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Behavior of Nonalternating Maleic Acid Copolymers in Aqueous Solution[†]

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A nonalternating 1:3 maleic acid−methyl methacrylate copolymer was synthesized and characterized, and its polyelectrolyte behavior was studied by potentiometric and conductometric titrations. Two intrinsic dissociation constants were found equal to 3.5 and 7.6, and only a slight influence of the nature of the counterions and of the presence of added salt (0.1 M) was observed. The transport coefficients, determined from conductometry, for mono- and divalent cations were in relatively good agreement with the values calculated from Manning theory, especially at low polymer concentrations. A conformational change around $\alpha_N \sim 0.25$ was confirmed by means of viscometric and fluorescence measurements.

Introduction

Maleic anhydride copolymers are largely used in biomedical applications[1] but also as antiscale agents, phosphate substitutes in detergent compositions, dispersants, flocculants, and soil conditioners.[2] They hydrolyze in water, and carboxylic polyelectrolytes are obtained, whose behavior in aqueous solutions is governed mainly by electrostatic interactions between polyions and counterions. This behavior is also influenced by the structural characteristics of maleic acid copolymers, such as the presence of two neighboring carboxylic groups in the maleic units, the hydrophilic/hydrophobic character of the comonomer, the polymer configuration. All these effects contribute to some characteristic features of maleic acid polyelectrolytes: the two-step dissociation and binding of counterions, conformational transitions induced by pH variation. Such data were reported in several papers regarding maleic acid copolymers with alkenes,[3] alkyl vinyl ethers,[4] styrene,[5,6] indene,[7] and *p*-styrenesulfonic acid.[8] Recently, the dissociation behavior of maleic acid−alkene copolymers was investigated and more than two pK_a values were determined ascribed to the existence of erythro and threo configurations.[9]

Maleic acid copolymers are obtained in most cases by hydrolysis of maleic anhydride copolymers that are generally known as 1:1 alternating copolymers.[2,10] Consequently, in maleic acid copolymers the distribution of the charges along the chain is more uniform than that for other copolymers. However, it would be interesting to investigate if the polyelectrolyte behavior is modified by the irregular distribution of the comonomers. A suitable candidate for this purpose is maleic acid−methyl methacrylate copolymer. Such a copolymer could be obtained by hydrolysis of the maleic anhydride−methyl methacrylate copolymer, which was found to have a chemical composition different from 1:1 moles.[11,12] Maleic acid−methyl methacrylate copolymers have proved efficient as growth crystal modifiers or corrosion inhibitors,[13] and these effects could be correlated with their polyelectrolyte behavior.

In this paper a nonalternating maleic acid−methyl methacrylate copolymer was synthesized, and its polyelectrolyte behavior was examined by means of potentiometry and conductometry. Viscometric and fluorescence measurements were also performed to identify the conformational transitions that could be expected considering the hydrophobic character of methyl methacrylate unit sequences.

Experimental Section

Polymer Synthesis. The copolymer (**I**) of maleic anhydride (MAn) with methyl methacrylate (MMA) was synthesized by

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radical polymerization in cyclohexanone at 80 °C to high conversion.[14] The monomers, the catalyst, and the solvent were purified before use according to the known methods. The copolymer was recovered by precipitation in diethyl ether, repeatedly washed with diethyl ether to remove residual monomers and dried at 40 °C under reduced pressure for 48 h. MAn–MMA copolymer was roughly characterized by conductometric titration with aqueous 0.1 N NaOH in 1:1 (vol) acetone–water mixture[15] and viscometric measurements in acetone at 30 °C.[16] The copolymer (**II**) of sodium maleate (NaM) with MMA was obtained from **I** by hydrolysis with diluted aqueous NaOH at 40 °C for 24 h. It can be noticed that although for other maleic anhydride copolymers the hydrolysis with water was possible at room temperature or by heating, for the copolymer with MMA such treatments were unsuccessful. The solution was desalted and the oligomers were removed by diafiltration through an ultramembrane Amicon PM10 in a 8200 Amicon cell equipped with an Amicon RS4 tank filled with pure water (conductivity lower than 3 μS). The diafiltration was stopped when the filtrate conductivity was lower than 10 μS and the copolymer **II** was recovered by freeze-drying. It was characterized by ^{1}H NMR spectra recorded in D_2O with a Bruker AM 300 MHz spectrometer and by steric exclusion chromatography (SEC). The SEC analyses were performed using a Waters 150C chromatograph equipped with an homemade viscometer, a multiangle laser light scattering (MALLS) DSP-F from Wyatt with two Shodex columns: SB 804 HQ and SB 805 HQ.[17] The eluent was a 0.1 M $NaNO_3$ solution, the flow rate was 1.0 cm[3] min^{-1}, and the feed was 0.4 mL of 1.0 g/L copolymer solution in aqueous 0.1 M $NaNO_3$. For weight average molecular weight (M_w) calculations from light scattering the value dn/dc = 0.141 mL/g was used, evaluated from refractometric measurements in 0.1 M $NaNO_3$ with a Brice Phoenix differential refractometer at λ = 546 nm.

From **II** the copolymer (**III**) of maleic acid (MAc) with MMA was delivered by passing a diluted solution of **II** through an ion exchange column filled with a sulfonic Dowex 50WX 820, 50 mesh resin. The aqueous solution of **III** was used as such for conductometric or potentiometric titrations. The chemical structures of **I**, **II**, and **III** copolymers are presented in Scheme 1.

