Polymer Nuclear Magnetic Resonance Spectroscopy. XIX. Carbon-13 Resonance Observations of Stereochemical Configuration

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ABSTRACT: It is shown that the direct spectra of ^{13}C in natural abundance give useful information concerning the tacticity of vinyl polymers. Poly(vinyl methyl ether), poly(styrene) (isotactic and "atactic"), poly(methyl methacrylate), and poly(propylene) (isotactic and "atactic") are examined. The discrimination of configurational sequences is at least equal to that possible in proton spectra at 220 MHz.

The ^{13}C nucleus is of great potential interest for the study of polymer chains because it permits direct observation of the molecular skeleton, and because its range of chemical shifts is very large, encouraging the hope of seeing finer substructure than can be seen in proton spectra. The observing sensitivity of ^{13}C is low, owing to its natural abundance of only 1.1% and to its relatively small magnetic moment, which is about one-fourth that of the proton. Not all of its properties are unfavorable, however. Its spin is $^1/_2$ and so it has no quadrupole moment. The use of multiple scan techniques on a field-frequency locked spectrometer together with signal enhancement by proton decoupling[2] has made it possible for high-resolution spectra of satisfactory signal-to-noise ratio to be obtained in a matter of hours.

Very little is known of the ^{13}C spectra of polymers. Schaefer[3] has shown that triad and pentad compositional sequences can be discriminated in ethylene oxide–maleic anhydride copolymers, and has measured configurational sequences in propylene oxide homopolymers.[3b] Horsley and Sternlicht[4] measured ^{13}C chemical shifts in amino acids and oligopeptides by observing the ^{13}CH proton side bands using an indor technique. They have also made direct measurements of the ^{13}C spectra of these compounds.[5] In this paper we report the measurement of configurational sequences in vinyl homopolymers by direct ^{13}C observations on unenriched samples.

Experimental Section

A. Materials. Poly(vinyl methyl ether) was obtained from the Monomer–Polymer Division of the Borden Chemical Co. and was found from measurements in *o*-dichlorobenzene at 220 MHz (not reported in detail here) to be predominantly isotactic, appearing to be similar to the material reported earlier.[6] Isotactic poly(styrene) ($\bar{M}_w$ = 494,000; $\bar{M}_v$ = 430,000) was obtained from P. I. Roth (3M Co.) and is the same as that used in a recent study.[7] "Atactic" poly(styrene) ($\bar{M}_w$ = 236,000; $\bar{M}_v$ = 201,000) was obtained from Monomer–Polymer. Poly(methyl methacrylate) was prepared using a free radical initiator, and had a P_m[8] of 0.24. Its 220-MHz spectrum has been previously reported.[9] Isotactic poly(propylene) was obtained from the Monomer–Polymer Division of the Borden Chemical Co., and the atactic polypropylene sample was a commercial polymer "Oletac 100" from Avi-sun Corporation.

B. Methods. Polymer solutions were approximately 50% (wt/vol) in chlorobenzene (except the poly(styrenes), which were dissolved in a mixture of chlorobenzene and $CHCl_3$) and were observed at *ca.* 50°. It is noteworthy that under these conditions, the proton spectra show very broad line widths and that sequences beyond triads cannot be clearly resolved. The ^{13}C spectra were observed by frequency sweep in the absorption mode at 25.14 MHz using a Varian HA-100 spectrometer. The samples were contained in 5 mm o.d. tubes (8 mm for poly(propylene)) with $^{13}CS_2$ as capillary reference and lock signal. Chemical shifts are expressed in parts per million upfield from the $^{13}CS_2$ resonance. Proton decoupling was performed in two ways: (a) by "off-resonance" decoupling,[10] which has the effect of diminishing the spacing in the multiplets (by a factor of about 5 in the present experiments) while preserving their form; and (b) by "white noise" decoupling,[11] which removes the coupling of all protons to ^{13}C. The first technique is employed in order to assign the peaks on the basis of their multiplet structure (see next section). Once assignments have been made in a general way, complete "noise" decoupling is employed in order to increase the effective signal-to-noise ratio.

Off-resonance decoupling and noise decoupling were done using a Varian V-3512-1 heteronuclear spin decoupler.

