High-Resolution Pulsed Carbon-13 Nuclear Magnetic Resonance Analysis of Some Polyelectrolytes

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Received September 8, 1970

ABSTRACT: Fourier transforms of the noise-decoupled, natural abundance, 22.6-MHz ^{13}C nmr free induction decays of some polyelectrolytes have been obtained. The polyelectrolytes investigated include atactic and isotactic poly(methacrylic acid), atactic and isotactic poly(acrylic acid), and a completely alternating copolymer of ethylene and maleic anhydride. The titration of the polyelectrolytes can be followed by the changing chemical shifts of the carboxyl carbons. Stereochemical differences between different segments within the atactic chains are both distinguishable in the ^{13}C nmr spectra and pH dependent. The pH dependence of these differences is related to a change in the ionization of the substituents rather than to a change in the local conformation of the chain which is constant.

The use of ^{13}C nmr in the elucidation of polymer structure is well established.[1-4] The chief obstacle to its widespread use to date has been the severe limitation of low sensitivity resulting from the character of the ^{13}C nucleus itself and from its natural abundance of only 1%. This limitation has been overcome by the use of Fourier transform nmr techniques.[5-8] By pulsing the ^{13}C radiofrequency instead of the usual restricted slow sweep, a complete ^{13}C nmr spectrum (in the form of its free induction decay) can be obtained in as little as 0.1 sec. Although such a spectrum is very noisy, it is practical to repetitively pulse thousands of times in a short period and accumulate these data in a time averaging computer. The normal absorption nmr spectrum can then be obtained from the free induction decay in just a few minutes by a Fourier transform performed by a small laboratory computer.

This article and the three immediately following will apply high-resolution, pulsed ^{13}C nmr techniques to a variety of polymer structure problems, including the conformations of some atactic polyelectrolytes in water, the stereochemistry of polyacrylonitrile, the monomer distribution in acrylonitrile–styrene copolymers, and the microstructure of cross-linked polymers. These are all problems which are intractable using proton nmr techniques.

Experimental Section

A. Nmr Experiments. Pulsed ^{13}C nmr spectra were obtained at 22.6 MHz using a Bruker HFX spectrometer. This spectrometer has four simultaneously available radio-frequency (rf) channels, including an analytical channel, a stabilization channel, and two irradiation channels. The ^{13}C analytical channel (22.6 MHz) has a crossed coil configuration and involves both rf transmission and center-band receiving in the usual way. The ^{19}F stabilization channel (84.7 MHz) uses a bridge circuit in which the receiver coil of the analytical channel is also tuned to the rf stabilization frequency. The stabilization channel is operated in a side-band CW mode. The remaining two channels involve only rf transmission for the purposes of multiple resonance experiments and consist of independent transmitter coils approximately orthogonal to the analytical receiver coil. These coils were tuned to the rf frequencies for ^{1}H (90.0 MHz) and ^{14}N (6.49 MHz). For the experiments reported here, the ^{14}N channel was not used.

The ^{13}C rf was produced by a Schomandl ND 30 M-B frequency synthesizer, the ^{19}F rf by an appropriate crystal (which also was connected to the audio side-band frequency of the stabilization channel), and the ^{1}H rf by a Hewlett-Packard 5105A-5110B frequency synthesizer. All of these frequencies were phase locked so that the stability of the field-frequency ratio established in the ^{19}F channel was maintained for all the other channels as well. The ^{13}C and ^{1}H frequencies were offset by simply varying the outputs of the respective frequency synthesizers.

The ^{13}C rf drove a Bruker BSV-2 pulse-shaping transmitter capable of producing a 60-W (into 50 ohms), square-wave pulse with a width variable between 20 and 200 μsec. (Although this power level is too low to produce a 90° pulse, weak, closely spaced pulses are not a severe limitation for many ^{13}C nmr applications.[5]) A 40-μsec pulse width was commonly used to irradiate the entire ^{13}C rf band, with correspondingly wider pulses used for irradiation of smaller sections of the rf band. The experiments were not critically dependent on the choice of pulse width. The ^{19}F rf was amplified by a low-power CW transmitter, a part of the HFX spectrometer. The ^{1}H rf was first phase modulated by a Hewlett-Packard 3722A noise generator and then amplified by the power section of a second Bruker BSV-2 transmitter, capable of an 18-W CW output. This permitted efficient decoupling[9] of all protons over a band width of about 800 Hz with an operating probe temperature of about 40°.

The pulse sequence timing was provided by the trigger output of a Fabri-Tek FT 1074, a 4096-channel computer. Only identical pulses with equal spacing were produced generating repetitive free induction decays. Delays between pulses ranging from 0.1 to 20 sec were successfully used.