Methods. pH measurements were performed with a Tacussel Minisis apparatus and a Tacussel combined glass electrode XC 100. LiOH or KOH aqueous 0.1 or 0.05 N solutions were used as titrating agents, and the titrations were performed at polymer concentrations $C_p = 5.5 \times 10^{-3}$ and 2.75×10^{-3} equiv/L, without added salt or with 0.1 M NaCl. In the case of titration with $Ca(OH)_2$, polymer concentration was 1.1×10^{-3} or 0.55×10^{-3} equiv/L and titrating base normality was 0.016 or 0.008, respectively, because of the low solubility of $Ca(OH)_2$ and Ca salt of the polymer. Generally, the polymer concentration calculated from titration attained 94–98% from theoretical value. We consider that, except the experimental precision, this difference can be due to some polymer adsorption onto ion-exchange resin during the delivering of acidic form **III**, because this difference was also observed for other maleic polyelectrolytes with well-established 1:1 compositions and some increases could be observed when M_w or C_p increased.[18]

The potentiometric data were used to determine pK_a values according to the usual relation:[19]

$$pK_a = pH + \log[(1 - \alpha_T)/\alpha_T] \qquad (1)$$

where K_a is the apparent dissociation constant, $\alpha_T = \alpha_H + \alpha_N$ means the fraction of ionized carboxylic groups, α_H is the degree of autodissociation, and α_N is the degree of neutralization. Calculations were made separately for each of the two carboxylic groups of maleic acid units.

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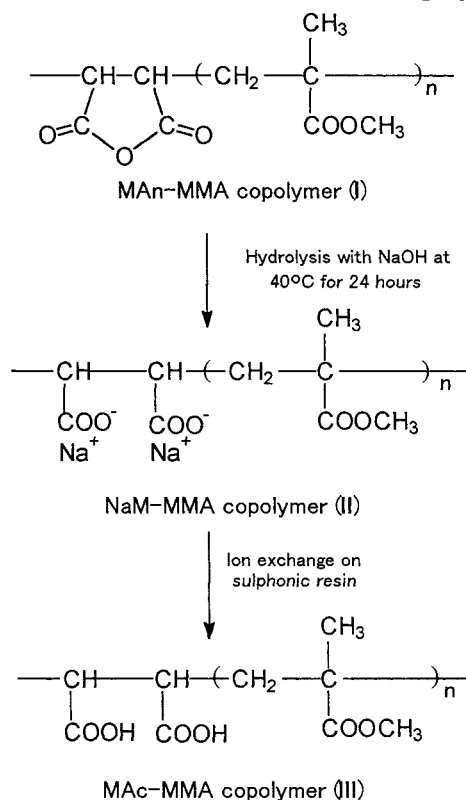
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Scheme 1. Chemical Structure of MAn–MMA (I), MAc–MMA (II), and NaM–MMA (III) Copolymers

The conductometric titrations were carried out using a Tacussel conductivity bridge type CD78 and a XE 130 cell, without added salt, at the same polymer concentrations and using the same titrating agents as above. All the titrations were performed at 25 ± 0.1 °C. The transport coefficients of monovalent (f^{M^+}) and divalent ($f^{M^{2+}}$) counterions and the equivalent conductivity of the polyion λ_p were calculated as usually[20] for $\alpha_N = 0.5$ and 1.0, assuming that f^{M^+} is independent of the monovalent counterion considered:

$$f^{M^+} = (\sigma_{K^+} - \sigma_{Li^+})/10^{-3}C_p(\lambda_{K^+} - \lambda_{Li^+}) \qquad (2)$$

and

$$\lambda_p = (\sigma_{Li^+} - 10^{-3}C_p f^{M^+}\lambda_{Li^+})/10^{-3}C_p f^{M^+} \qquad (3)$$

and

$$f^{M^{2+}} = \sigma_{Ca^{2+}}/10^{-3}C_p(\lambda_{Ca^{2+}} + \lambda_p) \qquad (4)$$

where σ_{K^+}, σ_{Li^+}, and $\sigma_{Ca^{2+}}$ are the conductivities at α_N 0.5 or 1.0 for neutralization with KOH, LiOH, or $Ca(OH)_2$, respectively, C_p is the polymer concentration, in equiv/L, and λ_{K^+}, λ_{Li^+}, $\lambda_{Ca^{2+}}$, and λ_p are the equivalent conductivities of K^{+}, Li^{+}, Ca^{2+}, and polyion, respectively.

The viscometric measurements were carried out using a capillary viscometer, Fica Viscomatic MS with a 0.5 mm capillary, at 25 ± 0.1 °C.

The fluorescence emission spectra of MAc–MMA aqueous solutions were recorded using a Perkin-Elmer LS-50B spectrofluorometer in the range 300–500 nm at an excitation wavelength of 335 nm. The solutions were added with 10^{-4} M ethanolic solution of pyrene as marker, so that the actual pyrene concentration was about 5×10^{-7} M, a value slightly lower than that of its solubility in water.

