Macromolecules 1985, *18*, 2154-2157

(3) Ranby, B.; Rabek, J. F. "Photodegradation, Photooxidation, and Photostabilization of Polymers"; Wiley: New York, 1975; Chapter 4.

(4) (a) David, C.; Demarteau, W.; Geuskens, G. *Eur. Polym. J.* **1970**, *6*, 537. (b) David, C.; Demarteau, W.; Derom, F.; Geuskens, G. *Polymer* **1970**, *11*, 61.

(5) Lukac, I.; Hrdlovic, P.; Manasek, Z.; Bellus, D. *J. Polym. Sci., A-1* **1971**, *9*, 69.

(6) (a) Golemba, F. J.; Guillet, J. E. *Macromolecules* **1972**, *5*, 212. (b) Dan, E.; Somersall, A. C.; Guillet, J. E. *Macromolecules* **1973**, *6*, 228; *Ibid.* **1974**, *7*, 233. (c) Dan, E.; Guillet, J. E. *Ibid.* **1973**, *6*, 230. (d) Kilp, T.; Guillet, J. E.; Merle-Aubry, L.; Merle, Y. *Ibid.* **1982**, *15*, 60.

(7) (a) Kiwi, J.; Schnabel, W. *Macromolecules* **1976**, *9*, 468; **1975**, *8*, 430. (b) Beck, G.; Dobrowlski, G.; Kiwi, J.; Schnabel, W. *Eur. Polym. J.* **1976**, *12*, 657. (c) Beck, G.; Kiwi, J.; Lindenau, D.; Schnabel, W. *Ibid.* **1974**, *10*, 1069.

(8) (a) Faure, J.; Fouassier, J.-P.; Lougnot, D.-J. *J. Photochem.* **1976**, *5*, 13. (b) Faure, J.; Fouassier, J.-P.; Lougnot, D.-J. *Nouv. J. Chim.* **1977**, *1*, 15. (c) Faure, J. *Pure Appl. Chem.* **1977**, *49*, 487. (d) Faure, J.; Fouassier, J.-P.; Lougnot, D.-J.; Salvin, R. *Eur. Polym. J.* **1977**, *13*, 891.

(9) (a) Small, R. D.; Scaiano, J. C. *Macromolecules* **1978**, *11*, 840. (b) Encinas, M. V.; Funabashi, K.; Scaiano, J. C. *Ibid.* **1979**, *12*, 1167. (c) Bays, J. P.; Encinas, M. V.; Scaiano, J. C. *Ibid.* **1980**, *13*, 815.

(10) Scaiano, J. C.; Stewart, L. C. *Polymer* **1982**, *23*, 913.

(11) (a) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495. (b) Holden, D. A.; Shephard, S. E.; Guillet, J. E. *Macromolecules* **1982**, *15*, 1481.

(12) Scaiano, J. C.; Lissi, E. A.; Stewart, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 1539.

(13) Bays, J. P.; Encinas, M. V.; Scaiano, J. C. *Macromolecules* **1979**, *12*, 348.

(14) (a) Whitten, D. G.; Punch, W. E. *Mol. Photochem.* **1970**, *2*, 77. (b) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; Haug, A.; Graber, D. R. *Ibid.* **1970**, *2*, 81. (c) Stermitz, F. R.; Nicodem, D. E.; Muralidharan, V. P.; O'Donnel, C. M. *Ibid.* **1970**, *2*, 87-89.

(15) (a) Scaiano, J. C.; Perkins, M. J.; Sheppard, J. W.; Platz, M. S.; Barcus, R. L. *J. Photochem.* **1983**, *21*, 137. (b) Casal, H. C.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 628.

(16) Netto-Ferreira, J. C.; Leigh, W. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 2617.

(17) (a) Carlson, G. L. B.; Quina, F. H.; Zarnegar, B. M.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 347. (b) Wilson, T.; Halpern, A. M. *Ibid.* **1981**, *103*, 2412.

(18) (a) Hrdlovic, P.; Lukac, I.; Zvara, I.; Kulickova, M.; Berek, D. *Eur. Polym. J.* **1980**, *16*, 651. (b) Nenkov, G.; Georgieva, T.; Stoyanov, A.; Kabaivanov, V. *Angew. Makromol. Chem.* **1980**, *91*, 69. (c) Shiraishi, F.; Seno, M.; Ishii, M.; Asahara, T. *J. Appl. Polym. Sci.* **1976**, *20*, 2429.

