polyethylene sample used was a Marlex 6009 type whole polymer. The critical concentration was measured by the phase–volume ratio method.[3-5]

Figures 5 and 6 sketch the general behavior of the lines of constant m_w and those of constant m_z. The latter are fully determined by eq 7 in terms of the m_w mapping. Conversely, the m_z mapping (together with its boundary $m_z = m_w$, see Figures 5 and 6) also fully determines the m_w mapping. This follows because, given $m_z = m_z(\varphi)$ at fixed temperature T, we can obtain $m_w = m_w(\varphi)$ by integrating eq 7 in its alternative form

$$m_z = [\partial(m_w\varphi)/\partial\varphi]_T \tag{8}$$

thus

$$m_w = [m_0\varphi_0 + \int_{m_0}^{m_z}(\mathrm{d}\ln m_z^*/\mathrm{d}\varphi)^{-1}\,\mathrm{d}m_z^*]/\varphi \tag{9}$$

The integration starts from any point ($m_0 = m_w = m_z$, $\varphi = \varphi_0$) on the fat lines in Figures 5 and 6, and proceeds horizontally to the right. In principle, the mappings of Figures 5 and 6 can be determined experimentally by finding the critical points of fractions with narrow distributions and known mixtures thereof. Once Figures 5 and 6 are known, a single measurement of the critical point (φ_c, T_c) determines both m_w and m_z of any polymer distribution. Measurements are now being carried out to collect the data needed for constructing graphs like Figures 5 and 6 for actual systems (cyclohexane–polystyrene and diphenyl ether–polyethylene).

Finally, it may be of interest to derive ψ and hence $g(\varphi, T)$ (eq 6) from the mappings in Figures 5 and 6. To this end, we may use the m_w mapping and evaluate ψ from it by integrating twice eq 4, thus

$$\psi = -\int_0^{\phi}\int_0^{y}\frac{1}{xm_w(x, T)}\,\mathrm{d}x\,\mathrm{d}y - (1 - \phi)\ln(1 - \phi) + \phi[g(0, T) - 1] \tag{10}$$

We have used

$$\left(\frac{\partial\varphi}{\partial\psi}\right)_{T,\varphi=0} = g(0, T) \tag{11}$$

which follows from eq 6. We deduce that $m_w(\varphi, T)$ does not fully determine g, except when supplemented by the value of g at infinite dilution ($\varphi = 0$), which arises as an integration constant.

Acknowledgment. The authors are indebted to Mr. L. A. Kleintjens (Centraal Laboratorium, DSM) for his skilful performance of the measurements underlying Figure 4.

Carbon-13 Nuclear Magnetic Resonance Analysis of Ethylene Oxide–Maleic Anhydride Copolymers

Jacob Schaefer

Central Research Department, Monsanto Company, St. Louis, Missouri 63166.

Received October 4, 1968

ABSTRACT: Natural abundance ^{13}C white noise decoupled nmr spectra of poly(ethylene oxide) and some ethylene oxide–maleic anhydride copolymers have been obtained at 25.1 MHz. The copolymer spectra are interpreted in terms of triads and pentads of monomers in the chain providing both short- and long-range information about chain structure. The relative chemical shifts of the carbons in the central units of these sequences are opposite to and more than an order of magnitude larger than those of the protons in the same units. The ^{13}C shifts correlate with differences in the local π-electron density, while the ^{1}H shifts correlate with neighbor anisotropic shielding effects of adjacent functional groups.

The ^{1}H nmr spectra of copolymers can usually be interpreted in terms of triads of monomer units in the chain.[1] The relative chemical shifts of the protons of a unit in the chain depend on the identity of the two nearest neighbor monomer units. (Only rarely are sizable effects of more distant units in the chain observed.[2]) For a given central unit even these triad shifts are generally small, amounting to only a fraction of a part per million. This makes interpretation of the spectra difficult, especially if the resonances show the dipolar broadening characteristic of proton nmr polymer spectra. In addition, the proton nmr spectra of most copolymers are complicated by spin–spin coupling which does not itself contain any sequence information and which often cannot be conveniently removed by homonuclear decoupling techniques.

