration steps, 5 μL of 0.1 M LiOH or 0.1 M NaOH was added at 22.0 ± 0.1 °C under an argon atmosphere to the PMA in LiCl or NaCl solutions, respectively. As equilibrium is found to be established rather slowly, after 5 min for each step no change in pH was observed, the duration of the titration was chosen such that the equilibration time for each step was 7 min. Back-titration with 0.1 M HCl at about 5 times excess salt or higher showed no difference with the forward titration. Titrations in TMACl were similar albeit that the temperature was thermostated at 24.5 °C.

The PMA concentration of the titrated samples was determined to be 2 times the value of the first clear inflection point, see Figures 3 and 4. This concentration differed ±0.5% from the calculated concentration based on a water content of 3.5% in dried PMA. This water content was determined by infrared spectroscopy. In addition, at high LiCl concentrations, the plateau at full neutralization of PMA is also observable and is exactly located at 2 times the first inflection point; see Figure 4.

Viscosity measurements on PMA at various degrees of neutralization were performed with a capillary viscometer (KPG-Ubbelohde-Viskosimeter, Kapillaere no. 0a). Measurements at four different PMA concentrations without added salt were done at 24.5 °C under a nitrogen atmosphere. Viscosity measurements in 0.01 and 0.1 M NaCl were done similarly but at 25 °C.

Self-diffusion coefficients of PMA in the solutions without added salt, as used for the viscometry measurements, were determined with pulsed field gradient (PFG) NMR. A Bruker AM 200 (4.7 T) wide bore magnet equipped with a home-built gas thermostat using pressurized air to a stability of 0.1 °C was used. All measurements were performed at 25 °C. The pulsed magnetic field gradient was generated by an actively shielded gradient coil capable of generating an amplitude up to 7.2 T m^{-1} at a maximum current of 20 A. The axis of the magnetic field gradient was parallel to the main magnetic field. The gradient coil was designed and manufactured at Massey University, Palmerston North, New Zealand, by Prof. P. T. Callaghan and co-workers. Rectangular gradient pulses, with carefully controlled rise and fall times (about 1 ms), were delivered by a Techron 7570 amplifier which was coupled to the spectrometer. The calibration of the gradient was performed by measuring the self-diffusion of pure water (2.30×10^{-9} m^2 s^{-1}).[26] We used 5 mm (o.d.) NMR tubes, in which the filling height was always between 5 and 6 mm to ensure good gradient homogeneity over the sample volume. Because of the large difference between the transversal and longitudinal relaxation rates of the ^1H nuclei of PMA, the stimulated echo sequence $^1/_2\pi-\mathrm{gp}-^1/_2\pi-^1/_2\pi-\mathrm{gp}$ was used.[27] The duration of the gradient pulses (gp) was 2.5 ms. After the gradient pulses a 1.0 ms delay was used before either applying the second RF pulse or acquiring the signal. The time duration between the two gradient pulses reported here was 31 ms. The amplitude of the gradient pulses ran from 2.18 to 11.10 A in 64 steps. The relaxation delay was taken as 4 s.

The drawn lines in Figures 3 and 4, and the experimental data of Kitano et al.[8,20] in Figure 9 were obtained by fitting the model predictions, eqs 8–10, to the experimental data. The algorithm was programmed in FORTRAN and ran on a personal computer. Randomness was introduced by drawing pseudorandom numbers (NAG library routine G05CAF) from a homogeneous distribution using the propagation rate, P_r or P_m, as decision threshold level. The degree of dissociation appeared to converge after evaluating for approximately 8000 consecutive sites on the chain. The racemic propagation rate of PMA, P_r, used in the modeling was determined at 0.655 by ^{13}C NMR.[15] The quality of the fit is hardly influenced by a small change in P_r. In PFA the mesomeric propagation rate, P_m, was chosen around 0.5 in the fitting procedure. Wang et al.[16] determined P_m for esterified PFA at ca. 50% and report slight dependence on the kind of esterification used. The best fit of the PFA data was obtained at a P_m of 0.45.