(19) Marvel, C. S.; Peterson, W. R.; Inskip, H. K.; McCorkle, J. E.; Taft, W. K.; Labbe, B. G. *Ind. Eng. Chem.* **1953**, *45*, 1532.

(20) (a) Gramain, P.; Libyre, R. *J. Appl. Polym. Sci.* **1970**, *14*, 383. (b) Kilp, T.; Houvenaghel-Defoort, B.; Panning, W.; Guillet, J. E. *Rev. Sci. Instrum.* **1976**, *47*, 1496. (c) Satne, R.; Mateo, J. L. *Rev. Plast. Mod.* **1983**, *46*, 611.

(21) Zasosov, V. A.; Metel'kova, E. I.; Milovanova, S. N. *Magy. Kem. Lapja* **1956**, *26*, 2499. See also: *Chem. Abstr.* **1957**, *51*, 4994*d*.

(22) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

(23) Scaiano, J. C.; Leigh, W. J., to be published.

(24) Hrdlovic, P., private communication.

(25) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506.

(26) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.

(27) Encinas, M. V.; Scaiano, J. C. *Chem. Phys. Lett.* **1979**, *63*, 305.

(28) Sandros, K. *Acta Chem. Scand.* **1964**, *18*, 2355.

(29) (a) Terenin, A.; Ermolaev, V. *Trans. Faraday Soc.* **1956**, *52*, 1042. (b) Forster, Th. *Discuss. Faraday Soc.* **1956**, *27*, 7. (c) Turro, N. J. *Pure Appl. Chem.* **1977**, *49*, 405. (d) Klopffer, W. *Spectrosc. Lett.* **1978**, *11*, 863.

(30) Guillet, J. E. *Pure Appl. Chem.* **1977**, *49*, 249.

(31) Das, P. K.; Scaiano, J. C. *Macromolecules* **1981**, *14*, 693.

Determination of the Tacticity and Analysis of the pH Titration of Poly(acrylic acid) by ^{1}H and ^{13}C NMR

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ABSTRACT: The tacticity, to triad and partial pentad resolution, of a commercial sample of poly(acrylic acid) was determined by ^{1}H and ^{13}C NMR. Curve deconvolution of the ^{13}C NMR spectrum for the methine resonances gave relative areas of 27, 50, and 23% for the rr, mr, and mm sequence, respectively, based on Schaefer's peak assignments. The use of Bernoullian statistics gave the corresponding probabilities of r and m configuration as 52% and 48%, respectively, establishing the atactic character of the polymer. This was confirmed by the ^{1}H NMR spectrum of the methylene protons. The simulated pentad spectrum was constructed on the basis of these probabilities and the experimental spectrum. The changes in chemical shift of the methine resonance for each tacticity and for the carbonyl resonance with changing pH were treated as typical polyelectrolyte titrations and analyzed by the extended Henderson–Hasselbalch and Mandel's equations. We found a small tacticity effect on the acid dissociation behavior of poly(acrylic acid).

Introduction

^{13}C NMR has been extensively used for elucidating the stereochemical sequence of vinyl polymers, such as poly(methyl methacrylate),[1] poly(vinyl acetate),[2] and polyacrylonitrile.[3] By comparison, there have been only a few studies[4-8] of poly(acrylic acid) (PAA), and these are incomplete. Schaefer[5] has reported on the triad sequence of the methine carbon for PAA by ^{13}C NMR. Comparing the spectrum of isotactic PAA with that of the atactic polymer, he found that the upfield portion of both the methine and methylene carbon resonances may be attributed to the meso (m) configuration and, by default, the downfield region to the racemic (r) configuration. Furthermore, it was shown that the tacticity of the methine and methylene carbons was observed only at high pH. At low pH the resonance for each carbon nucleus was a single peak, shifted upfield. Interestingly, the carbonyl peak was insensitive to tacticity at both high and low pH. Watts,[7] in contrast, ascribed the downfield component of the methylene carbon resonances to the m configuration and the upfield component as a mixture of both m and r configurations. His assignments, however, were made on an unjustified extrapolation of the ^{1}H NMR results. In the first part of this paper, we will provide a quantitative solution to the tacticity of PAA by ^{13}C NMR at the triad level and propose a pentad analysis as well.

The acid dissociation constant (pK_a) of a polyelectrolyte generally depends on the mole fraction of charged sites (α).