The extensive range of ^{13}C chemical shifts, the absence of significant dipolar broadening, and the simplicity of spectra in which all spin–spin interactions can be removed by heteronuclear decoupling make the ^{13}C nmr analysis of copolymers attractive enough to overcome the disadvantage of low sensitivity. This paper reports the analysis of the natural abundance ^{13}C nmr spectra of some ethylene oxide–maleic anhydride copolymers.

Experimental Section

Natural abundance ^{13}C nmr spectra were obtained using a Varian HA-100 spectrometer operating at 25.1 MHz. An

---

(1) For a recent review see James C. Woodbrey in "The Stereochemistry of Macromolecules," Vol. III, A. D. Ketley, Ed., Marcel Dekker Inc., New York, N. Y., 1968.

(2) For some examples see K. H. Hellwege, U. Johnsen, and K. Kolbe, *Kolloid-Z.*, **214**, 45 (1966), and U. Johnsen and K. Kolbe, *ibid.*, **220**, 145 (1967).

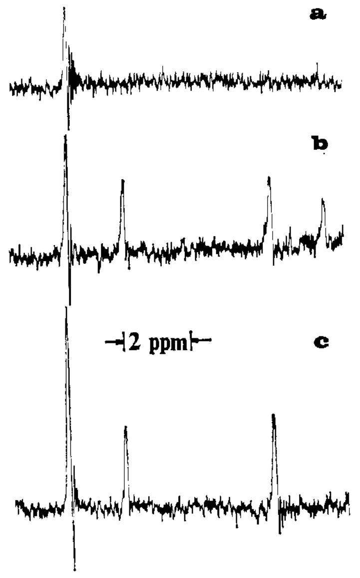

Figure 1. White noise spin-decoupled, natural abundance 25.1 MHz ^{13}C nmr spectra of $CDCl_3$ solutions of (a) poly(ethylene oxide), (b) ethylene oxide–maleic anhydride copolymer containing 74% ethylene oxide, and (c) ethylene oxide–maleic anhydride copolymer containing 80% ethylene oxide. Only the resonances from the ethylene oxide units are shown. Spectrum a is the accumulation of 400 scans and spectra b and c are the accumulations of 1600 scans. Each scan swept 250 Hz in 25 sec. All sweep scales are equal. The magnetic field increases from left to right.

internal field–frequency lock signal was provided by ^{13}C-enriched methanol included in the solvent. Carbon–proton spin–spin interactions were removed by white noise modulation techniques.[3] The 100-MHz output of a Hewlett-Packard 5105A-5110B frequency synthesizer was phase modulated by a Hewlett-Packard 3722A noise generator, amplified by a Boonton 230A radiofrequency power amplifier, and applied to the coils of a double-tuned, thermostated nmr probe. This permitted simultaneously decoupling all protons over a band width of about 500 Hz with an operating probe temperature of no more than about 40°. Low-power, frequency-swept spectra were obtained and accumulated by driving a Beckman 9010 function generator with the ramp voltage (reversed in sign) from a Varian C-1024 time-averaging computer operating in the internal trigger mode.

Details of the synthesis and characterization (by glpc and proton nmr) of the ethylene oxide–maleic anhydride copolymers will be presented elsewhere.[4] The copolymer is a poly(ester ether), $-C(=O)CH=CHC(=O)O(CH_2CH_2O)_X-$, in which consecutive maleic anhydride units do not occur and which has an average molecular weight of about 5000. Samples for nmr analysis were made from approximately 10% (by weight) solutions of polymer in $CDCl_3$ or DMSO, each solvent containing about 25% (by volume) ^{13}C-enriched methanol. Standard 5-mm o.d. nmr tubes were used.