In order to obtain useful spectra under the conditions described, it is necessary to increase the signal-to-noise ratio by means of spectrum accumulation. This was accomplished using a Varian C-1024 time-averaging computer. The number of scans employed varied from 100 to 3125 and is indicated in the caption for each spectrum.

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(1)(a) Varian Associates; (b) Bell Telephone Laboratories, Inc.

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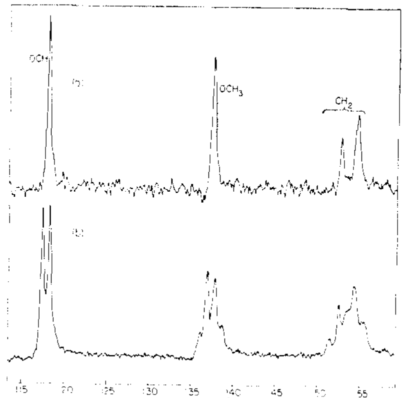

Figure 1. Natural abundance ^{13}C spectra of poly(vinyl methyl ether) (25.14 MHz); 50% (wt/vol) solution in chlorobenzene at *ca.* 50°; (a) protons completely decoupled (50 scans); (b) decoupling "off-resonance" (1038 scans).

The signal-to-noise ratio is increased substantially in the decoupled spectra by the nuclear Overhauser effect. If the observed ^{13}C nucleus normally undergoes spin-lattice relaxation only by interaction with the irradiated proton, the enhancement will be given by

$$\frac{I}{I_0} = 1 + {}^1/_2\left(\frac{\gamma^{1}\mathrm{H}}{\gamma^{13}\mathrm{C}}\right) \simeq 3$$

This theoretical factor has been attained within experimental error for $H^{13}CO_2H$ by Kuhlmann and Grant.[12] Possible variations in enhancement make quantitative measurements of different types of carbon nuclei doubtful in the spectra reported here, but should not affect the relative intensities of the resonances of carbons which differ only in configuration.

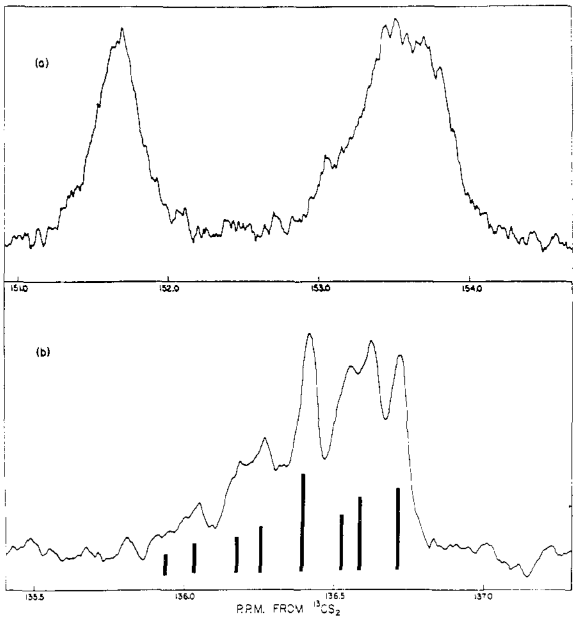

Figure 2. Expanded ^{13}C spectrum of (a) the β-methylene carbons (2128 scans) and (b) the methoxyl carbons of poly(vinyl methyl ether) (200 scans); same conditions as in Figure 1a. The noise level in b is relatively high; bars mark those features believed to represent real peaks.

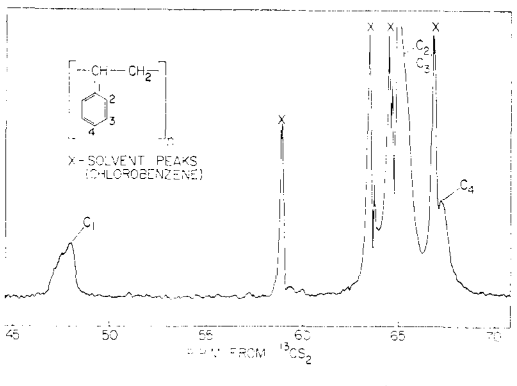

Figure 3. ^{13}C spectrum of the aromatic carbons of "atactic" poly(styrene), 50% solution (wt/vol) in chlorobenzene–chloroform solvent at *ca.* 50°; protons decoupled. The peaks marked X are from chlorobenzene (1639 scans).