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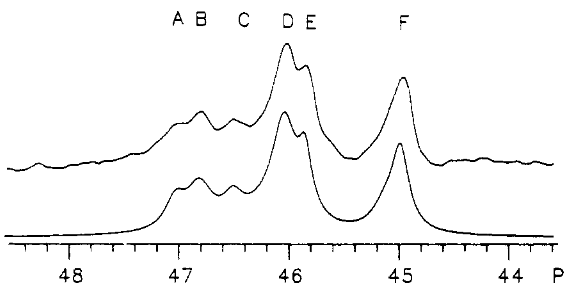

Figure 1. ^{13}C NMR spectrum of CH for PAA at 75 °C in D_2O (5% w/v) at pH 12. Upper trace: spectrum for 10 732 acquisitions under the conditions described in the Experimental Section. Lower trace: the reconstructed spectrum from the deconvoluted peaks with a rms error of <1%.

The change of pK_a with respect to α is due primarily to an electrostatic effect.[9] The titration data can be treated in principle according to Manning's model.[10] Alternatively, the data can be treated empirically either with the extended Henderson–Hasselbalch (HH) equation[11] or Mandel's equation.[12] Relatively little work has been done on the NMR pH titration of polyelectrolytes. The titration behavior of PAA may be determined by ^{13}C NMR by plotting chemical shifts vs. pH. Schaefer[5] worked at three different pH's (2, 5, and 8) in order to maximize tacticity effects, but he made no attempt to titrate PAA. Prosser et al.,[8] however, did titrate this polymer using ^{13}C NMR to monitor the change in ionization state, and they used the HH equation to calculate $pK_{1/2}$ from the change in chemical shift of the carbonyl carbon, where $pK_{1/2}$ is the value of pK_a at $\alpha = 0.5$. In this paper, we will examine the titration behavior of PAA in more detail and analyze the influence of tacticity on pK_a.

Experimental Section

PAA (Celanese Water Soluble Polymers) with a weight-average molecular weight of 10 000–20 000 was used as received. The ^{13}C NMR spectra were obtained by using a GE 300 WB spectrometer (NT series) equipped with an 1180e computer and a 293c pulse programmer. The concentration of PAA was 5% w/w. This concentration was sufficient to minimize any changes of chemical shifts with dilution of the polymer. The tacticity studies were performed on D_2O solutions at 75 °C. The NMR titrations were done at 25 °C with the polymer dissolved in H_2O. Pulse angles of 62° (27 μs), repetition rates of 5.5 s, sweep widths of ±7575 Hz, and 16K data points were used to acquire the free induction decays. Dioxane was used as an internal chemical shift reference (66.5 ppm relative to tetramethylsilane). Nuclear Overhauser effects (NOE) were determined by the ratio of the peak intensity of the fully proton-decoupled and gated-decoupled (decoupler off during delay time) spectra. The repetition rate for this measurement was at least 10 times the longest spin–lattice relaxation time (T_1). The T_1 values were obtained from the inversion recovery pulse sequence[13] using a composite 180° pulse with delay values of 0.025, 0.08, 0.2, 1.0, and 3.0 s. The T_1 values were calculated by using a nonlinear three-parameter fitting procedure.[14] Curve deconvolution was accomplished with the NMCCAP program provided by the GE software using a completely Lorentzian line shape. ^1H NMR experiments were performed at 80 °C on 0.5% (w/v) D_2O solutions. The pH's were adjusted with 5-μL additions of 9 N sodium hydroxide and recorded on an Orion Research Model 701 A pH meter with a microcapillary Ingold combination electrode and with no D_2O corrections.

Results and Discussion

Determination of Tacticity of PAA. The ^{13}C NMR spectra of PAA were recorded in full through the pH range 1–13. There was no fine structure apparent in the spectra at low pH, whereas at high pH there was good resolution for the methine carbon, poor resolution for the methylene carbon, and a single peak for the carbonyl carbon. The methine carbon resonances obtained at 75 °C showed some pentad sensitivity, whereas at 25 °C only triad sensitivity was observed. The proton-decoupled ^{13}C spectrum of the methine carbon of PAA at 75 °C (Figure 1) appeared as six resolved peaks at 46.98, 46.75, 46.41, 45.99, 45.85, and 44.95 ppm, labeled A through F, respectively. The methylene region (Figure 2) has three major peaks at 38.65, 37.06, and 36.15 ppm, G through I. Finally, the carbonyl carbon, spectrum not shown, exhibited no apparent tacticity. Schaefer reports[5] three principle peaks for the methine carbon of atactic PAA and one principle peak for isotactic PAA that corresponds to the upfield peak of the atactic polymer. Consequently, we assign peaks A, B, and C to the rr sequence, D and E to the mr or rm sequence, and F to the mm sequence. The rr resonance has three components and represents pentad sensitivity. Schaefer shows one methylene peak for isotactic PAA, which corresponds to peak I that we assign to the m diad.