For comparison purpose, a poly(acrylic acid) sample LE 286 purchased as 24% aqueous solution from Coatex (Genay, France)

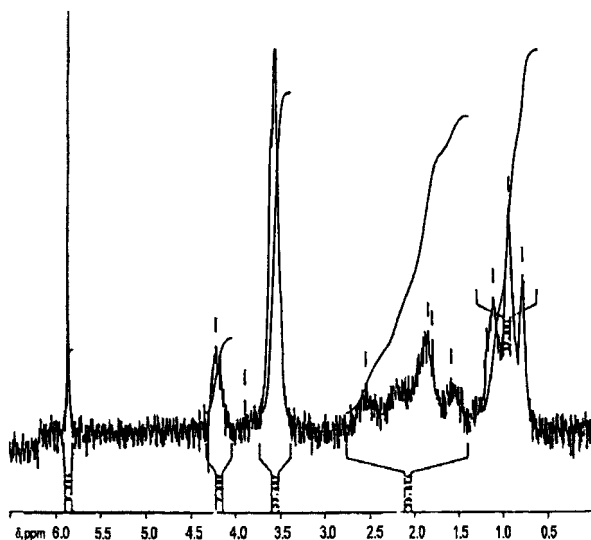(20) Milas, M.; Shi, X.; Rinaudo, M. *Biopolymers* **1990**, *30*, 451.

Figure 1. ^{1}H NMR spectrum of NaM−MMA copolymer in D_2O using sodium maleate (NaM) as internal standard. $C_p = 1.67 \times 10^{-3}$ g/mL; $C_{NaM} = 3.11 \times 10^{-6}$ mol/mL; $T = 60$ °C.

was used, having a weight average molecular weight of 306 000 determined by SEC. The sample was purified by diafiltration and ion exchange as described above.

Results and Discussion

Polymer Preparation and Characterization. According to the previous data, the copolymerization of MAn with MMA produces copolymers with a composition different from 1:1 moles. The composition of our polymer was determined from potentiometric and conductometric titrations of the corresponding free acid **III**. The value of the mass per equivalent for the sodium form was 230 ± 12 g/equiv. Correspondingly the average mass of repeating unit was 460 and the ratio between maleic and MMA units was 1:3 (moles). To confirm this composition ^{1}H NMR spectra were recorded for the sodium salt **II** in D_2O. The peaks in the spectrum can be assigned according to the literature data[11] as follows: the three peaks centered at 0.78, 0.93, and 1.10 ppm are due to the α-CH_3 from the MMA unit, the peak at 3.56 ppm is due to $COOCH_3$ protons of the MMA unit, and peaks at 1.58, 1.78, 1.83, and 2.54 ppm are due to methine and methylene protons from maleic and MMA moieties, respectively. The recording of spectra using sodium maleate as internal standard allowed calculation of the ratio between NaM and MMA units as 1:3.2 (moles). An example of the NMR spectrum is shown in Figure 1.

From potentiometric, conductometric, and NMR measurements it can be accepted that $n = 3$ in Scheme 1. It can be seen that the ratio between the integrals of peaks at 1.5−2.5 and 3.56 ppm is in agreement with this copolymer composition. The splitting in the peak due to the α-CH_3 can be considered as the effect of the sequence distribution and of the tacticity and cotacticity.[11] In the IR spectrum of the copolymer **I**, two bands at 1090 and 1150 cm^{-1} can be observed,[21] attributable to the sequences greater than three MMA units.[22] The presence of hydrophobic MMA sequences can be related to the difficulty to hydrolyze the maleic ring of this copolymer in mild conditions, while for other maleic anhydride copolymers with vinyl acetate, *N*-vinylpyrrolidone, or styrene the

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hydrolysis occurred easily.[18] The copolymer composition found by conductometric titration of anhydride form in acetone−water as usual was different, but in this case the titration curve is quite flat and aqueous potentiometric or conductometric titration of acidic form **III** is much more sensitive, as will be shown later. More, the acidic form can be carefully purified by diafiltration, while the anhydride form strongly retains unreacted maleic anhydride.

The weight average molecular weight M_w of the copolymer was determined by SEC analysis on sodium salt **II**. It was found $M_w = 82\ 700$ with a polydispersity index $M_w/M_n = 1.35$, which is an acceptable value for a polymer obtained by radical polymerization. The M_w value is different from the value 35 800 roughly estimated from viscometric measurements of **I** in acetone. The difference is explained by the separation of low molecular weight fractions during diafiltration and by the fact that K and a values from the literature can be not convenient for this copolymer composition.

Potentiometric Titration of the Copolymer. This paper tries to demonstrate the role of the distribution of the ionic sites along the polymeric backbone on the electrostatic properties. In this view, one investigates the behavior of the copolymer 1:3 in diluted solutions and we compare the experimental data with those obtained, as a reference, with a poly(acrylic acid) (PAA) sample. These two polymers have different average charge parameters, $\zeta = 2.8$ for PAA and 1.4 for MAc−MMA copolymer. Nevertheless, another important difference is that in the copolymer an alternance of one C−C and on average seven C−C bonds separate the carboxylic groups; on the opposite, in PAA the distribution is regular and two C−C bonds separate the ionic sites.

The most sensitive parameters reflecting the effective electrostatic effect are the activity of counterions and the apparent pK_a, which gives the intrinsic pK, pK_0, from extrapolation to zero charge of the polymer. These two aspects were investigated and discussed in the following.

A given quantity of the copolymer was transformed to the acidic form and neutralized as usual by different hydroxides. The use of different hydroxides having the same valence allows testing for the existence of an ionic selectivity. The use of counterions with different valence as well as the addition of external salt permit testing for the electrostatic effects; especially, the external salt screens the long-range electrostatic interactions, and it is well-known that polyelectrolytes behave like neutral polymers in a large excess of salt.