The FT 1074 was used to sample the receiver output after completion of the irradiating pulse. By changing the sampling rate between 100 and 1000 μsec per computer channel,

(1) J. Schaefer, *Macromolecules*, **2**, 210 (1969).
(2) J. Schaefer, *ibid.*, **2**, 533 (1969).
(3) L. F. Johnson, F. Heatley, and F. A. Bovey, *ibid.*, **3**, 175 (1970).
(4) M. W. Duch and D. M. Grant, *ibid.*, **3**, 165 (1970).
(5) R. R. Ernst and W. A. Anderon, *Rev. Sci. Instrum.*, **37**, 93 (1966).
(6) R. R. Ernst, *Advan. Magn. Resonance*, **2**, 1 (1966).
(7) E. D. Becker, J. A. Ferretti, and T. C. Farrar, *J. Amer. Chem. Soc.*, **91**, 7784 (1969).
(8) W. Horsley, H. Sternlicht, and J. S. Cohen, *ibid.*, **92**, 680 (1970).
(9) R. R. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966).

the observed frequency range could be conveniently varied from 5000 to 500 Hz, respectively. Frequency components higher than the chosen sweep width were essentially eliminated by analog filtering using a 48 db/octave Multimetric AF 420 tunable active filter between the receiver and the FT 1074.

The normal nmr spectrum was obtained from the accumulated free induction decay by a Fourier transform.[10] This was accomplished using a Fast Fourier Transform program based on the Cooley–Tukey algorithm and written for a Digital Equipment Corporation PDP-8/I computer interfaced to the FT 1074.[11] The version of the FFT program used in these experiments makes no phase corrections, and calculates the amplitude spectrum which is the square root of the sum of the squares of the absorption and dispersion spectra. The amplitude spectrum is independent of the receiver phasing and approximately independent of phase shifts introduced by delays between the time of the pulse and the time the receiver output is first sampled. The main practical difference between amplitude and absorption spectra is in line shape. Narrow lines in the amplitude spectrum tend to be somewhat too broad at the base so that very weak lines adjacent to very strong lines are sometimes lost in the tail of the stronger line.

The line positions in the spectrum were read as channel locations in the FT 1074 with an accuracy of ± 1 channel. The accuracy achieved in the frequency domain depends on the number of computer channels employed and the sampling rate. Line positions are accurate to $\pm 1/2$(sampling rate $\times$ number of channels). For example, line positions are accurate to ± 1 Hz when 1024 computer channels are internally swept at a rate of 1000 μsec/channel. The spectrum was plotted using an X–Y recorder driven by the FT 1074.

The nmr sample cells were provided by Wilmad Glass Co. and consisted of a 13-mm o.d. tube containing a removable, concentric, slightly narrower, 5-cm long inner tube which tapered to 5 mm, about 2 cm above the region of the receiver coil. Inner tubes with a 3-mm diameter at the receiver coil were also used. Hexafluorobenzene was placed in the inner tube and provided a ^{19}F stabilization signal while the analytical sample was in the outer section of the cell. The entire assembly was spun by an air turbine.

Carbon-13 chemical shifts were measured in parts per million downfield from external tetramethylsilane and are denoted by δ_C. In order to remove bulk susceptibility effects, the TMS signal was obtained from a dilute solution of the TMS in the same solvent as used for the analytical samples.

The choice of TMS as a ^{13}C chemical-shift reference seems appropriate for several reasons. Almost all ^{13}C resonances appear at lower field than TMS, so that the same sort of δ scale in parts per million can be used as is common for proton nmr spectra. Also, as ^{13}C nmr analysis becomes more popular, it will be convenient to use the same reference material in the same sample for both proton and ^{13}C nmr spectra. Tetramethylsilane can be used both as an external and an internal reference because of its compatibility with most solvents. Finally, TMS is not subject to undue solvent effects.

When ^{13}C chemical shifts are referenced to other standards, the reference material will be denoted explicitly in the subscript. For example, for a variety of solvents, including chlorobenzene, pyridine, dimethyl sulfoxide, and methylene chloride, $\delta_C = 192.8 - \delta_{CS_2}$, within 0.1 ppm. (The CS_2 resonance must be obtained from a dilute solution of CS_2 rather than from the neat liquid, the latter resulting in a value 0.75 ppm to lower field for the apparatus described above.)

For measurements using water as a solvent, TMS is, of course, not appropriate. Instead, the methyl carbon resonance of the sodium salt of trimethylsilylpropanesulfonic acid (TPS), $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$, was used.

B. Synthesis of Polymers. Atactic poly(methacrylic acid) and poly(acrylic acid) were prepared by free radical polymerization of 10 vol % of the monomer in benzene using 2,2′-azobis(2-methylpropionitrile) as initiator. Isotactic poly(methacrylic acid) was obtained from the hydrolysis[12] of a highly isotactic sample of poly(methyl methacrylate), the latter prepared at 0° by polymerization of the monomer using phenylmagnesium bromide as a catalyst.[13] Isotactic poly(acrylic acid) was obtained from hydrolysis of a sample of isotactic poly(methyl acrylate) prepared from the monomer in toluene at −79° using lithium aluminum hydride as a catalyst.[12] Atactic poly(methyl methacrylate) was obtained from Du Pont as Lucite 40. The ethylene–maleic anhydride copolymer was prepared by a high-pressure (about 600 psi) copolymerization of ethylene and maleic anhydride in ethylene dichloride using benzoyl peroxide as initiator.