Results

The potentiometric titrations of 5 mN PMA in different salt solutions over a salt concentration range from no added salt up to 1 M of added salt exhibit an inflection point at half neutralization; see Figure 3. The plateau at full neutralization becomes clear at high LiCl and NaCl concentrations. The shape of the titration curves passes through two different stages over the experimental salt concentration range; see Figure 4. The first stage is from zero to about 4 times excess salt, where long-range electrostatic interactions are present and decrease with increasing salt concentration. In the range from 5 times or more excess salt the long-range electrostatic interactions are screened totally and the short-range electrostatic interactions inside the polymer chain appear to be still present. Therefore, the model was fit to the PMA titration curves obtained in this regime. Figure 3 shows the results for 5 mN PMA with three types of salts at 50 mM, and Figure 4 shows the results for PMA at various LiCl concentrations. As expected, at zero LiCl concentration the model cannot be applied. From 5 up to 40 times excess LiCl the model satisfactorily describes the experimental data. The parameters are summarized in Table 1. We have also used a variation of the model where the intrinsic p*K* values for different sites could vary independently. The obtained values for the various intrinsic p*K* values did not differ significantly and were henceforth left equal.

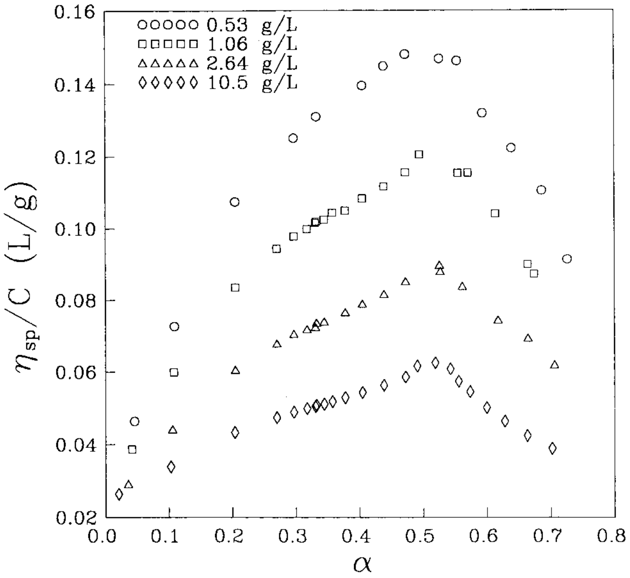

Figure 5. Effect of charging with NaOH on the reduced specific viscosity of PMA at different polymer concentrations and zero salt.

Table 1. Parameters Obtained by Fitting the Random Ising Model to the Experimental Potentiometric Titration Curves (Figures 3 and 4)

[polyacid], mN	polyacid	[salt], mM	salt	pK_0	ϵ_r	ϵ_m	P_r
4.9	PMA	25	LiCl	4.3	2.4	1.3	0.655
4.9	PMA	48	LiCl	4.2	2.35	1.25	0.655
4.9	PMA	98	LiCl	3.95	2.25	1.1	0.655
27	PMA	1000	LiCl	3.35	2.05	1.05	0.655
5.1	PMA	50	NaCl	4.2	2.85	1.35	0.655
4.5	PMA	45	TMACl	4.25	3.65	2.6	0.655
4.5	PMA	90	TMACl	4.2	3.75	2.5	0.655
4.5	PMA	445	TMACl	3.95	3.9	2.5	0.655
4.5	PAA	45	LiCl	4.87	0.75	0	1

The influence of charging on the reduced viscosity at zero salt concentration for four PMA concentrations is shown in Figure 5. From these measurements it is expected that the intrinsic viscosity at zero salt concentration has a maximum at $\alpha = 0.5$. At the lowest of the four PMA concentrations, the specific viscosity η_{sp} was determined for 0.01 M NaCl (Figure 6). Also, for 0.1 M NaCl the intrinsic viscosity at several degrees of dissociation has been determined by extrapolation of the specific viscosity data, shown in Figure 7, over a concentration range from 0.5 to 3.5 g L^{-1} of PMA. All these figures show the general tendency: an increase in η_{sp}/C or $[\eta]$ up to about $\alpha = 0.5$ and a decrease for higher α. The relative decreases of η_{sp}/C from $\alpha = 0.5$ to 0.67 at ± 0.5 g L^{-1} of PMA at zero salt and 0.01 and 0.1 M NaCl are almost equal, i.e., 25, 28, and 29%, respectively.