The curve relating the pH with the degree of neutralization for the copolymer presents an unusual aspect; during neutralization with monovalent hydroxides one transition is observed in pH (around pH = 7) corresponding to half the neutralization of the polymer. An example is given in Figure 2; on this graph the neutralization is performed with LiOH and KOH and the pH and the derivative are plotted as a function of the degree of neutralization α_N. In the limit of precision of the experiments, no selectivity between Li$^+$ and K$^+$ is observed.

When a divalent hydroxide is used, a two-step neutralization curve is obtained with transitions at $\alpha_N = 0.5$ and 1.0; the derivative clearly shows these two steps (Figure 3). The neutralizations were performed also at different polymer concentrations from 2.75×10^{-3} to 5.5×10^{-3} equiv/L, and no specific modification of the results was obtained. At the end, the neutralization was performed in the presence of an excess of external salt (0.1 M NaCl). The results are given in Figures 4 and 5. The presence of salt screens at least partly the electrostatic interactions
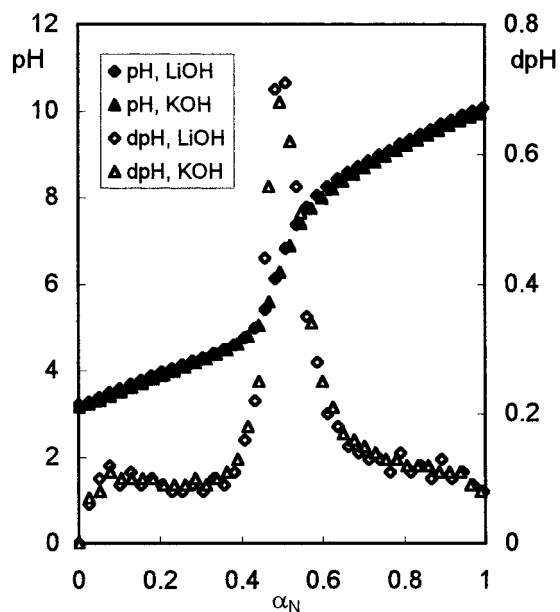
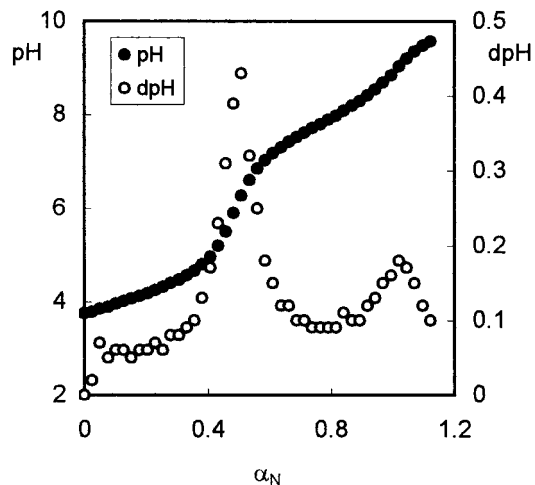**Figure 2.** Titration curves of MAc–MMA with LiOH and KOH without added salt. $C_p = 5.45 \times 10^{-3}$ equiv/L.

Figure 3. Titration curve of MAc–MMA with Ca(OH)$_2$ without added salt. $C_p = 1.10 \times 10^{-3}$ equiv/L.

between neighboring ionic groups. In this case even in the presence of a monovalent hydroxide a two-step neutralization is obtained. In addition the pH values along the curves are lower than those obtained without salt, which is indicative of the decrease of the pK_a.

These series of results allow plotting the apparent pK_a as a function of the degree of neutralization. Due to the difference between the acidities of the two carboxylic groups located on two successive carbons, their neutralization was considered separately. The results in the presence of monovalent and divalent counterions as a function of the degree of neutralization of each carboxyl, α_T, are given in Figures 6 and 7. For the first acidity, one takes into account the autodissociation of the polyelectrolyte determined from the pH measurements. In this case the pK_a varies only slightly (from 3.73 to 3.90 up to 4.1–4.3 depending on the polymer concentration); in these conditions, the maximum charge parameter for the complete neutralization of the first carboxylic group must be assumed as $\zeta = 0.7$. Nevertheless, this variation looks very low. Then in the absence of external salt p$K_a \sim 4$, it is also nearly the same value in the presence of monovalent and divalent counterions. This is also an unusual situation.
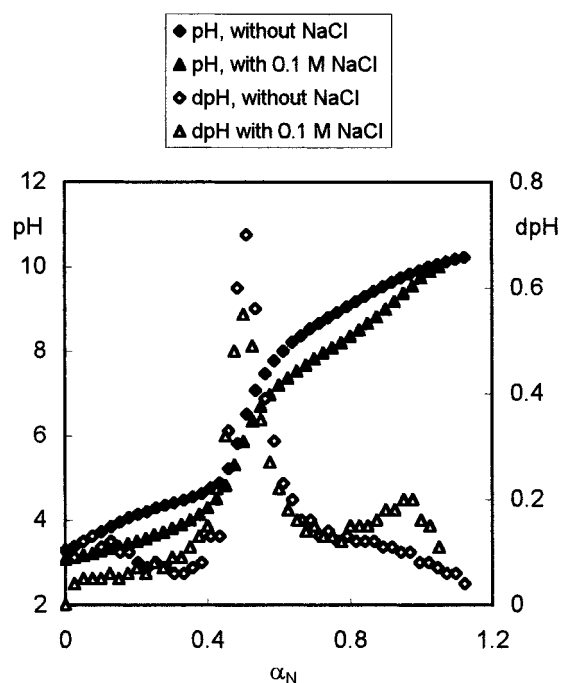