All of these materials are high polymers, the ethylene–maleic anhydride copolymer having the lowest weight-average molecular weight, a value of about 30,000.

Samples for nmr investigations were prepared as 15% (wt/vol) solutions in the appropriate solvents, water for the polyelectrolytes and chlorobenzene for the poly(methyl methacrylates).

Results

A. Poly(methacrylic acid). The noise-decoupled ^{13}C nmr spectrum of atactic poly(methacrylic acid), $+CH_2C(CH_3)(COOH)+_x$, at pH 11 is shown in Figure 1a. The lowest field line (δ_{TPS} 189.5) is assigned to carboxyl carbon, the highest field line (δ_{TPS} 22) to methyl carbon; those at $\delta_{TPS} \sim 48$ are assigned to quaternary carbon, with the very weak, barely discernible line at about δ_{TPS} 55 assigned to the methylene carbon. These assignments are similar to those made by Johnson, Heatley, and Bovey[3] interpreting the ^{13}C nmr spectrum of poly(methyl methacrylate). The carboxyl and quaternary carbon assignments can be confirmed by an off-resonance experiment (Figure 1b) in which the proton decoupling frequency has been shifted from its optimum value by about 500 Hz. The carboxyl and quaternary lines, arising from carbons which have no direct coupling with protons, are not substantially affected.

The spectrum obtained from highly isotactic poly(methacrylic acid) at pH 11 is shown in Figure 1c. The spectrum is relatively simple, and has sufficiently sharper lines so that the methylene carbon resonance is now clearly discernible. (The two lines centered around δ_{TPS} 139.5 arise from the carbons of hexafluorobenzene, whose ^{19}F signal is used in the field-frequency control system. The varying intensities of these signals from spectrum to spectrum are due to the use of different concentrations of C_6F_6 in different kinds of sample cells.)

(10) I. J. Lowe and R. E. Norberg, *Phys. Rev.*, **107**, 46 (1957).
(11) The program was supplied by Fabri-Tek Instruments, Inc., Madison, Wis.
(12) M. Nagasawa, T. Murase, and K. Kondo, *J. Phys. Chem.*, **69**, 4005 (1965).
(13) The isotactic triad concentrations of some of the poly(methyl methacrylates) prepared in this way have been characterized by proton nmr as greater than 96%: R. C. Ferguson, *Macromolecules*, **2**, 237 (1969).

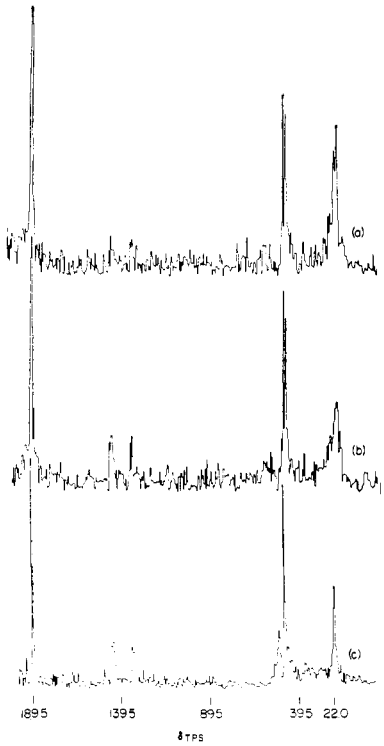

Figure 1. Fourier transforms of the natural abundance ^{13}C nmr free induction decays of water solutions (a) of atactic poly(methacrylic acid) at pH 11 with all proton–carbon spin–spin interactions removed, (b) of the same material with these interactions only partially removed, and (c) of isotactic poly(methacrylic acid) at pH 11 with spin–spin interactions removed. The free induction decays were obtained by sampling the receiver output using 1024 channels of a time averaging computer internally swept at a rate of 100 μsec/channel; 4000 scans were accumulated. The total time required for data accumulation and manipulation was 7 min for each spectrum.