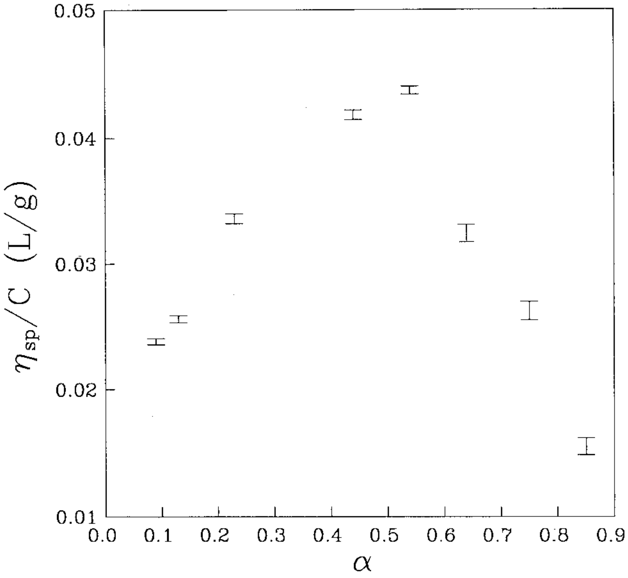

Figure 6. Effect of charging with NaOH on the reduced specific viscosity of PMA at 10 mM NaCl. The concentration of ionizable groups was 8.8 mN.

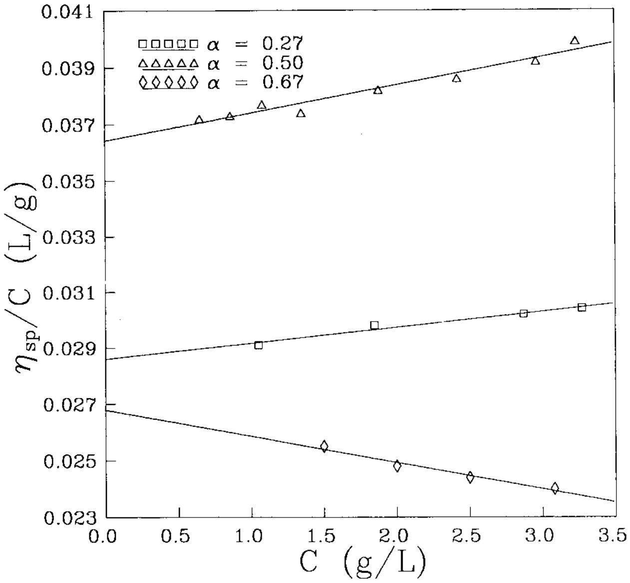

Figure 7. Reduced specific viscosity dependence on the PMA concentration at different degrees of dissociation at 100 mM NaCl.

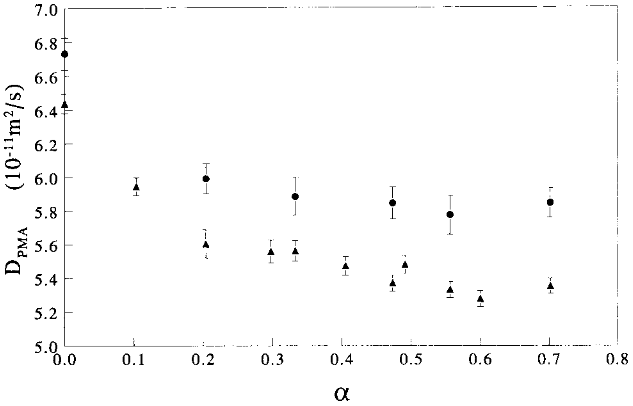

Figure 8. PMA self-diffusion coefficient as a function of the degree of neutralization at PMA concentrations: 10.5 g/L (▲) and 2.64 g/L (●).

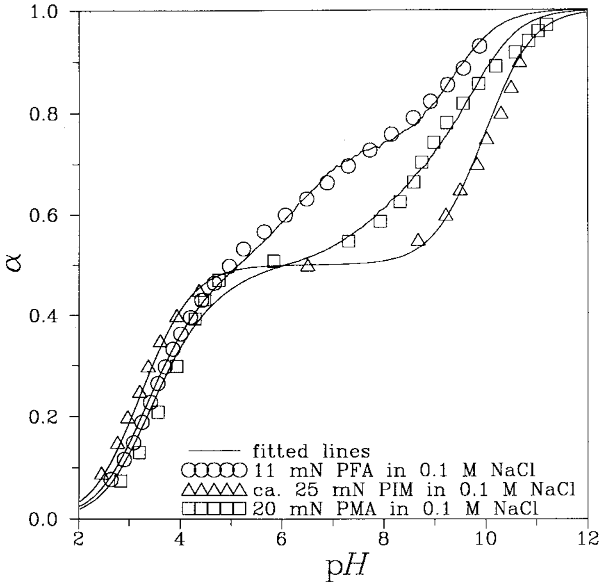

Figure 9. Experimental titration data of PMA, PIM, and PFA in salt solutions measured by Kitano et al.[8,20] Modeling parameters are given in Table 2.

