Use of Noise-Modulated Partial Decoupling in the Interpretation of the Carbon-13 Nuclear Magnetic Resonance Spectra of Polymers

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ABSTRACT: In a decoupling experiment with random noise, a component of the central line of a triplet is unaffected by the perturbation of the random noise. This component, which involves antisymmetric spin states independent of the spatially coherent noise, stays sharp even when the decoupling is incomplete and other kinds of lines in the spectrum are broadened. Since the methylene-carbon triplet has such a component while the methine-carbon doublet does not, this simple partial decoupling experiment can be used to distinguish methine- from methylene-carbon lines. In the ^{13}C spectra of some polymers, this is, in fact, the most direct way of identifying the two kinds of lines. As an illustration, methine- and methylene-carbon line assignments are made for the ^{13}C nmr spectrum of a high molecular weight, solid poly(propylene oxide), even though similar assignments, based either on spin–lattice relaxation times or single-frequency off-resonance decoupling experiments, are ambiguous.

The first step in the interpretation of a proton-decoupled ^{13}C nmr spectrum of a polymer is the decision of which lines arise from which kinds of carbons. The characteristics of quaternary- and methyl-carbon lines are sufficiently unique that their identification is seldom a serious problem, but for the main-chain methine and methylene carbons, the assignment is often difficult. As illustrated by the chemical shift correlation diagram of Figure 1, either line can occur at higher relative magnetic field, and, in fact, the two kinds of lines sometimes occur very close to one another. Because of low sensitivity and highly complex multiplets, single-resonance, fully coupled ^{13}C polymer nmr spectra are usually not of value in helping to distinguish between the methine- and methylene-carbon lines of the decoupled spectra.

In general, there are three techniques available for making such ^{13}C line assignments: (1) comparison of the decoupled spectra of similar model systems, (2) the use of spin–lattice relaxation times, and (3) the use of various double-resonance schemes. The first of these techniques is unsatisfying in that a suitable model system is not always available. In addition, even when models with known spectra are available, the extrapolation from the model system to the real system can never be made with absolute confidence. The second technique relies on the fact that ^{13}C spin–lattice relaxation times in most molecules are dominated by dipolar interactions between a carbon and its directly bonded proton or protons.[1] The fewer the number of protons involved in the coupling, the weaker the interaction, and the longer the spin-lattice time. Thus, a methine-carbon spin–lattice relaxation time is usually just twice as long as that of a methylene carbon in the same molecule, and this difference can be easily distinguished in a two-pulse, partially relaxed Fourier transform experiment.[2] However, for some kinds of polymers, the spin–lattice relaxation times are not simply related to the number of directly bonded protons. This situation occurs for polymeric elastomers such as poly(propylene oxide), $\leftarrow\!OCHCH_3CH_2\!\rightarrow_x$, in which the relaxation times are influenced by the segmental motion of the chain which is distinctly anisotropic. The anisotropy destroys the simple inverse proportionality between the spin–lattice relaxation time of a poly(propylene oxide) main-chain carbon and the number of directly bonded protons. This is true even though the integrated intensities of the main-chain carbon lines are the same, consistent with a predominantly dipolar relaxation mechanism.[3] (The observed Overhauser enhancement is 2.5 ± 0.1.)

The partially relaxed Fourier transform spectra of the main-chain carbons of a solid poly(propylene oxide)[4] illustrate this point (Figure 2). The spectra were obtained using a Bruker HFX-90 spectrometer operating at 22.6 MHz. Two lines are observed which can be attributed to the methine and methylene carbons.[5] The two lines are about 50 Hz apart and are fairly well resolved, but they are just about indistinguishable in their response to a two-pulse 180–*t*–90 sequence. This is also true for dilute solutions of the same high molecular weight polymer,[6] as well as for a low molecular weight version of poly(propylene oxide).[7] A plot of the observed integrated intensities of the methine- and methylene-carbon lines of the latter polymer, as a function of the delay time in a 180–*t*–90 experiment, is shown in Figure 3. The spin–lattice relaxation times are given by the respective slopes, and while they are not identical, they clearly do not differ by a factor of 2, as do the corresponding slopes obtained from similar experiments performed on solutions of isotactic polystyrene. For solutions of the more rigid polystyrene, an isotropic description of the segmental motion is adequate;[3] this means that, in effect, all the carbons in the main chain can be considered to be moving in the same simple manner and at the same rate. Thus, the relative spin–lattice relaxation times are inversely proportional to the number of directly bonded protons, just as for many nonpolymeric molecules of intermediate size. For more flexible polymers, such as poly(propylene oxide), this simple

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(1) A. Allerhand, D. Doddrell, and R. Komoroski, *J. Chem. Phys.*, **55**, 189 (1971).