Results

The 25.1-MHz natural abundance ^{13}C-[^1H(noise)] nmr spectra of poly(ethylene oxide) and the ethylene oxide units of two ethylene oxide–maleic anhydride copolymers of different composition are shown in Figure 1. The copolymer spectra can be interpreted in terms of triads of monomers in the chain. By comparison to the single line of the poly(ethylene oxide) spectrum in Figure 1a, the lowest field copolymer line in Figure 1b is assigned to A*A*A triads. (The notation A = $-CH_2CH_2O-$ and B = $-C(=O)CH=CHC(=O)O-$ is used.) The highest field line in Figure 1b is assigned to B*A*B triads since this line does not appear in Figure 1c, which is the spectrum of a copolymer with a lower maleic anhydride content.[5] The remaining two lines of the spectra of Figures 1b and 1c are assigned to the two different types of carbons in B*A*A,A*A*B triads. The line assignments are presented in Table I. The relative triad concentrations obtained from these assignments are given in Table II and compared to the corre-

TABLE I

LINE ASSIGNMENTS FOR ^{13}C NMR SPECTRA OF ETHYLENE OXIDE UNITS OF ETHYLENE OXIDE–MALEIC ANHYDRIDE COPOLYMERS

Sequence			Line position[a] (Hz) at 25.1 MHz
$-\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O$	$\mathit{C}H_2\mathit{C}H_2O$	$\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O-$	339
$-\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O$	$\mathit{C}H_2CH_2O$	CH_2CH_2O-	379
$-CH_2CH_2O$	$CH_2\mathit{C}H_2O$	$\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O-$	
$-\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O$	$CH_2\mathit{C}H_2O$	CH_2CH_2O-	484
$-CH_2CH_2O$	$\mathit{C}H_2CH_2O$	$\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O-$	
$-CH_2CH_2O$	$\mathit{C}H_2\mathit{C}H_2O$	CH_2CH_2O-	528

[a] As measured downfield from the spin-decoupled line of $^{13}CH_3OH$ present as 25% (by volume) in $CDCl_3$ at 40°. Accuracy is ±1 Hz.

TABLE II

RELATIVE TRIAD CONCENTRATIONS FROM NMR ANALYSES OF ETHYLENE OXIDE–MALEIC ANHYDRIDE COPOLYMERS[a]

Ethylene oxide in copolymer,[b] mol %	Nuclear probe	A*A*A	B*A*A, A*A*B	B*A*B
74	^{13}C	0.38	0.52	0.10
74	^1H	0.39	0.52	0.09
80	^{13}C	0.50	0.50	0.00
80	^1H	0.50	0.49	0.01

[a] Estimated accuracy is ±0.03 for ^{13}C triads and ±0.01 for ^1H triads. [b] See ref 5.

---

(3) R. R. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966).

(4) J. Schaefer, D. A. Bude, and R. J. Katnik, in preparation.

(5) The two copolymers differ in composition by only 6% but were prepared from reaction mixtures in which the ratio of reactants differed by a factor of 2. It is a property of the $SnCl_4$ catalyst that monomer distributions which are distinctly different in some respects can be generated in chains whose total compositions are almost the same, if the ratio of reactants is varied. For example, the BAB contents of two different propylene oxide–maleic anhydride copolymers (where A is propylene oxide and B is maleic anhydride) prepared using $SnCl_4$ as catalyst differ by a factor of 4 even though the over-all compositions of the two chains are identical [R. J. Kern and J. Schaefer, *J. Amer. Chem. Soc.*, **89**, 6 (1967)].

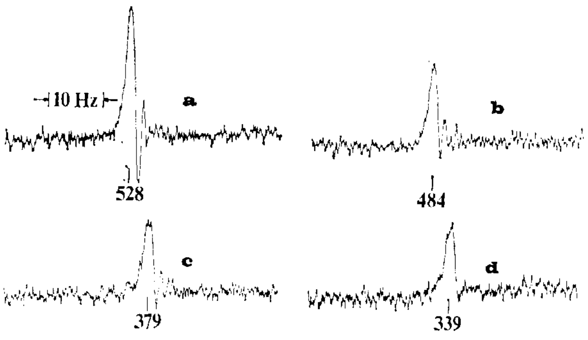

Figure 2. An expanded scale version of Figure 1b. The spectrum shown here was taken in four parts with the lowest field region appearing in a and the highest field in d. The center of the spectrum of Figure 1b in which no resonance appears is not shown. The numbers below the lines give the separation in hertz at 25.1 MHz downfield from the spin-decoupled resonance of $^{13}CH_3OH$. Spectra a, b, and c are the accumulations of 1000 scans and spectrum d is the accumulation of 4000 scans. Each scan swept 50 Hz in 10 sec. Slower sweep rates did not result in narrower lines. All sweep scales are equal. The magnetic field increases from left to right.