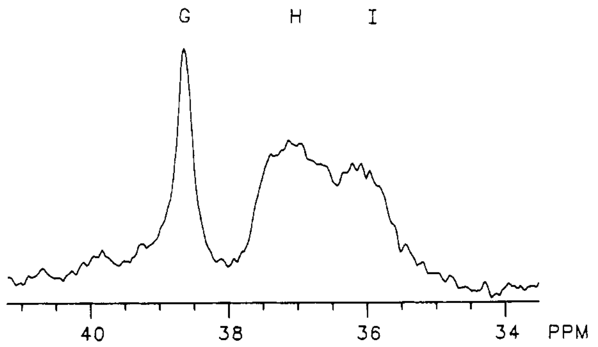

Figure 2. ^{13}C NMR spectrum of CH_2 for PAA under the same experimental conditions described in the caption of Figure 1.

Table I
Peak Assignments, T_1, NOE, and Peak Areas for PAA[a]

carbon	configuration	measured region, ppm	NOE (+0.1)	T_1 (+0.001)	area, %[b]
CH	rr	46.3–47.2	2.2	0.306	27
	mr (+rm)	45.4–46.3	2.2	0.290	50
	mm	44.7–45.4	2.3	0.293	23
CH_2		38.1–39.1	2.7	0.159	23
		35.5–38.0	2.5	0.158	77
CO_2		178.6	1.2	2.497	

[a] 5% w/v in H_2O adjusted to pH 12 and at 75 °C. [b] Estimated error ±5%.

Triad tacticity of the methine carbon is estimated from the combined peak areas, which are 27, 50, and 23% for the rr, mr, and mm sequences, respectively. The intensities of these peaks may be influenced by T_1 and NOE.[15] As shown in Table I, the T_1 values for each methine resonance are nearly equal. Since the experiment utilized repetition rates of more than 10 × T_1, the areas in this respect require no correction. Furthermore, NOE measurements show only slightly different values for the three regions (Table I), and these differences are within the experimental error estimated at ±5%; therefore, no corrections for peak areas were necessary for the proton-decoupled spectrum.

The probability for the m configuration and r configuration, calculated from peak areas based on Bernoullian statistics,[16–18] are 48 and 52%, respectively. With these values, a simulated spectrum to pentad resolution is constructed, which is shown in Figure 3, and the contribution to the area of each sequence is given in Table II. The simulated spectrum was generated by using the following assumptions: (1) the mm-, mr-, and rr-centered resonances do not overlap; (2) the pentad distribution follows Bernoullian statistics; and (3) the line widths for all tacticities are equal. The last assumption is based on the fact that

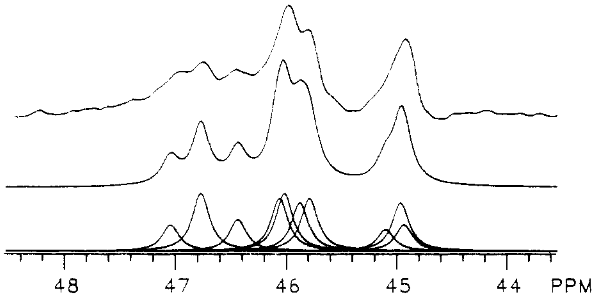

Figure 3. ^{13}C NMR spectrum of CH for PAA under the same experimental conditions described in the caption of Figure 1 compared to the reconstituted curve (middle trace) based on the pentad analysis (lower trace) with a rms error of <1%.