Figure 4. Effect of external salt on the potentiometric titration curves of MAc–MMA with monovalent cations. Titrating agent: KOH, 0.085 N; $C_p = 5.45 \times 10^{-3}$ equiv/L.
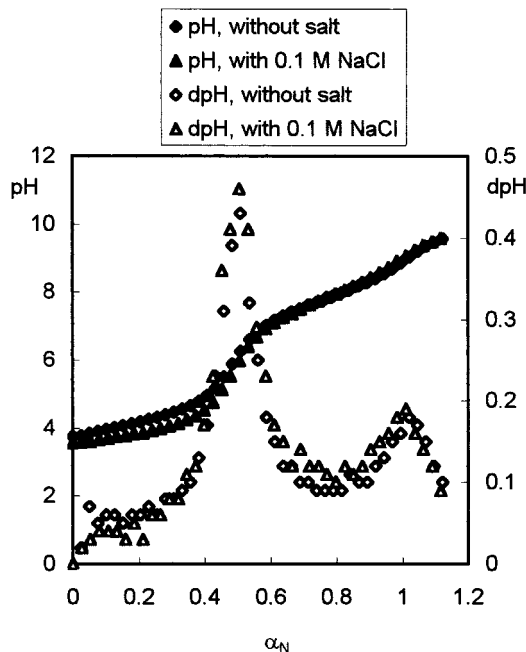

Figure 5. Comparison between potentiometric titration curves of MAc–MMA with Ca(OH)$_2$ without and with added salt. $C_p = 1.07 \times 10^{-3}$ equiv/L.

For the second acidity, the pK_a is also nearly constant: with monovalent hydroxide p$K_a = 8.4$–9.0 depending on the polymer concentration and the degree of neutralization, but with divalent counterions pK_a is constant and lower due to the strong interaction between carboxylic groups and Ca^{2+} ions decreasing the effective charge; p$K_a \sim 7.7$.

At the end we have considered the role of the presence of external salt. The variations of pK_a are given in Figures 8 and 9. The pK_a decreases due to the screening of electrostatic interactions. For the neutralization with KOH, the pK_a varies between 3.45 and 3.6 for the first step and between 7.6 and 8.4 for the second acidity, which
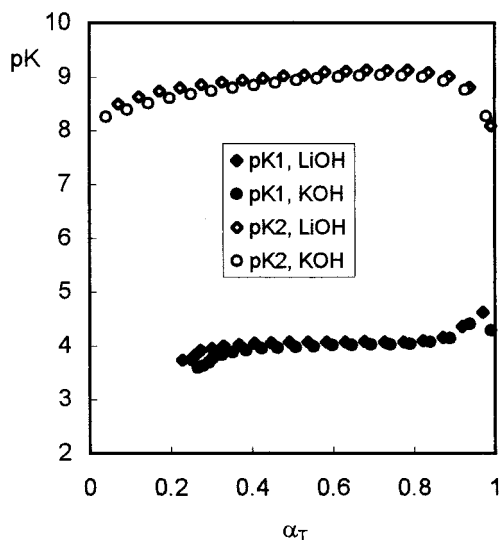
Figure 6. pK_{a1} and pK_{a2} of MAc−MMA using monovalent bases, without external salt. $C_p = 5.45 \times 10^{-3}$ equiv/L.
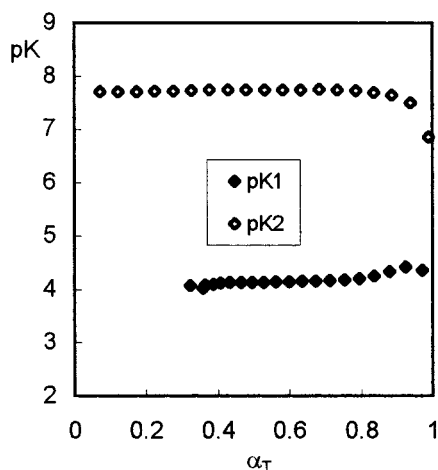

Figure 7. pK_{a1} and pK_{a2} of MAc−MMA obtained with Ca-(OH)$_2$, without added salt. $C_p = 1.10 \times 10^{-3}$ equiv/L.
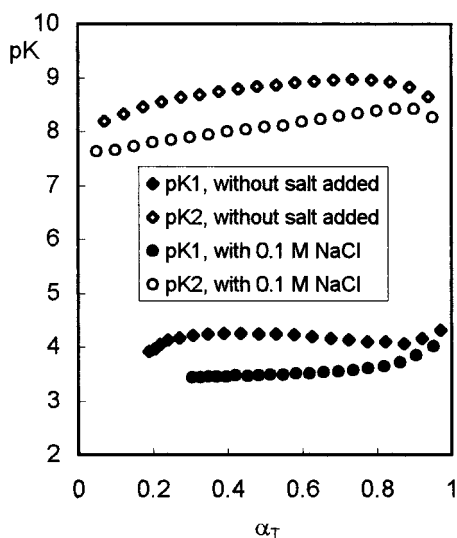

Figure 8. Effect of external salt on the plot $pK_a = f(\alpha_T)$ by titration with monovalent base. Titrating agent KOH, 0.045 N; $C_p = 5.45 \times 10^{-3}$ equiv/L.