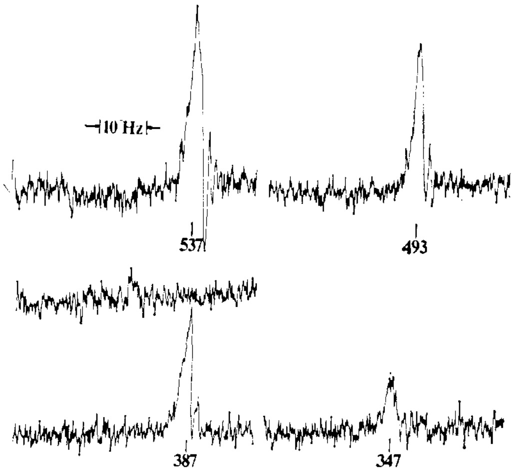

Figure 3. White noise spin-decoupled, natural abundance 25.1 MHz ^{13}C nmr spectrum of a DMSO solution of the ethylene oxide–maleic anhydride copolymer containing 74% ethylene oxide. Only the resonances from the ethylene oxide units are shown. The numbers below the lines give the separation in hertz downfield from the spin-decoupled resonance of $^{13}CH_3OH$. Thus the magnetic field increases from left to right and from up to down. The spectrum was obtained in five parts indicated by the breaks in the figure. Each part is the accumulation of 2500 scans, 50 Hz/10 sec/scan. The observing frequency was always swept from 2550 to 2500 Hz. The ^{13}C-enriched methanol upper side-band lock frequencies were 1975, 2025, 2075, 2125 and 2175 Hz. The centers of the white noise decoupling irradiation bands for these values of the lock frequencies were 99.991620.0, 99.991820.0, 99.992020.0, 99.992220.0, and 99.992420.0 MHz, respectively. The ^{13}C center-band frequency was 25.142070 MHz.

sponding values obtained from proton nmr analysis.[4] The two sets of results are in agreement.

Expanded scale spectra of the ethylene oxide units of the copolymer of Figure 1b in both $CDCl_3$ and DMSO are presented in Figures 2 and 3, respectively, and show very little additional structure. Spectra are presented

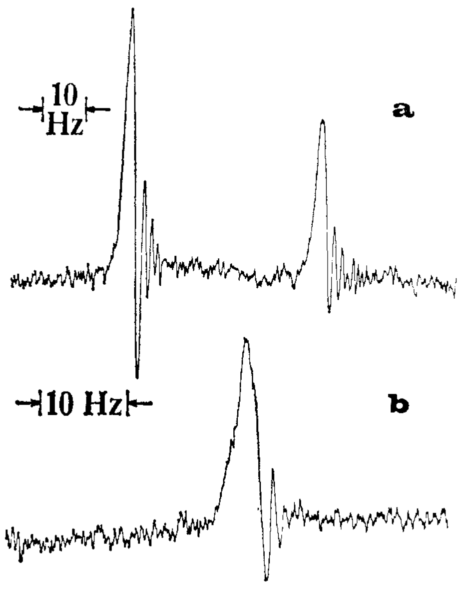

Figure 4. (a) A reduced scale version of the spectra shown in Figures 2a and 2b so that both lines appear in each scan. The spectrum is the accumulation of 1600 scans of 100 Hz/10 sec/scan. The magnetic field increases from left to right. (b) A repetition of the spectrum of the lowest field line shown in Figure 3. The spectrum shown here is the accumulation of 5000 scans of 50 Hz/10 sec/scan. The asymmetry of the lowest field line of Figure 3 is also seen in this figure and may be attributed to the very weak influence of next-nearest neighbors in the chain when DMSO is the solvent.