Table II
Simulated Methine Carbon Resonance for Pentad Sensitivity

triad	pentad	chemical shift, ppm
rr	mrrm	47.03
	mrrr	46.76
	rrrr	46.44
mr	rmrm	46.07
	rmrr	45.98
	mmrm	45.85
	mmrr	45.76
mm	rmmr	45.05
	mmmr	44.94
	mmmm	44.92

T_1 is proportional to T_2 (spin–spin relaxation time) in the extreme narrowing region. Since the line width is proportional to T_2, it follows that equal T_1 values predict equal line widths. Under these conditions only the position of each resonance was varied manually in a curve-deconvolution program to yield the lowest root mean square error between the observed and calculated composite spectra, Figure 3.

Since pentad sensitivity was displayed in the observed spectrum of the rr region, it was possible to predict the ordering of the rr-centered pentads with some confidence. As shown in Table II, these peaks are, left to right, mrrm, mrrr (and rrrm), and rrrr. Interchanging mrrm with rrrr results in a noticeably poorer fit. The ordering for the mm-centered pentads is hampered by poor resolution, and only the mmmr (and rmmm) can be assigned with confidence.

The fully decoupled spectrum of the methylene carbon, Figure 2, despite the poor resolution, may be analyzed according to the m and r content established above. The spectrum was deconvoluted by the same procedure as used for the methine carbon resonances. The peak identified as G accounts for 23% of the total CH_2 area. However, this analysis is complicated by the presence of a spurious peak.[19] It is easily identified in acidic solutions as a separate peak upfield from the principle CH_2 resonances. It moves downfield with increasing pH and at pH 12 contributes 9.4% to the peak areas of H or I. Its presence is confirmed by the T_1 studies, appearing as an inverted peak when the rest of the CH_2 peaks are nulled. After correction for this spurious peak is made, the contribution of the area of peak G to the total area of the CH_2 resonance is 25%.

On the basis of the diad distribution established above, m = 0.48 and r = 0.52, the Bernoullian tetrad distribution may be calculated as follows: mmm = 0.11, mmr and rmm = 0.24, rmr = 0.12, mrr and rrm = 0.26, and rrr = 0.14. The poorly resolved CH_2 spectrum of PAA, except for peak G of Figure 2, can be analyzed in terms of the tetrad distribution. Peak G may be assigned to one of the two major tetrads or a combination of two minor ones. On the basis of an approximate analysis of line width, the former is more likely. The tetrad choice for G, mmr (and rmm) or mrr (and rrm), is not clear-cut, based on the approximately equal areas for this polymer and conflicting earlier assignments.[5-7]

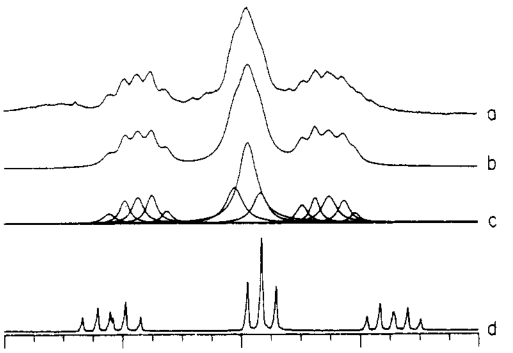

Figure 4. ^1H NMR of CH_2 of PAA at 80 °C in D_2O (0.05 M) at pH 2 and for 2400 acquisitions: (a) experimental spectrum, (b) reconstructed spectrum from curve c, (c) deconvoluted spectrum based on the expected spin–spin coupling pattern; (d) ^1H NMR of CH_2 of a mixture of m and r 2,4-dimethylglutaric acid at 25 °C in D_2O (0.5 M) at pH 2.

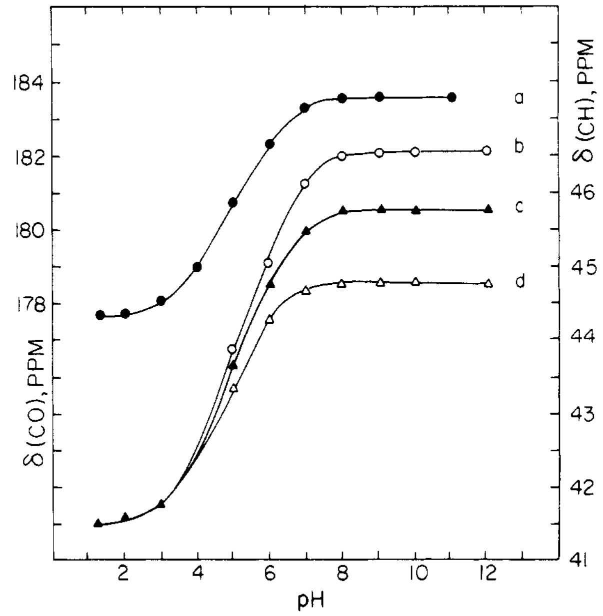

Figure 5. Chemical shift vs. pH for the carbonyl carbon (a) and for the methine carbons (b = rr sequence, c = mr sequence, and d = mm sequence) of PAA at 25 °C.