is lower than that usually found in absence of salt for polyacids. For neutralization with divalent hydroxide, one gets pK_a 3.47−3.68 for the first acidity, which is nearly
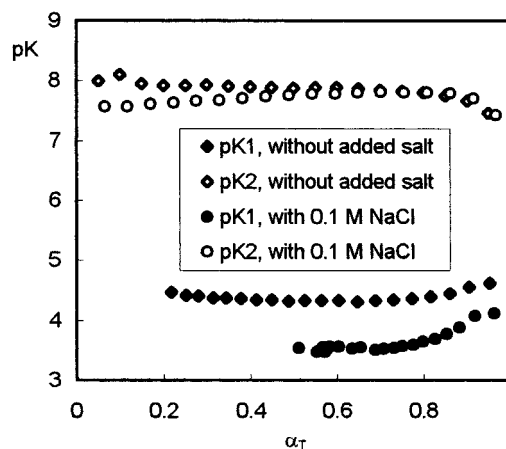

Figure 9. Effect of external salt on the plot $pK_a = f(\alpha_T)$ by titration with Ca(OH)$_2$. $C_p = 1.07 \times 10^{-3}$ equiv/L.

Table 1

	$pK_{0,1}$	$pK_{0,2}$	ref
comonomer in copolymers			
ethylene	3.65	6.40	3a
propylene	3.40	7.40	3a
isobutylene	2.72	8.83	3a
	3.00	9.20	3c
2-methylpentene		9.35	3a
styrene		7.75	3a
	(NaCl, 0.01 M)		6
alkyl vinyl ethers	3.50	6.60	4a
low molecular models			
succinic acid	4.16	5.61	23
maleic acid	1.83	6.07	23

in the same range with monovalent counterions. In contrast, for the second one, $pK_a = 7.56-7.80$; this variation is lower than with monovalent ions but very close to the values obtained in absence of external salt ($pK_a = 7.7$).

From all these results it is clearly established that the two carboxylic functions behave as independent from each other as far as the pK_a is concerned. From the data obtained in the presence of salt excess or in the presence of divalent counterions, approximated values for the two intrinsic pK values can be proposed: $pK_{0,1} = 3.5$ and $pK_{0,2} = 7.6$.

This may be due to the position of −COOH on the two neighboring carbons with a large inductive effect as observed with low molecular weight diacids. Then, there is no role of the repartition of comonomers in the chain. The pK_0 values are comparable with the values reported for other maleic acid copolymers but different from the values of saturated or unsaturated low molecular models (Table 1).[23]

Comparison with Poly(acrylic acid). The neutralization of PAA with monovalent hydroxide is compared with that of the copolymer in Figure 10. This clearly indicates the difference between the two polymers. For PAA only one transition in pH is shown at $\alpha_N = 1$, and a progressive increase of pK_a with α_T is obtained as usual in polyacids. On the pK_a vs α_T plot, it can be seen that with monovalent counterions the pK_a varies from 4.9 to 7.4 as a function of the degree of ionization (from 0.046 to 1.0) going through 6.55 for half neutralization; with divalent counterion pK_a varies from 5.08 to 5.80 going through 5.66 for the pK_a at half neutralization (i.e., the same charge density as the copolymer for the whole neutralization) (Figure 11). The pK_a change found for the

(23) *CRC Handbook of Chemistry and Physics*, 75th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1994; pp 8−46.
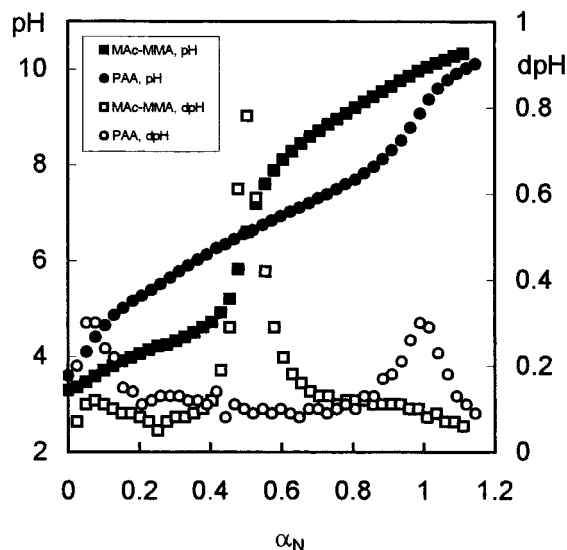
Figure 10. Comparison between potentiometric titration curves of MAc−MMA and PAA with a monovalent base, in absence of external salt. $C_p = 5.45 \times 10^{-3}$ and 5.16×10^{-3} equiv/L, respectively. Titrating agent: LiOH, 0.085 N.
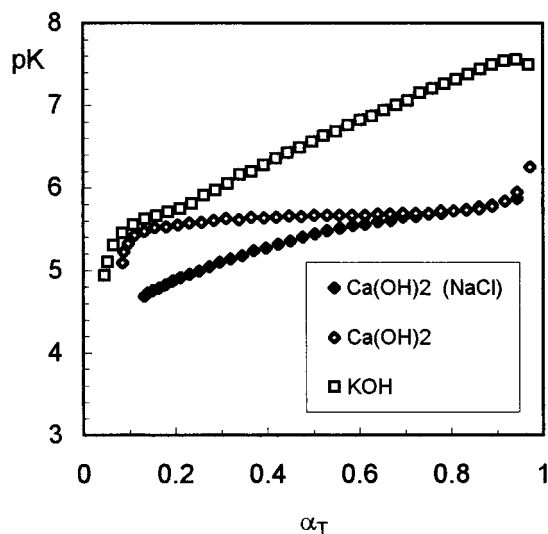