Results and Discussion

A. Poly(vinyl methyl ether). In Figure 1 are shown the ^{13}C spectra of poly(vinyl methyl ether) with (a) complete "noise" decoupling and (b) off-resonance decoupling. In b, the α and methoxyl carbons are readily identifiable as the expected doublet and quartet, respectively. The β carbons appear as two overlapping triplets near 155 ppm. These become two well-separated singlets in spectrum a, and from their relative intensities are assigned to racemic and *meso* carbons, in order of increasing chemical shift.

In Figure 2, the β-methylene (a) and methoxyl (b) carbon spectra are shown expanded tenfold. There are indications of fine structure in the *meso*-β-carbon resonance. The methoxyl resonance appears to be the most sensitive to stereochemical configuration. At least eight peaks can be distinguished, so we must be resolving pentad sequences.

B. Poly(styrene). In Figure 3 is shown the aromatic region of "atactic" polystyrene. The peaks marked X, arising from the chlorobenzene solvent, partially overlap those of the 2, 3, and 4 carbons of the phenyl groups. The C_1 carbon resonance at *ca.* 47.5 ppm appears promising for structural studies. Its general form resembles that of the α-proton resonance in poly(β,β-d_2-styrene).[13] In Figure 4(a) is shown the expanded C_1 spectrum. It is clear that here also pentad sequences are being resolved. In Figure 4(b) the spectra of "atactic" and isotactic poly(styrene), obtained from a solution containing both, are shown. This establishes the position of the *mmmm* pentad resonance and also indicates that, in common with all other free radical polymers measured, the "atactic" polymer is probably predominantly syndiotactic, for most of the spectral intensity is upfield from the isotactic resonance. A complete assignment of pentad peaks will require spectra of higher signal-to-noise ratio.

C. Poly(methyl methacrylate). In Figure 5, spectrum a shows the resonances of all the carbons except the carbonyl carbon. Assignments, obtained from the "off-resonance" spectrum (not shown), are indicated on each peak. The triad α-methyl carbon peaks show the same pattern as the α-methyl proton spectrum.[9] A similar but smaller splitting is discernible in the

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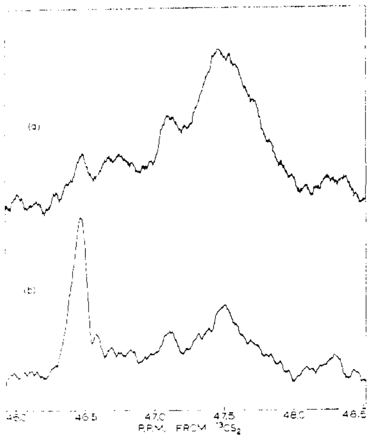

Figure 4. (a) Expanded aromatic C_1 spectrum of "atactic" poly(styrene), same conditions as Figure 3 (3125 scans); (b) C_1 spectrum of mixed atactic and isotactic poly(styrene) (593 scans).

quarternary carbon (*i.e.*, α-carbon) resonance at *ca.* 148 ppm. More interesting is the carbonyl carbon spectrum (b). This shows a clear splitting into pentad resonances; it has the same profile as the α-methyl proton resonance at 220 MHz, but is its mirror image, differing in this respect from the other carbon peaks in this polymer and in the other polymers described in this paper. (Schaefer[3] has observed a similar reversal for the proton and ^{13}C spectra of ethylene oxide–maleic anhydride copolymers.) It is also noteworthy that (on a parts per million scale) the ^{13}C carbonyl spectrum is spread over a tenfold greater range of chemical shifts than the α-CH_3 spectrum.