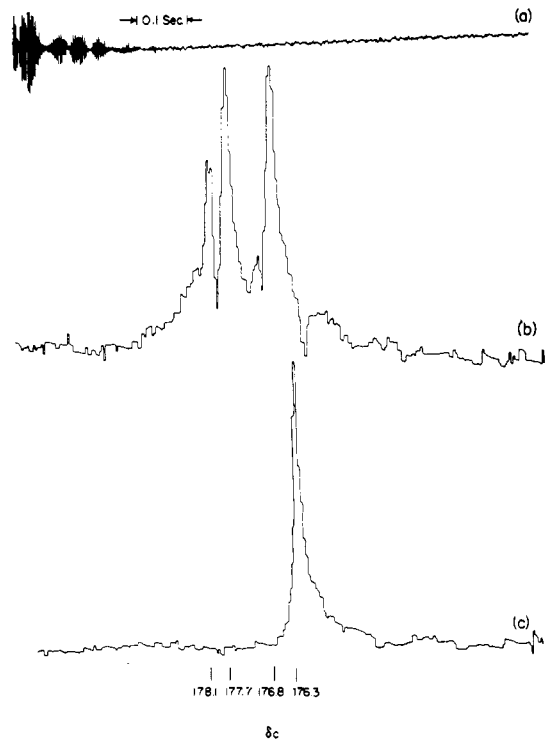

Figure 2. (a) The noise-decoupled, natural abundance, carbonyl ^{13}C nmr free induction decay of a solution of atactic poly(methyl methacrylate) in chlorobenzene, (b) its Fourier transform, and (c) the corresponding Fourier transform of a solution of highly isotactic poly(methyl methacrylate). The free induction decay was obtained by sampling the receiver output using 1024 channels of a time averaging computer internally swept at a rate of 1000 μsec/channel; 16,000 scans were accumulated in 4.5 hr. The transform required 30 sec.

The identification of the material whose spectrum appears in Figure 1c as highly isotactic poly(methacrylic acid) was made on the basis of the ^{13}C nmr spectrum of the precursor poly(methyl methacrylate). This spectrum and that of a predominantly syndiotactic poly(methyl methacrylate) are shown in Figures 2 and 3. Both the carbonyl carbon spectrum (Figure 2) and quaternary carbon spectrum (Figure 3) of the former material consist of essentially single lines with chemical shifts consistent with isotactic assignments. (The chemical shift values differ from those quoted by Johnson, Heatley, and Bovey[4] by about 1 ppm, resulting from the fact that those authors used neat CS_2 as an external reference material.)

The spectral line shapes and intensities of the poly(methyl methacrylate) spectra obtained with delays between pulses on the order of 20 sec were the same as those obtained with delays of only 1 sec, and the same as the previously reported CW spectra.[4] These parameters were also independent of frequency offsets of the ^{13}C rf carrier. The effective transverse relaxation times for viscous polymer solutions are sufficiently short that very small pulse spacings can be used without affecting the ^{13}C nmr line shape or position.[6] This may not always be true for the pulse spacing of 0.1 sec occasionally used to obtain spectra with sweep widths of

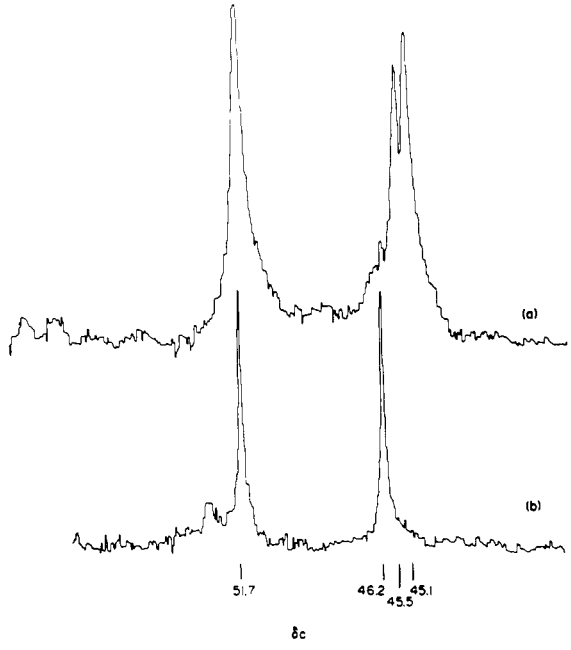

Figure 3. The ^{13}C nmr spectra of the ester methyl and quaternary carbons of (a) atactic and (b) isotactic poly(methyl methacrylate). The spectra were obtained as described in the caption to Figure 2.

5000 Hz. Although no obvious distortions are apparent, spectra obtained using very short pulse spacings are used only for qualitative purposes.

An expanded version of the ^{13}C nmr spectrum of the carboxyl carbon of atactic poly(methacrylic acid) at pH 5 is shown in Figure 4a. Because of the rapid exchange of carboxyl protons, each structurally unique carboxyl carbon produces a single ^{13}C nmr line whose position depends on the pH. Two major lines are observed in Figure 4a and, in order of increasing magnetic field, are assigned to syndiotactic and heterotactic triads, respectively. Just as for the free-radical-initiated poly(methyl methacrylate), this polymer is predominantly syndiotactic with the isotactic triad concentration very low, in this case, not observable.[14] At pH 11 the distinction between the different stereochemical configurations has disappeared (Figure 4b), and the single observed line is shifted about 2 ppm to lower field. Similar downfield shifts have been observed and discussed by Hagen and Roberts in studies of small carboxylic acids.[15] The carboxyl carbon resonance from the isotactic poly(methacrylic acid) at pH 11 appears at the same field position as that from the atactic carboxyl carbon at this pH (Figure 4c).