(2) A. Allerhand and D. Doddrell, *J. Amer. Chem. Soc.*, **93**, 2777 (1971).

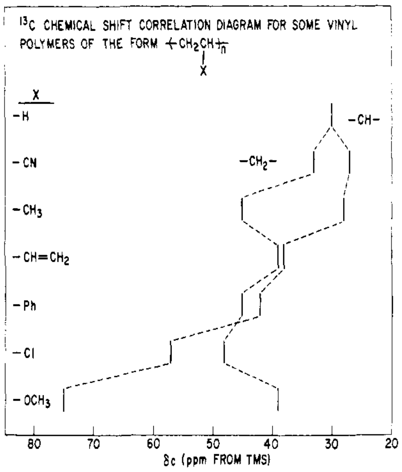
(3) J. Schaefer and D. F. S. Natusch, *Macromolecules*, **5**, 416 (1972).

(4) The polymer has a molecular weight on the order of 200,000, and was prepared using a triethylaluminum–acetylacetone–water catalyst. The sample was supplied by R. J. Herold, General Tire and Rubber Co., Akron, Ohio.

(5) The basis for this conclusion is given later in the text.

(6) The spin–lattice relaxation times of the two main-chain carbons were measured as 550 and 725 msec, with an error of about ±10%. The polymer was present in a 5% (wt/vol) concentration in *o*-dichlorobenzene at 40°.

(7) The polymer has a molecular weight on the order of 2000, and was prepared by base catalysis. It is identified as Union Carbide poly(propylene glycol) 2025.



CONFIGURATIONAL SEQUENCE, IN ORDER OF INCREASING MAGNETIC FIELD

—CH—	—CH$_2$—	α-CARBON
—	—	—
S,I*	UNRESOLVED	I,S*
UNRESOLVED	S,I	I,S
UNRESOLVED	S,I	I,S
UNRESOLVED	S,I	I,S
S,I	S,I	—
UNRESOLVED	S,I	—

*TENTATIVE

Figure 1. A ^{13}C chemical shift correlation diagram for the main-chain carbons of some typical vinyl homopolymers. In general, unless the α substituent is strongly electron withdrawing, the deshielding β effect shifts the methylene-carbon line to lower field than the methine-carbon line. The right-hand side of the diagram shows the effect of steric configuration on relative chemical shifts. I and S refer to iso- and syndiotactic dyads for methylene carbons and to iso- and syndiotactic triads for methine and α carbons.

description is not adequate, and the various kinds of carbons in the main chain must each be considered to be moving in its own way and at its own rate. The differences in rates of motion alter the relative efficiencies of dipolar coupling to directly bonded protons. Using spin–lattice relaxation times in this situation to identify methine and methylene carbons can be ambiguous and, in general, should be avoided.

The most popular version of the third of the general techniques for making ^{13}C line assignments, carbon–proton double resonance, is single-frequency off-resonance decoupling.[8] This method makes use of the fact that in a single-frequency ^{1}H off-resonance decoupling experiment (with a sufficiently intense decoupling field) long-range spin–spin interactions can often be suppressed, thereby revealing simple, characteristic spin multiplets with reduced coupling constants. The multiplets arise only from coupling of carbons with their directly bonded protons. Thus, methine- and methylene-carbon spectra appear as doublets and triplets, respectively. However, if the methine- and methylene-carbon lines are, as in the spectra of some polymers, broad or poorly resolved, or closely spaced and complicated by effects due to steric and structural irregularities, then the single-frequency off-resonance decoupled spectra do not exhibit easily identifiable spin-multiplet patterns. For example, single-frequency off-resonance spectra of the methine- and methylene-carbon region of the solid poly(propylene oxide) consisted of a single, poorly resolved, uninterpretable multiplet.