D. Poly(propylene). Figures 6(a) and 6(b) show, respectively, the complete spectra of highly isotactic and atactic samples of poly(propylene). In the first of these, three singlets are observed, as expected. The chemical shifts are in reasonable agreement with those calculated from additive parameters obtained by Grant and Paul[14] from the ^{13}C chemical shifts in small linear and branched alkanes. Thus the calculated shifts of the methyl, methine, and methylene carbons (referred to $^{13}CS_2$) are, respectively, 173, 166, and 146 ppm, compared to the experimental values of 172, 165, and 147 ppm.

In the spectrum of the atactic poly(propylene), Figure 6(b), all three carbon resonances show stereochemical fine structure. The methyl resonances fall into three distinct groups, which we have assigned as indicated in Figure 6(b) to isotactic, heterotactic, and syndiotactic triads on the basis of a chemical shift comparison with the isotactic polymer. Pentad resonances may also be distinguished but the resolution is insufficient to allow an assignment. The triad intensities indicate that the atactic polymer is essentially of random configuration.

The methine carbon is little affected by the polymer stereochemistry. However, the methylene carbon resonance is split into several components, attributable to tetrad resonances.

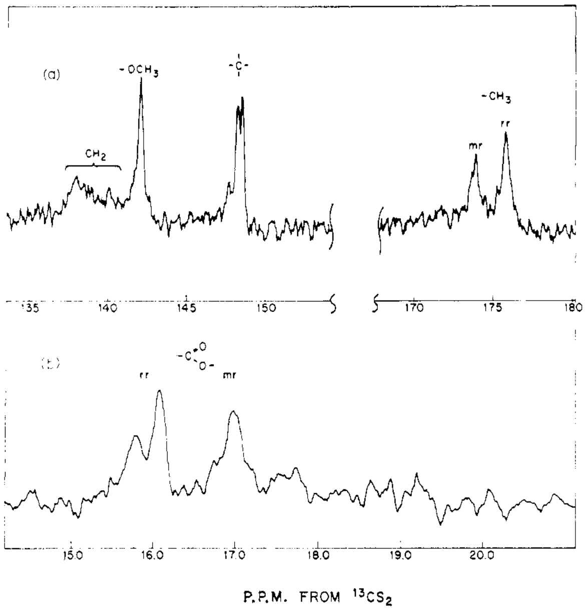

Figure 5. ^{13}C spectrum of predominantly syndiotactic poly(methyl methacrylate); (a) all carbons except the carbonyl carbon, assigned as indicated (225 scans); (b) carbonyl carbon spectrum. Observed using 50% (wt/vol) solution in chlorobenzene at *ca.* 50° (269 scans).

In conclusion, ^{13}C high-resolution nmr promises to be a useful addition to the range of techniques available for studying macromolecules in solution. The information obtained is often complementary to that obtained from proton spectra, and one can also envisage situations where it may be the only method of attack, for instance in studying the conformations of α,α-disubstituted poly(olefins).

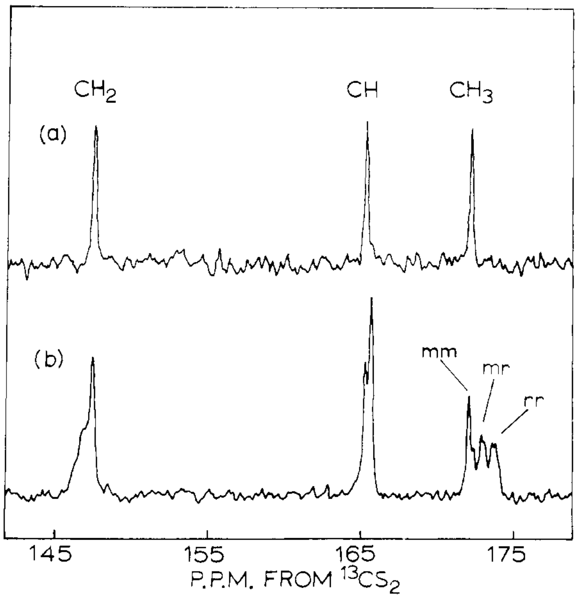

Figure 6. ^{13}C spectrum of poly(propylene): (a) an isotactic sample, *ca.* 5% (wt/vol) in *o*-dichlorobenzene at 60° (100 scans); (b) an atactic sample, *ca.* 30% (wt/vol) in *o*-dichlorobenzene at 60° (100 scans).

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