The behavior of the quaternary carbon resonance of poly(methacrylic acid) with changing pH is substantially different from that of the carboxyl carbon and is shown in Figure 5. At lower pH, resonances which are assigned to heterotactic and syndiotactic triads in the atactic polymer are observed, with the effects of next-nearest steric configurational neighbors splitting these lines. The position of the major syndiotactic triad line is at high field relative to the other quarternary carbon lines, a reversal from the relative positions of the carboxyl carbon lines of the same triads. Comparing relative intensities with the relative intensities of the carboxyl carbon lines in the same sequences indicates that some of the resonances from the quaternary carbons in syndiotactic triads may be shifted downfield from the major line by next-nearest neighbor shielding. At higher pH, all of the lines have been shifted to lower field by about 1 ppm, but most of the stereochemical distinctions remain (Figure 5b). The resonance of the quaternary carbon of the isotactic poly(methacrylic acid) at the higher pH (Figure 5c) is at lower field than any of the lines of the atactic polymer, which is consistent both with the ordering of the line assignments for the atactic polymer and the absence of any significant concentration of istotactic triads in the atactic (predominantly syndiotactic) polymer.

B. Poly(acrylic acid). The ^{13}C nmr spectra of free-radical-initiated poly(acrylic acid), $+CH_2CH(COOH)+_x$, over a wide pH range have also been obtained. The carboxyl carbon spectra are less interesting than those of poly(methacrylic acid) in that only a single line is observed. The carboxyl carbon resonance is sensitive to the pH but, except for some broadening

(14) Comparing intensities from similar carbons which differ only in structural or steric configurations several bonds distant is acceptable. Under these conditions differences in nuclear Overhauser effects will be small, as will differences in relaxation times. See ref 6 for a discussion of relative line intensities in Fourier transform nmr spectra.

(15) R. Hagen and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 4504 (1969).

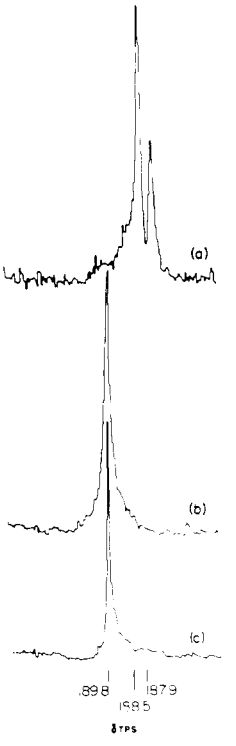

Figure 4. The ^{13}C nmr spectra of the carboxyl carbon of atactic poly(methacrylic acid) at (a) pH 5 and (b) pH 11. (c) The corresponding spectrum of isotactic poly(methacrylic acid) at pH 11. The spectra were obtained as described in the caption to Figure 2.

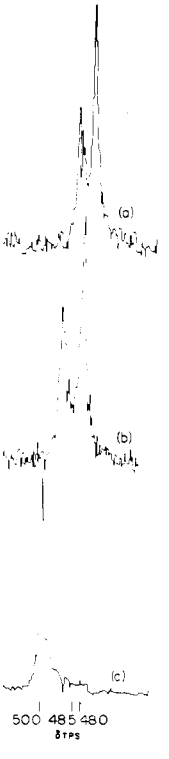

Figure 5. The ^{13}C nmr spectra of the quaternary carbon of atactic poly(methacrylic acid) at (a) pH 5 and (b) pH 11. (c) The corresponding spectrum of isotactic poly(methacrylic acid) at pH 11. The spectra were obtained as described in the caption to Figure 2.