Figure 11. Plot $pK_a = f(\alpha_T)$ by titration of PAA with KOH and Ca(OH)$_2$, without or with added salt. $C_p = 5.16 \times 10^{-3}$ equiv/L with KOH and 0.98×10^{-3} equiv/L with Ca(OH)$_2$. NaCl = 0.1 M.

copolymer is clearly very different from the progressive increase of pK_a with α_T found for PAA. From this plot a value of p$K_0 = 4.3$ can be estimated for PAA.

The pK_0 of the PAA, corresponding to the pK of an independent carboxylic group, given in the literature are 4.13,[3c] 4.03,[24] or 4.6.[25] This value is higher than that obtained previously for the first acidity of the copolymer: 3.5.

Another important difference is the autodissociation of the first carboxylic group in the copolymer. Calculated from the pH measurement α_H is 0.23 at $\alpha_N = 0$ for the copolymer and 0.046 at the same ionic concentration $C_p = 5.21 \times 10^{-3}$ equiv/L for PAA. This is relative to the lower pK_0 of the copolymer.

Conductometric Titration. The neutralization was performed under the same conditions as for potentiometry.
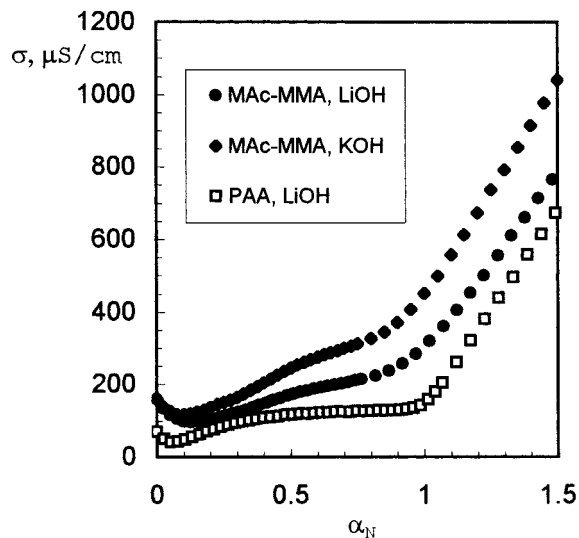
(24) Chang, C.; Muccio, D. D.; St. Pierre, T. *Macromolecules* **1985**, *18*, 2154.
(25) Dautzenberg, H.; Jaeger, W.; Koetz, J.; Philipp, B. *Polyelectrolytes. Formation, Characterization and Application;* Munchen-Hanser Verlag: Munchen, 1994; p 133.

Figure 12. Conductometric titration curves of MAc−MMA and PAA with monovalent bases. $C_p = 5.45 \times 10^{-3}$ and 5.16×10^{-3} equiv/L, respectively.
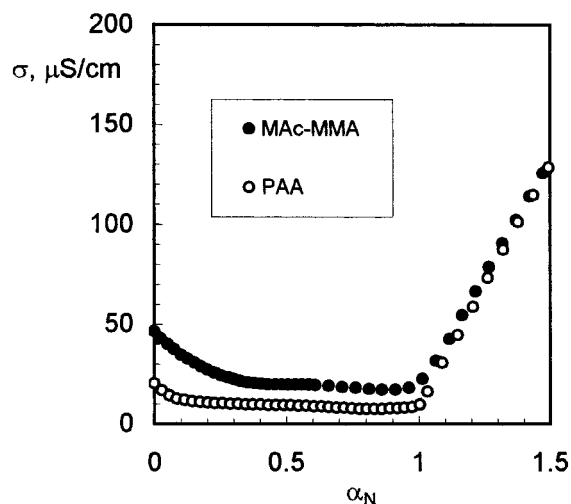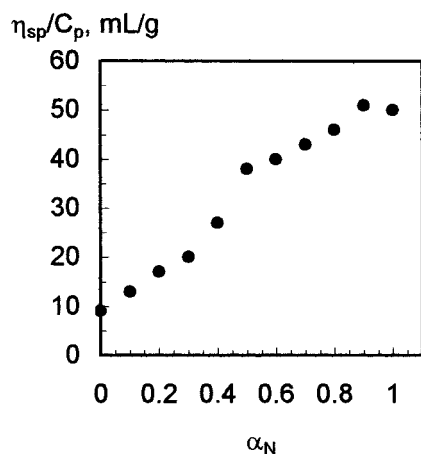

Figure 13. Comparison between potentiometric titration curves of MAc−MMA and PAA with Ca(OH)$_2$. $C_p = 1.07 \times 10^{-3}$ and 0.98×10^{-3} equiv/L, respectively.

As proposed previously[20] the analysis of the conductivity during successive neutralizations by LiOH or KOH allows determination of the transport coefficient for monovalent f^{M^+} and the ionic mobility of the fraction of polymeric chain having one ionic site λ_p. Then from the knowledge of λ_p, one gets the transport coefficient for divalent counterions $f^{M^{2+}}$.