In this situation the line assignments may still be possible using the results of a *noise-modulated* partial-decoupling experiment. Ernst has shown that in a decoupling experiment with random noise, a component of the central line of a triplet, arising from the weak coupling of a nucleus of spin $^1/_2$ with two different, magnetically equivalent nuclei also of spin $^1/_2$, is unaffected by the perturbation of the random noise.[9] This component, which involves antisymmetric spin states independent of the spatially coherent rf noise,[10] stays sharp even when the decoupling is incomplete and all other kinds of protonated-carbon lines in the spectrum are broad. This experiment can therefore be used to distinguish methine from methylene, since the methylene-carbon triplet has such a component while the methine-carbon doublet does not. Thus, any remaining sharp line in the spectrum can immediately be associated with the methylene-carbon resonance. This simple directness is the basis for expecting that noise-modulated partial decoupling experiments may

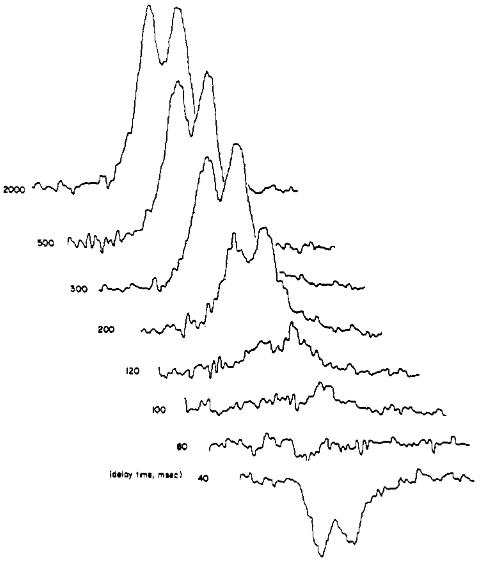


Figure 2. Partially relaxed Fourier transforms of the ^{1}H spin-decoupled natural-abundance ^{13}C free-induction decays of the methine and methylene carbons of a solid poly(propylene oxide). The repetition time of the 180–t–90 pulse sequence was 5 sec. Delay times between the two pulses are indicated in the figure.

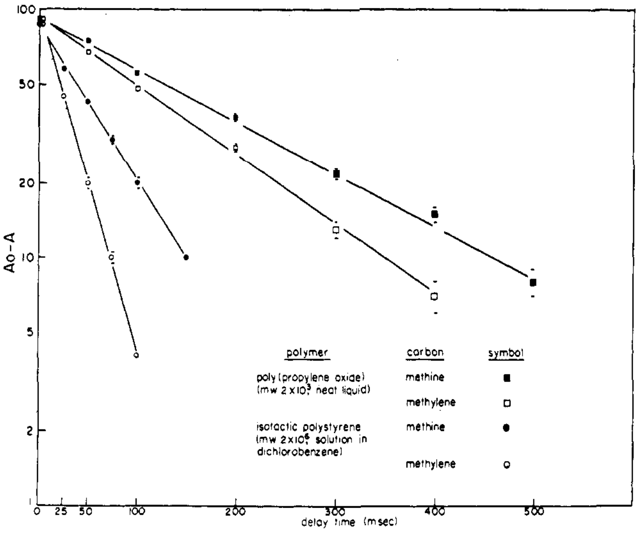


Figure 3. A plot of integrated intensities of main-chain carbons of two polymers as a function of the delay time, t, in a partially relaxed Fourier transform experiment using a 180–t–90 pulse sequence. The observed integrated intensity is A, and the integrated intensity observed in a normal Fourier transform spectrum is A_0. The spin–lattice relaxation time, T_1, can be extracted from the slope of such a plot, since $A = A_0[1 - 2\exp(-t/T_1)]$.

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(8) H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 7445 (1969).

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

(10) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, Oxford, 1961, p 506.

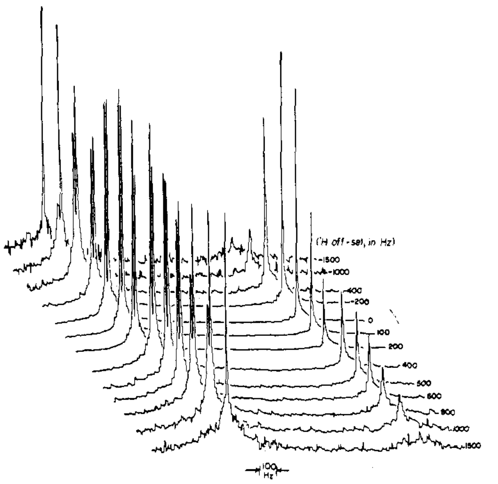

Figure 4. The ^{13}C nmr amplitude spectra of propylene glycol as a function of the frequency offset of the center frequency of the noise-modulated ^{1}H rf for a decoupling field intensity of $\gamma H_2/2\pi = 1200$ Hz.

permit ^{13}C line assignments even though other double-resonance experiments are complicated and indecisive.