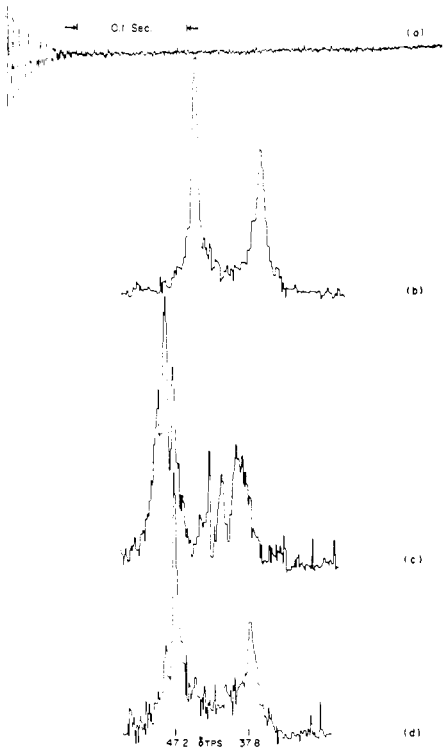

Figure 6. (a) The noise-decoupled, natural abundance ^{13}C nmr free induction decay from a water solution of poly(acrylic acid) at pH 5 and (b) its Fourier transform. Only the methine and methylene carbon regions are shown. The corresponding spectra of (c) poly(acrylic acid) at pH 8 and of (d) isotactic poly(acrylic acid) at pH 8. The free induction decay was obtained by sampling the receiver output using 1024 channels of a time averaging computer internally swept at a rate of 400 μsec/channel; 16,000 scans were accumulated in less than 2 hr. The transform required 30 sec. The isotactic poly(acrylic acid) solution was four times more dilute than the others. As long as the pH is the same, the chemical shifts of the polyacids are independent of the concentration within experimental error.

at high pH, is insensitive to steric configuration. However, the methine and methylene carbon spectra of poly(acrylic acid) are sensitive to steric configuration as shown in Figure 6. At high pH, the lower field methine carbon resonance splits into three lines (Figure 6c) with intensity ratios of about 1:2:1, consistent with assignment to syndio-, hetero-, and isotactic triads and with the known random steric configuration of this polymer.[16] The methylene carbon region at this pH is very complicated, indicating a sensitivity to long-range steric configuration. Isotactic sequences contribute mostly to the high-field portions of both methine and methylene regions as established by comparison to the spectrum of the predominantly isotactic polymer at high pH, shown in Figure 6d.

The pH-dependent shifts of various carbons in iso- and syndiotactic triads of poly(methacrylic acid) and poly(acrylic acid) relative to the shifts of the corresponding carbons in heterotactic triads are shown in Figure 7. Only relative chemical shifts measured from the same solution are plotted to avoid errors in the accurate determination of the pH of occasionally very viscous polymer solutions. The relative shifts fall along two approximately straight lines. One line represents those steric configurations whose carbon resonances are at low field relative to the resonances of corresponding carbons in heterotactic sequences at each pH, and the other represents those resonances at high field. The same segmental, steric configurations are not represented by the same line for both polyacids. This is not surprising since these two polyacids are members of different classes of vinyl polymers having significantly different kinds of steric interactions, local conformations, and hence relative ^{13}C chemical shifts.

C. Ethylene–Maleic Anhydride Copolymers. The carboxyl carbon resonances of completely alternating ethylene–maleic anhydride copolymers, $+CH_2CH_2CH(COOH)CH(COOH)+_x$, are shown in Figure 8. At extremely low pH, only a single major line is observed (Figure 8a) with a minor line probably due to small concentrations of structural defects or end effects. At somewhat higher pH, the carboxyl carbon line is split into two lines about 0.15 ppm apart (Figure 8b). This pattern is maintained even at pH values as high as 11. The separation of the lines is unaffected by the addition of salts to the solution and only slightly reduced by the addition of methanol. Resolving the copolymer carboxyl lines at high but not low pH is opposite to the situation for poly(methacrylic acid) but similar to the situation for poly(acrylic acid). The two copolymer lines are assigned to iso- and syndiotactic placements of adjacent carboxyl groups with longer range effects not observable because of the intervening ethylene units. The two tactic placements are present in equal concentrations because of the apparent absence of any selectivity when the maleic anhydride units in the chain are hydrolyzed to form the polyelectrolyte. The choice of which line belongs to which steric configuration is, at this point, arbitrary. No stereochemical information is available from the spectra of the other carbons of the copolymer which are broader and unresolved.

Even though a rather narrow sweep range was used to obtain the spectra of Figures 8a and 8b (500 Hz), the improvement in sensitivity using pulsed rather than continuous wave techniques can be appreciated by comparison of these two spectra with the CW spectra of Figures 8c and 8d. The CW spectra are of the same samples, obtained in comparable lengths of time, using the same basic spectrometer. The improvement in the signal to noise ratio is more than an order of magnitude. This is expected theoretically[5] since the ratio of longitudinal to transverse relaxation times for a moderately viscous polymer solution is seldom much greater than one even though both relaxation times are short.

The dependence on pH of the chemical shift of the carboxyl carbon of the ethylene–maleic anhydride copolymer is presented in Figure 9. Because it is easier to remove the first carboxyl proton of the dibasic acid, there is a pronounced break in the titration curve which is easily seen from both nmr and potentiometric data, the latter having been reported earlier.[17] The separation of the two carboxyl steric dyad lines does

(16) K. Matsuzaki, T. Uryu, A. Ishida, T. Ohki, and M. Takeuchi, *J. Polym. Sci., Part A-1*, 5, 2167 (1967).

(17) See the discussion in H. Morawetz, "Macromolecules in Solution," Interscience, New York, N. Y., 1965, p 355.