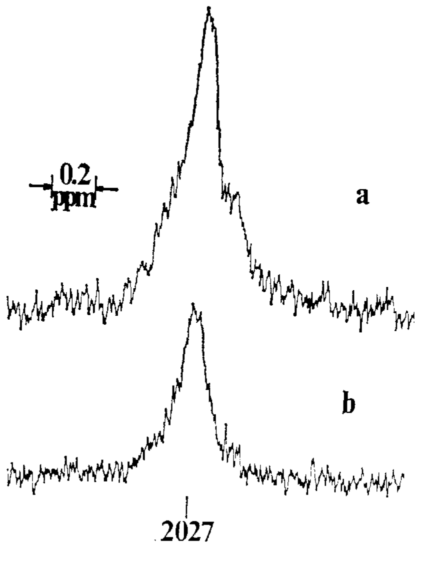

Figure 5. White noise spin-decoupled, natural abundance 25.1 MHz ^{13}C nmr spectra of $CDCl_3$ solutions of ethylene oxide–maleic anhydride copolymer containing (a) 74% ethylene oxide and (b) 80% ethylene oxide. Only the resonances of vinyl carbons in the maleic anhydride units are shown. The number below the line gives the separation in hertz downfield from the spin-decoupled resonance of $^{13}CH_3OH$. Spectrum a is the accumulation of 4000 scans and spectrum b of 2500 scans each of 50 Hz/10 sec/scan. The magnetic field increases from left to right. The center of the white noise decoupling irradiation band was varied over a range of 250 Hz in order to obtain maximum decoupling.

TABLE III

LINE ASSIGNMENTS FOR ^{13}C NMR SPECTRA OF MALEIC ANHYDRIDE UNITS OF ETHYLENE OXIDE–MALEIC ANHYDRIDE COPOLYMERS

Sequence					Line position[a] (Hz) at 25.1 MHz
$-\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O$	CH_2CH_2O	$\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O$	CH_2CH_2O	$\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O-$	2912.0
$-\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O$	CH_2CH_2O	$\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O$	CH_2CH_2O	CH_2CH_2O-	2914.5
$-CH_2CH_2O$	CH_2CH_2O	$\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O$	CH_2CH_2O	$\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O-$	
$-\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O$	CH_2CH_2O	$\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O$	CH_2CH_2O	CH_2CH_2O-	2916.5
$-CH_2CH_2O$	CH_2CH_2O	$\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O$	CH_2CH_2O	$\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O-$	
$-CH_2CH_2O$	CH_2CH_2O	$\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O$	CH_2CH_2O	CH_2CH_2O-	2919.0

[a] As measured downfield from the spin-decoupled line of $^{13}CH_3OH$ present as 25% (by volume) in $CDCl_3$ at 40°. Accuracy is ±0.5 Hz.

in Figure 4 which give an idea of the reproducibility of the results.

The spectra of the maleic anhydride units of the two copolymers are shown in Figures 5 and 6. The spectra of the vinyl carbons are broad and structureless (for a wide range of decoupling bands) while the spectra of the carbonyl carbons have narrow lines (0.5 Hz), which can be interpreted in terms of pentads of monomers in the chain. The pentad line assignments are straightforward and are made by comparing the intensities of the lines in the two spectra, by remembering that consecutive B units do not occur, by realizing that BABAA, AABAB sequences are improbable and BABAB sequences very improbable in the lower maleic anhydride containing copolymer of Figure 6b but not in the copolymer of Figure 6a, and by counting the number of nmr unique carbonyl carbons in the central unit of each pentad. These assignments are presented in Table III and the relative pentad concentrations (in agreement with values from proton nmr measurements[4]) are given in Table IV.

Discussion

The relative chemical shifts of the central carbons of the ethylene oxide units in the triads listed in Table I cover a range of almost 10 ppm compared to a range of about 0.5 ppm for the corresponding relative proton shifts.[4,6] The improvement in the separation of resonances along with the simplicity of a totally spin-decoupled spectrum are advantages which are not as critical to the successful analysis of this particular copolymer as they would be in the analysis of more complicated systems such as, for example, certain biopolymers.