In order to confirm the diad distribution established above, the ^1H NMR analysis of CH_2, known to be useful for this purpose,[7] was undertaken. The ^1H NMR spectrum of PAA for the methylene proton at pH 2, characterized by multiplets at 1.98, 1.79, and 1.65 ppm, is shown in Figure 4a. The model compound, an equimolar mixture of m and r 2,4-dimethylglutaric acid, Figure 4d, is characterized by the previously assigned peaks[20] at 2.02 and 1.54 ppm for the m configuration and 1.77 ppm for the r configuration. The peak areas, obtained from curve deconvolution are 23.1%, 52.0%, and 24.6% for the peaks centered at 1.98, 1.79, and 1.65 ppm, respectively. This result is in good agreement with the analysis of the methine carbon by ^{13}C NMR.

^{13}C NMR pH Titration. The ^{13}C NMR pH titrations of the methine carbon for each tacticity and the carbonyl carbon, one peak, are displayed in Figure 5. Deprotonation with increasing pH resulted in a downfield shift of

Table III
Acid Dissociation Constants of PAA

	methine carbons			
	mm	mr (+rm)	rr	carbonyl carbon
		HH Equation		
$\mathrm{p}K_{1/2}$	4.73	5.05	5.22	4.97
n	1.65	1.78	1.80	1.75
correlation coeff	0.99	0.99	0.99	0.99
		Mandel's equation		
$\mathrm{p}K_{\mathrm{i}}$	3.91	4.09	4.22	4.03
a	1.93	1.99	2.08	2.09
b	−0.46	−0.18	−0.21	−0.42
n^a	1.85	2.04	2.08	1.96
$\mathrm{p}K_{1/2}{}^a$	4.76	5.03	5.21	4.97

[a] HH parameters calculated from Mandel's equation.

each resonance. The extended HH treatment was used to calculate the $\mathrm{p}K_{\mathrm{a}}$ and $\mathrm{p}K_{1/2}$ according to

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

where α is calculated as the fraction of total chemical shift change given by

$$\alpha = \frac{\delta - \delta_{\min}}{\delta_{\max} - \delta_{\min}} \quad (2)$$

where δ is the observed intermediate ^{13}C chemical shift at intermediate pH's and $\delta_{\max}$ is the maximum chemical shift and $\delta_{\min}$ is the minimum chemical shift at the extremes of pH. A linear regression fit of pH gives $\mathrm{p}K_{1/2}$ and n as the intercept and slope, respectively. The results for rr, mr, and mm configurations of methine carbon and for the carbonyl carbon are given in Table III. The correlation coefficient in each case is very close to 1, which suggests that PAA does not change conformation abruptly during the course of titration.[12]

The $\mathrm{p}K_{1/2}$ for each CH triad tacticity is slightly but significantly different. The most acidic tacticity corresponds to the mm sequence and the least acidic to the rr sequence. The CH mr (and rm) configuration and the carbonyl cation are characterized by similar and intermediate values of $\mathrm{p}K_{1/2}$. The slopes for each titration are also slightly different and indicate convergent p*K*'s at low pH, i.e., low charge state.

By another approach, Mandel[12] expressed $\mathrm{p}K_{\mathrm{a}}$ (or pH + log ((1 − α)/α)) as a series expansion on α

$$\mathrm{p}K_{\mathrm{a}} = \mathrm{p}K_{\mathrm{i}} + a\alpha + b\alpha^2 \quad (3)$$

where $\mathrm{p}K_{\mathrm{i}}$ is the intrinsic dissociation constant and a and b are the coefficients for the α terms. The results based on eq 3 are also shown in Table III, and they show the same trends in p*K* as described above. The self-consistency of these two empirical equations[20] is made clear in the calculation of n and $\mathrm{p}K_{1/2}$ of the extended HH equation from the a and b parameters of Mandel's treatment by means of

$$n = 1 + 0.575(a + b) \quad (4)$$

The results of these calculations for $\mathrm{p}K_{1/2}$, but not for n (Table III), are consistent with the results obtained from the extended HH.