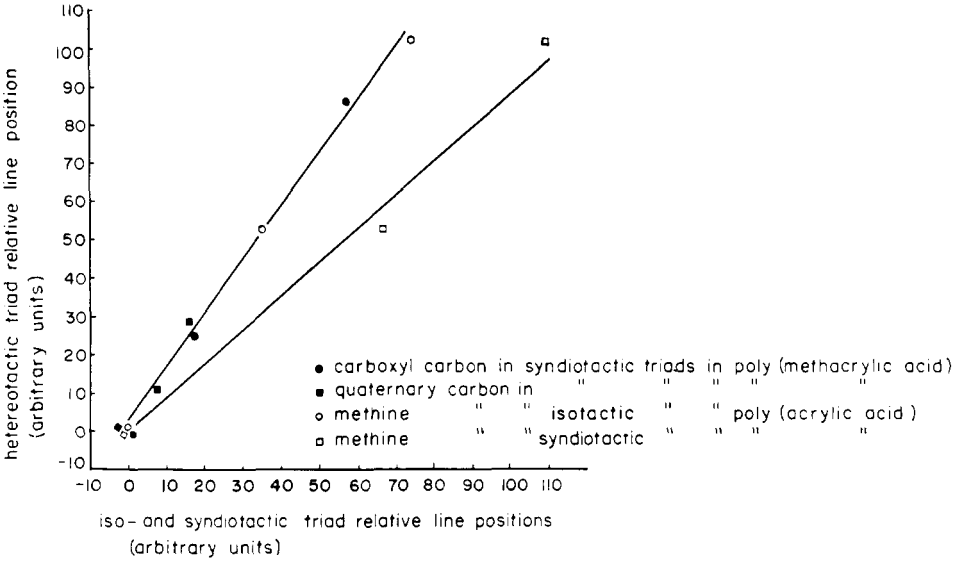

Figure 7. A plot of the ^{13}C chemical shifts of carbons of poly(methacrylic acid) and poly(acrylic acid) in iso- and syndiotactic triads relative to the shifts of the corresponding carbons in hetereotactic triads for several pH values.

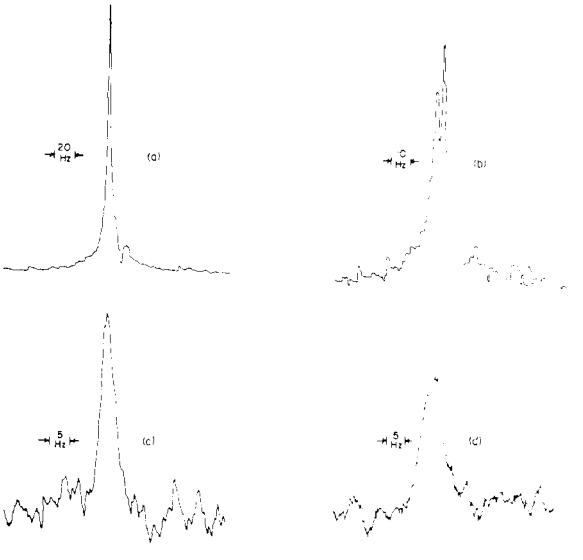

Figure 8. The ^{13}C nmr spectra of the carboxyl carbons of a water solution of ethylene–maleic anhydride at (a) pH 1.75 and (b) pH 3.88. The spectra were obtained as described in the caption to Figure 2 except that only 4000 scans were accumulated during a 1-hr period for (b). The corresponding spectra obtained with the spectrometer operating in the CW mode are presented in (c) and (d), respectively. The CW spectra are the accumulations of 500 scans, each scan taken at a rate of 5 Hz/sec and covering a sweep width of 125 Hz. The total time required to obtain each of these two spectra was 3.5 hr.

not have the same kind of pH dependence as illustrated in Figure 10. The two lines are little better resolved at pH 11 than they were at pH 4.

Discussion

The water solutions of poly(methacrylic acid), poly(acrylic acid), and the ethylene–maleic anhydride copolymer have ^{13}C nmr spectra which are pH dependent in a significant way. That is, the dependence is more than just a shift of the entire spectrum, but rather involves a change in the degree to which stereochemical differences within the chains are distinguishable. There are two possible principal causes for these relative line shifts: (1) a change in the nature of the substituents (together with the solvent surrounding the substituents) and (2) a change in the local conformation of the chain. Both of these can alter the relative electron density distribution in chain segments of different configuration. Only one of these effects seems to be operative

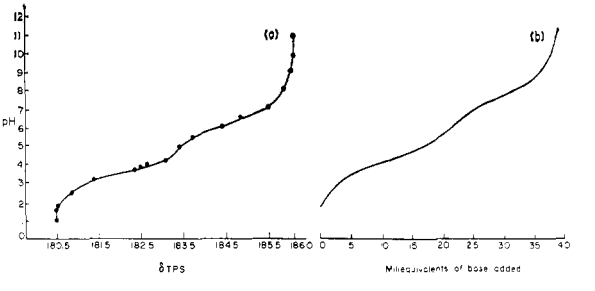

Figure 9. (a) A plot of the chemical shift of the carboxyl carbon of a water solution of ethylene–maleic anhydride as a function of the pH. (b) A similar plot obtained from an ordinary potentiometric titration. The break in the titration curve is due to the dissimilarity of the two carboxyl groups.