The curves obtained for the neutralization by monovalent and divalent counterions are given in Figures 12 and 13, respectively. A comparison with the behavior of PAA is also performed. The first evidence is that the initial degree of autodissociation of the copolymer is larger than that of the PAA. This is also the same information as obtained by potentiometry when the initial pH values of the acidic solutions are considered.

The fractions of free H$^+$ determined from conductivity, at the same polymer concentration $C_p = 5.4 \times 10^{-3}$ equiv/L are respectively 0.150 and 0.037 for the copolymer and the PAA. The dissociation of the copolymer is attributed to the first acidity.

The fraction f^{M^+} for monovalent counterions in the first part of the neutralization (i.e., $\alpha_{H^+} = 0.5$) is 0.85. Corresponding to the structural value of the charge

Figure 14. Dependence of reduced viscosity of MAc−MMA upon α_N. $C_p = 5.45 \times 10^{-3}$ equiv/L; titrating agent KOH, 0.085 N.

Figure 15. Plot of I_1/I_3 ratio against α_N for MAc−MMA. $C_p = 5.45 \times 10^{-3}$ equiv/L; titrating agent KOH, 0.085 N.

parameter $\zeta = 0.7$; the predicted value of f^{M^+} from the Manning theory should be 0.93. The equivalent mobility of the copolymer was determined with a good precision; one found $\lambda_p = 40$ cm^2 Ω^{-1} equiv^{-1} in agreement with the value obtained for large ions. For complete neutralization $f^{M^+} = 0.61$ when the predicted theoretical value is 0.62 ($\zeta = 1.4$). Concerning the long-range electrostatic interactions which impose the distribution of counterions, the experimental values agree with predicted value from polyelectrolyte theory.

With divalent counterions $f^{Ca^{2+}} = 0.36$ and 0.18 for the first half of neutralization and the complete neutralization of the copolymer, respectively, at $C_p = 1.08 \times 10^{-3}$ equiv/L. These values are too low compared to the values obtained with monovalent counterions; the theoretical prediction expects a ratio of 2 between the monovalent and divalent values of f. In fact one observes an important role of the polymer concentration. At 0.51×10^{-3} equiv/L $f^{Ca^{2+}} = 0.465$ and 0.37 for the first half and complete neutralization, respectively, in agreement with the theory. This effect was also observed for PAA (with a phase separation).

Again, from the comparison between the prediction and the experimental data for the transport coefficient, a relatively good agreement is obtained; the effect of polymer concentration in the presence of divalent counterions is important as usual with flexible polyelectrolytes.

Conformation of the Copolymer. To follow the change in conformation of the copolymer in relation with its charge density, we have determined the reduced viscosity as a function of the degree of neutralization. The results are plotted in Figure 14. As usual with polyelectrolytes, the viscosity increases when the net charge increases: it appears as a rapid increase in the viscosity for $\alpha_N > 0.25$, and the viscosity levels off in the range of the higher degrees of neutralization.

To confirm this change in the conformation, a fluorescence test was performed using a probe, the pyrene, for which the fluorescent spectrum is modified following the polarity of the environment. The ratio between the two characteristic bands I_1/I_3 as a function of the degree of neutralization is given in Figure 15. For the acidic form, the pyrene is located in hydrophobic zones but over a
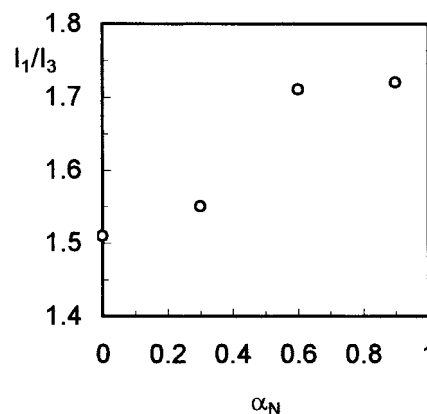
critical degree of neutralization, $\alpha_N > 0.25$, its environment becomes more hydrophilic. Such modifications were also observed for other copolymers of maleic acid with hydrophobic comonomers such as styrene, indene, or alkyl vinyl ethers connected with some discontinuity in the plot of pK function of ionization degree;[4a,6,7] they were attributed to a conformational transition from a compact to an expanded coil upon ionization of the first carboxylic groups.

Conclusion

The copolymer of maleic acid with methyl methacrylate having a 1:3 (moles) composition and a nonalternating monomer distribution was synthesized and characterized by different techniques. The structural charge parameter is 1.7, but the carboxylic groups are not regularly distributed along the chain. Comparison with PAA is discussed to point out the role of the distribution of the carboxylic groups on the electrostatic properties.

The two distinct intrinsic pK_0 values for the copolymer are given equal to 3.5 and 7.6. The neutralization proceeds in a two-step mechanism contrary to PAA. The autodissociation of the acidic form is also larger than that for PAA; it signifies that this local charge dissociation does not agree with polyelectrolyte behavior. In fact, the two carboxylic groups have a different environment and behave as isolated sites. This behavior seems to be independent of the number n of consecutive MMA monomers in the chain.

From conductometry, the transport coefficients are determined for mono- and divalent counterions. The values, especially at low concentrations, agree relatively well with the predicted values calculated from the Manning theory for polyelectrolytes. In this respect, the long-range electrostatic potential controls the distribution of the counterions, then it is the average distance between the carboxyl groups along the chain and not their precise repartition which imposes the electrostatic properties. In addition, during neutralization a change in conformation occurs around $\alpha_N \sim 0.25$ as shown by viscometry and fluorescence.