The $\mathrm{p}K_{1/2}$ and n values obtained by ^{13}C NMR titration are close to the literature values obtained by potentiometric titration reported by Monjol and Champetier.[21] They found $\mathrm{p}K_{1/2} = 5.35$ and $n = 1.7$ for atactic PAA at 10^{-2} M polymer concentration and 0.1 N NaCl salt concentration at 15 °C. The results, theirs and ours, are surprisingly close given the difference in experimental conditions.

The effect of tacticity on the acid dissociation of PAA is small, but the trends are clear: $\mathrm{p}K_{\mathrm{mm}} < \mathrm{p}K_{\mathrm{mr}} < \mathrm{p}K_{\mathrm{rr}}$. The p*K* of the carboxyl associated with the mr (and rm) sequence of CH is approximately equal to the p*K* determined from the CO titration and to the average of the other two carboxyl sequences. Our results, however, are at odds with the potentiometric titration results of Kawaguchi and Nagasawa,[22] who show the syndiotactic tactic polymer, r > m, to be a slightly stronger acid than the isotactic polymer, m > r. From Clark's report[23] on the potentiometric titration of 2,4,6-heptanetricarboxylic acid, $\mathrm{p}K_{\mathrm{a}}$ = 5.00, 4.87, and 4.90 for mm, mr, and rr isomers, respectively. Since these values are so close, it is difficult to draw conclusions based on the different configurations. No doubt the conformational freedom of the low molecular weight model, and to a certain extent the polymer, moderate the configuration effects on $\mathrm{p}K_{\mathrm{a}}$.

Registry No. PAA (homopolymer), 9003-01-4.

References and Notes

(1) Peat, I. R.; Reynolds, W. F. *Tetrahedron Lett.* **1972**, *14*, 1359.
(2) Wu, T. K.; Ovenall, W. F. *Macromolecules* **1974**, *7*, 776.
(3) Schaefer, J. *Macromolecules* **1977**, *4*, 105.
(4) Muroga, Y.; Noda, I.; Nagasawa, M. *J. Phys. Chem.* **1969**, *73*, 667.
(5) Schaefer, J. *Macromolecules* **1971**, *1*, 98.
(6) Matsuzaki, K.; Kanat, T.; Kawamura, T.; Matsumoto, S.; Uryu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 1961.
(7) Watts, D. C. *J. Biomed. Mater. Res.* **1979**, *13*, 423.
(8) Prosser, H. T.; Richards, C. P.; Wilson, A. D. *J. Biomed. Mater. Res.* **1982**, *16*, 431.
(9) Morawetz, H. "Macromolecules in Solution"; Wiley: New York, 1975; p 344.
(10) Manning, G. S. *J. Phys. Chem.* **1981**, *95*, 870.
(11) Katchalsky, K.; Spitnik, P. *J. Polym. Sci.* **1947**, *2*, 432.
(12) Mandel, M. *Eur. Polym. J.* **1970**, *6*, 807.
(13) Freeman, R.; Kempsell, S. P.; Levitt, M. H. *J. Magn. Reson.* **1980**, *38*, 453.
(14) Kowalewski, J.; Levy, G. C.; Johnson, L. F.; Palmer, L. *J. Magn. Reson.* **1977**, *26*, 533.
(15) King, J.; Bower, D. I. *Makromol. Chem.* **1983**, *184*, 879.
(16) Randall, J. C. "Polymer Sequence Determination ^{13}C NMR Method"; Academic Press: New York, 1977; p 71.
(17) Bovey, F. H. "High Resolution NMR of Macromolecules"; Academic Press: New York, 1972; p 146.
(18) The sequence distribution also fit first-order Markov statistics, which is not surprising for this atactic polymer.
(19) The spurious peak is assumed to be an end-group peak; however, at 9.4% the calculated M_{n} is not consistent with a M_{w} of 15 000. To refine this calculation it would be necessary to correct for T_1 and NOE.
(20) Fenyo, J. C.; Laine, J. P.; Muller, G. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 193.
(21) Monjol, P.; Champetier, G. *Bull. Soc. Chim. Fr.* **1972**, 1313.
(22) Kawaguchi, Y.; Nagasawa, M. *J. Phys. Chem.* **1969**, *73*, 4382.
(23) Clark, H. K. *Makromol. Chem.* **1965**, *86*, 107.