The behavior of the PMA self-diffusion coefficient in salt free solution at the two highest concentrations as used for viscometry is shown as a function of the degree of neutralization in Figure 8. At low α a decrease in the self-diffusion coefficient upon neutralization is observed. A further increase of α does not cause any significant change in the self-diffusion of PMA.

Discussion

From the model parameters in Table 1 it is seen that the intrinsic charge affinity pK_0 of PMA slightly decreases with increasing salt concentration but largely remains unaffected by the different salts. However, the interaction parameters ϵ_r and ϵ_m for LiCl, NaCl, and TMACl are strongly dependent on salt type. One would expect that with decreasing bare counterion size the charge interactions decrease because the smaller ions may be able to situate themselves between the charged sites of the polyacid by which a more effective screening is achieved. Also, an increasing counterion concentration should therefore decrease the charge interactions. This is indeed found for the interaction parameters for Li^+. However, increasing the TMACl concentration gives rise to an increase in ϵ_r. This demonstrates that the interaction parameters used here are not entirely of electrostatic nature but that other modes of interaction are involved as well. These modes mainly have to be short ranged and might be quite large; otherwise, the assumption made that the next nearest-neighbor interactions are negligible will not be valid. Indeed, the salt concentrations used in most of the experiments reported here are too low to suppress the electrostatic next-nearest-neighbor interactions completely. The exact nature of these other modes of short-range interactions will be further discussed in the following.

Another assumption made in the model is that no conformational changes occur in the polyacid with a change of its charge density. When, for instance, the rotation around the $-C-C-$ bond would be possible, the probabilities of the two kinds of nearest-neighbor interaction may be changed with the degree of neutralization. However, this rotation does not seem to occur because this would lead to a great similarity in the

Table 2. Parameters Obtained by Fitting the Random Ising Model to the Potentiometric Titration Curves of Kitano et al.[8,20] (Figure 9)

[polyacid], mN	polyacid	[salt], mM	salt	pK_0	ϵ_r	ϵ_m	P_r
20	PMA	100	NaCl	3.7	2.9	1.35	0.655
11	PFA	100	NaCl	3.6	4.15	1.35	0.54
25(≈)	PIM	100	NaCl	3.45	5.8	0.5	0
10	PAA	100	NaCl	4.5	0.76	0.76	noinfluence

titration curves of PMA and PFA, and this is not the case. Also, the back-titration of neutralized PMA with HCl might be affected. However, no hysteresis effect in the titration curves is observed.

The model is also expected to be applicable to PFA, which is only stereochemically different from PMA. Therefore, we also fit the model to the experimental titration data on PFA as measured by Kitano et al.[8,20] and we included their data on the similar molecules PMA, PAA, and PIM. The resulting model parameters are summarized in Table 2. The salt concentration for PMA is 2 times higher than the one reported here (see Table 1), and this explains the lower pK_0 value. The experimental data on PAA show a similar dependence, even though the counterion type differs. The interaction parameters ϵ_r and ϵ_m, however, do not differ when Na^+ is considered as the counterion. It is reassuring that measurements performed on the same system by different groups yield the same model results.

An interesting feature, observed from Table 2, is the difference between the values for the racemic bond parameters ϵ_r for PMA and PFA. One expects these values to be equal, as is the case for the values for the mesomeric bond interaction parameter ϵ_m. To explain this difference, one should consider other modes of stabilization of charges on the polyelectrolyte chains. One such mode involves adjacent charged and uncharged carboxylic groups connected by racemic bonds that have the possibility of sharing a proton, in which case, indeed, local stabilization of the charge[28,29] takes place. For mesomeric bonds this is sterically impossible. PMA consists mainly of racemic bond sequences and therefore is expected to stabilize charges better than isolated carboxyl pairs. This may result in a lower interaction parameter ϵ_r for PMA than for PFA. Around $\alpha = 0.5$ the number of stabilized charges in PMA will be optimal and in this part of the fitted curves the ϵ_r will be overestimated, which may cause the deviation from the experimental data, as demonstrated in Figure 3.