The narrowness of the ^{13}C nmr lines shown in Figures 2 and 3 (less than 2 Hz) and the almost complete lack

TABLE IV

RELATIVE PENTAD CONCENTRATIONS FROM NMR ANALYSES OF ETHYLENE OXIDE–MALEIC ANHYDRIDE COPOLYMERS[a]

Ethylene oxide in copolymer,[b] mol %	Nuclear probe	AA*B*AA	AA*B*AB, BA*B*AA	BA*B*AB
74	^{13}C	0.83	0.17	0.00
74	^{1}H	0.80	0.20	0.00
80	^{13}C	0.53	0.29	0.18
80	^{1}H	0.57	0.28	0.14

[a] Estimated accuracy is ±0.03 for both ^{13}C and ^{1}H pentads. [b] See ref 5.

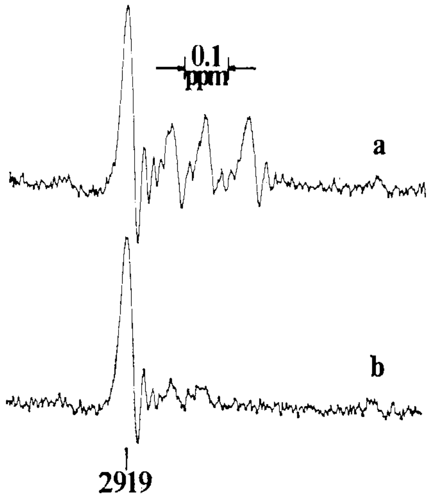

Figure 6. White noise spin-decoupled, natural abundance 25.1 MHz ^{13}C nmr spectra of $CDCl_3$ solutions of ethylene oxide–maleic anhydride copolymer containing (a) 74% ethylene oxide and (b) 80% ethylene oxide. Only the resonances of the carbonyl carbons in the maleic anhydride units are shown. The number below the line gives the separation in hertz downfield from the spin-decoupled line of $^{13}CH_3OH$. Both spectra are the accumulations of 1250 scans, 25 Hz/25 sec/scan. The magnetic field increases left to right.

---

(6) The proton nmr spectra of very similar copolymers are discussed in R. J. Kern and J. Schaefer, *J. Amer. Chem. Soc.*, **89**, 6 (1967), and in J. Schaefer, R. J. Kern, and R. J. Katnik, *Macromolecules*, **1**, 107 (1968).

of any structure to these lines (with the exception of a shoulder on the line in Figure 2d and some reproducible asymmetry in the lines in Figure 3) mean that observable long-range shielding effects are not *general* features of ^{13}C nmr spectra of copolymers at 25.1 MHz. The effect on the chemical shifts of the ethylene oxide units in these ethylene oxide–maleic anhydride copolymers due to variation of next-nearest neighbor monomer units is no more than a few tenths of a hertz even though the effect of varying nearest neighbors is several hundred hertz.

However, the spectra of the carbons in the maleic anhydride units in the same copolymers are affected by long-range shielding effects. Assuming no unusual relaxation effects, the broadness of the vinyl carbon spectra of the maleic anhydride units (Figure 5) can be attributed to the sensitivity of these kinds of carbons to shielding differences in next-nearest neighbors, triply removed neighbors, and so on. The broad band is the sum of many lines. Unfortunately, in this particular system, the broadness ruins the usefulness of these spectra.

The spectra of the carbonyl carbons do not suffer from this defect. Narrow lines are obtained (Figure 6) which do provide long-range information, but only about adjacent units in the chain twice removed. More distant units have no observable effect. The range of relative chemical shifts induced by next-nearest neighbors is about 0.3 ppm compared to a range of 0.02 ppm for the relative chemical shifts of the vinyl protons in the same pentad sequences.[4] Thus the carbonyl carbon pentad lines are completely resolved simplifying intensity measurements.