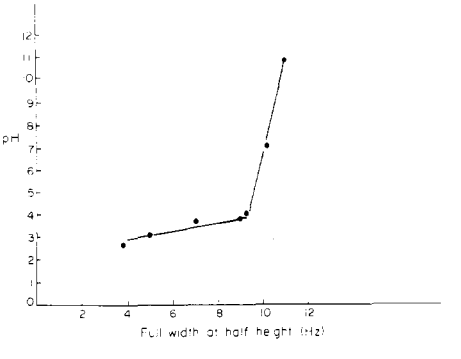

Figure 10. A plot of the width of the carboxyl carbon resonance of a water solution of ethylene–maleic anhydride as a function of pH.

here as suggested by the form of the pH dependence of the relative shifts (*cf.* the following).

Despite the fact that a detailed explanation is not yet available as to how the charge on a carboxyl group affects the chemical shifts of both the carboxyl and adjacent carbons,[15,18] it is clear that the observed shifts are dependent both on the degree of ionization of the carboxyl group and on the charge-dependent parameters of the connecting covalent bonds. The fact that we are dealing here with *relative* shifts of carbons in different segmental configurations, rather than with an absolute shift of a carbon in a single configuration,[19] means that only *differences* in bonding parameters (resulting from the effects of *differences* in steric configuration and hence conformation) are of importance. A significant abrupt change in the local conformation of a vinyl polymer would affect these small differences in bond parameters since all the corresponding carbons in the various steric configurations are unlikely to be affected in exactly the same way by such a change. Hence, a local conformational change for poly(methacrylic acid) and poly(acrylic acid) would produce a change in slope in a plot of the shifts of carbons in iso- and syndiotactic triads *relative* to those in heterotactic triads. We suggest that the absence of a significant break or change in slope in the plot of relative shifts for different pH values (Figure 7) indicates the absence of a local conformational change for these two polyacids.[20]

This conclusion has additional experimental support. In an independent study,[21] Muroga, Noda, and Nagasawa showed that isotactic poly(acrylic acid) underwent no significant change in local conformation as a function of pH. They determined this on the basis of an absence of any pH dependence of the vicinal proton–proton coupling constant which is known to be sensitive to geometry. The coupling constant was independent of pH even though the relative chemical shifts of the nonequivalent methylene protons were not.

A definite statement cannot be made in interpreting the change in the ethylene–maleic anhydride ^{13}C nmr spectra as a function of pH. A plot of relative shifts of carbons in different steric configurations against pH does show a pronounced break (Figure 10), but it is not clear whether this break is due to a change in the local conformation or to a drastic change in the chemical shift dependence on charge as the second of the two carboxyl groups is titrated in the dibacid acid. (The same break is obtained regardless of whether the data are plotted as in Figure 7 or as in Figure 10.) Nevertheless, the smallness of the pH dependence, involving a maximum relative shift of only 0.15 ppm despite the proximity of the two carboxyl groups, and the absence of a pH dependence of the spectra of the other carbons in the polymer suggest that any change in the local chain conformation is small. Thus, an unchanged *local* conformation[22] in fairly concentrated water solutions under a variety of conditions seems to be a general feature of a wide range of synthetic polyelectrolytes.

Acknowledgment. The author thanks Dr. E. M. Mottus, Central Research Department, Monsanto Co., for preparation of the isotactic poly(methyl methacrylate) and Mr. D. A. Bude, also of Central Research Department, for preparation of the other polymers used in this study.

(18) W. J. Horsley and H. Sternlicht, *J. Amer. Chem. Soc.*, **90**, 3738 (1968).

(19) Eventually a reliable theoretical understanding of ^{13}C chemical shifts and their relationship to nearby charge centers will permit the use of the absolute shifts for characterization of biological as well as synthetic polyelectrolytes.

(20) Even though only a few points are available for each plot, they were taken at crucial pH values on both sides of the inflection points of the titration curves of the concentrated polyacid solutions. For poly(methacrylic acid) the pH values were chosen as 5, 7, and 11, while for poly(acrylic acid) the values were 2, 5, and 8.

(21) Y. Muroga, I. Noda, and M. Nagasawa, *J. Phys. Chem.*, **73**, 667 (1969).

(22) Even though the short-range, local conformation is unchanged, a long-range interaction between charged segments may still result in an expansion of a polyion. See M. Fixman, *J. Chem. Phys.*, **41**, 3772 (1964), and ref 17.