The value of the racemic bond interaction parameter ϵ_r for PIM is even larger than that for PFA. The aliphatic isobutylene parts may cause an inductive electron-forwarding effect and therefore deprotonation will be harder to achieve. Also, because of this electronic effect, the carboxyl group may have a higher effective charge, which results in a stronger interaction strength. Increasing the size of the aliphatic group, which increases the electron-forwarding effect, in copolymers of maleic acid increases the interaction strength.[30] Also, a modification of the water structure[31] around the polyacid may give some stabilization of the charges. Because TMACl is an apolar counterion, this might be the reason for the increasing value of ϵ_r for PMA with increasing TMACl concentration. Between the proton-sharing stabilized pairs on PIM, there still seems to be a small electrostatic interaction that almost equals the interaction strength between neighboring charges on a PAA chain. Since the charge-stabilized pairs of PIM are further apart than the neighboring charges on PAA, one would not expect this "long-range" interaction on PIM. More insight in the magnitude of the interaction parameters ϵ_r and ϵ_m of the polyacid can be obtained by considering the pK values of the associated monomers.[32] Fumaric acid in 0.1 M NaCl has a pK_1 of 2.85 and pK_2 = 4.10. Succinic acid differs from fumaric acid through the trans double bond, which is replaced by a single bond, and its pK_1 and pK_2 are 4.00 and 5.24, respectively. From these differences between the pK_1 and pK_2 values for both acids an estimation of the interaction parameter can be calculated to be 0.65. The ϵ_m in PMA and PFA in 0.1 M NaCl as shown in Table 2 is 2 times this value, and this indicates that the freedom of the monomers in the chain is far less than that of the monomers. For maleic acid the pK_1 = 1.70 and the pK_2 = 5.84 results in an interaction parameter of 3.54, which lies exactly between the ϵ_r values 2.9 and 4.15 of PMA and PFA, respectively. In maleic acid, which has a double cis bond, no neighboring carboxyl group is present that can stabilize a charge like across a racemic bond of PMA and will therefore have a larger interaction. In PFA the value for ϵ_r is higher than the interaction parameter of maleic acid. The PFA chain seems to force carboxyl pairs in such a way that they are closer together than in maleic acid. The smaller value for ϵ_r in PMA in relation to the one for maleic acid may probably also be due to the freedom of motion inside the chain that is absent in the monomers because of the double bond.

The viscometric behavior of PMA as a function of degree of charging, α, is also found to be independent of the type of salt. The absolute values of the specific viscosity η_{sp}, however, do depend on salt concentration. The increase of η_{sp} up to $\alpha \approx 0.5$ is probably due to the expansion of the polymer coil caused by the increasing repulsion between the segments upon charging. At $\alpha \approx 0.5$ the specific viscosity reaches a plateau such as also has been found for PFA by Kitano et al.[8] and by Oosawa[33] for PAA at full dissociation. Additional charging does not induce a further increase of the specific viscosity, as is also evidenced by the self-diffusion coefficient as measured with PFG-NMR (Figure 8), and it may be deduced that the decrease in viscosity beyond 50% charging is an intermolecular effect. Further evidence for attractive interactions is provided by dynamic light-scattering experiments, which demonstrate aggregation upon further charging. Attractive interactions between highly charged polymers have also been reported by, e.g., Ise,[34] Muthukumar,[35] Nicolai,[36,37] and recently, Tanahatoe et al. for their sodium−poly(styrenesulfonate) system.[38]

Conclusion

The picture that emerges from the above analysis of the titration behavior of PMA is that the stabilization at 50% charging over more than 2 pH units, as evidenced by the titration curves in Figures 3 and 4, is largely due to the interaction between neighboring protonation sites, albeit that the interaction strength depends on the type of bond, racemic and mesomeric, between the carboxylic groups, which leads to two independent interaction parameters in the model. A comparison with the polymer PFA, only differing in stereochemistry, leads to identical parameters for the interaction across the mesomeric bonds. The interaction parameters for the interaction across the racemic bonds differ, probably because of the possibility of local charge stabilization due to proton sharing between adjacent carboxylic groups. The latter effect cannot be quantified by the present model.

The viscometric and PFG-NMR data provide evidence for increasing attractive intermolecular interactions that lead to aggregation upon charging. Nevertheless, the potentiometric titration curves are found to be experimentally independent of polymer concentration in the investigated range. It may therefore be concluded that during the charging of PMA no conformational transition takes place and that hence the interaction parameters are largely enthalpic in character.

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