In addition to being more than an order of magnitude larger, the relative triad and pentad ^{13}C chemical shifts listed in Tables I and III are opposite to those of the corresponding proton shifts. That is, the carbon resonances from A $\mathit{C}H_2\mathit{C}H_2O$ A and AA $\mathit{C}(=O)CH=CH\mathit{C}(=O)O$ AA appear at lower field relative to those from B $\mathit{C}H_2\mathit{C}H_2O$ B and BA $\mathit{C}(=O)CH=CH\mathit{C}(=O)O$ AB, respectively, while the proton resonances from A $C\mathit{H}_2C\mathit{H}_2O$ A and AA $C(=O)C\mathit{H}=C\mathit{H}C(=O)O$ AA appear at higher field relative to those from B $C\mathit{H}_2C\mathit{H}_2O$ B and BA $C(=O)C\mathit{H}=C\mathit{H}C(=O)O$ AB, respectively.[4,6] These reversals cannot be attributed to an unusual solvent effect since the relative shifts are the same in both $CDCl_3$ and DMSO, two quite different solvents. Strong associations between the copolymer and methanol are not responsible since methanol is not a solvent for this copolymer. Furthermore, the triad reversal is in contrast to measurements on some families of small molecules. Measurements of ^{13}C and ^1H chemical shifts in systems such as CH_3X, CH_3CH_2X, $CHX=CHX$, and C_6H_5X (where the electronegativity of X is a variable) have shown that trends in the two kinds of chemical shifts are the same in these systems when the two kinds of nuclei are directly bonded.[7]

The reversals can be explained by assuming that the ^{13}C and ^1H shifts are primarily determined by different factors. Empirical calculations have indicated that the dominant effect in determining large, relative chemical shifts between *carbon* nuclei whose local environments are comparable is the influence of differences in the surrounding electron density distribution.[8] Neighboring bond anisotropy effects can be ignored. Removing electron density (by any mechanism) produces a downfield shift and increasing electron density produces an upfield shift. Since an important contributing valence structure for α,β-unsaturated ketones may be written as $-C^+H-CH=C(O^-)-$,[9] the maleic anhydride units in the chain can be considered sources of available conjugated π-electron density for adjacent units. Thus the electron densities at the carbon nuclei in B $\mathit{C}H_2\mathit{C}H_2O$ B and BA $\mathit{C}(=O)CH=CH\mathit{C}(=O)$AB are probably increased relative to A $\mathit{C}H_2\mathit{C}H_2O$ A and AA $\mathit{C}(=O)CH=CH\mathit{C}(=O)$AA, respectively, and so their resonances will appear at higher field, as is observed. However, the much smaller, reversed, relative proton shifts in the central units of the same sequences are most likely due primarily to the neighbor anisotropic shielding effects of the carbonyl and vinyl groups (known in other systems to produce similar proton shifts[10]) rather than to the influence on the protons of the conjugated π-electron density in the chain backbone. Thus, in general, correlations between ^{13}C and ^1H chemical shifts in complicated molecules should not be expected[11] and those observed in some small molecules may have been exceptions.

In summary, the future of ^{13}C nmr analysis of polymers is promising. First, a stable and sensitive ^{13}C nmr spectrometer can be assembled using the widely available Varian HA-100 as the basic unit. Second, depending on the type of carbon observed, both short- and long-range information about chain structure can be obtained. And finally, interpretation of the totally spin-decoupled spectra is simple because of the large, relative chemical shifts and because even the smaller ^{13}C shifts seem to correspond fairly well to our intuitive ideas about the electron density distributions in molecules.

Acknowledgment. The author wishes to thank Mr. W. B. Frasure for valuable assistance in modifying the HA-100 spectrometer.

---

(7) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961); *Tetrahedron Lett.*, 468 (1961); G. B. Savitsky and K. Namikawa, *J. Phys. Chem.*, **67**, 2755 (1963).

(8) V. B. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 5319 (1967), and references sited therein.

(9) This is the basis for an explanation of the Michael reaction. See, for example, L. F. Feiser and M. Feiser, "Organic Chemistry," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1956, p 699.

(10) See, for example, the discussion of long-range shielding effects in N. S. Bhacca and D. H. Williams, "Applications of Nmr Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964.

(11) Opposite trends in ^{13}C and ^1H chemical shifts of directly bonded nuclei have also been observed in small ring compounds and attributed to the unique electronic character of ring methylene groups (G. E. Maciel and G. B. Savitsky, *J. Phys. Chem.*, **69**, 3925 (1965)) and in charged systems and attributed to electric field perturbations (W. J. Horsley and H. Sternlicht, *J. Amer. Chem. Soc.*, **90**, 3738 (1968)).