The use of noise-modulated, partially decoupled ^{13}C nmr spectra to distinguish methine- from methylene-carbon lines is illustrated by the spectra of propylene glycol, $HOCH_2CHCH_3OH$, shown in Figure 4. A noise generator was used to phase modulate the ^{1}H rf producing a decoupling bandwidth of over 1000 Hz. The power distribution of the decoupling field resulting from this simple phase modulation is not flat over the entire bandwidth.[9,11] This fact becomes readily apparent when a modest decoupling field intensity is used, as was the case for the spectra of Figure 4. For offsets of the center of the ^{1}H rf of on the order of 1000–1500 Hz, the effective decoupling has been reduced to the point where only the transition which involves the antisymmetric spin states is still sharp and easily observed. Similar results were obtained by keeping the ^{1}H rf approximately centered in the frequency band usually defined by ^{1}H chemical shifts and reducing $\gamma H_2/2\pi$ by about 10 dB. These results permit the straightforward identification of the higher field line of the low-field pair as due to the methylene carbon. As shown in Figure 4, the identification for propylene glycol can be made even though amplitude rather than absorption spectra are used.

Noise-modulated partial-decoupling experiments performed on the more complicated spin systems of the low molecular weight liquid poly(propylene oxide) and of the high molecular weight solid poly(propylene oxide) are shown in Figures 5 and 6, respectively. In these experiments the ^{1}H rf was approximately centered in the frequency range usually defined by ordinary proton chemical shifts and the intensity of the decoupling field was reduced. In both sets of experiments, despite the relatively broad lines of the polymers, a component of a line is observed which is not further broadened under conditions of noise-modulated partial decoupling. This identifies, for both polymers, the methylene-carbon line as the higher field line of the low-field pair. For the solid polymer, the assignment is, perhaps, less ambiguous than those based either on spin–lattice relaxation times or single-frequency off-resonance decoupling.

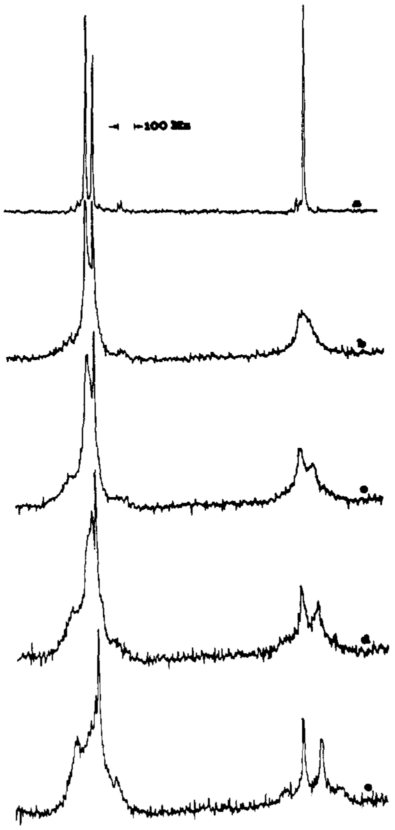

Figure 5. The noise-modulated partially decoupled ^{13}C nmr spectra of a low molecular weight liquid poly(propylene oxide) for approximate values of the decoupling field intensity, $\gamma H_2/2\pi$, of (a) 2500, (b) 250, (c) 75, (d) 25, and (e) 10 Hz. The spectrum of (a) is essentially fully decoupled. The minor lines in this spectrum are due to end effects in the chain. The spectral density of the power distribution of the decoupling field is not flat over the entire noise-modulated bandwidth, but falls off at either end. Thus, for weak decoupling field intensities, the methyl carbon (directly bonded to its high-field methyl protons) appears to be the least fully spin decoupled. A component of the high-field line of the low-field pair remains sharp independent of the intensity of the noise-modulated decoupling field.

The assignment for the high molecular weight polymer is not complicated by the possibility that the positions of some major methylene-carbon lines are shifted downfield to the methine-carbon region due to the influence of various steric or structural environments on relative chemical shifts.[12] This can be shown by analysis of the ^{13}C nmr spectra of dilute solutions of high molecular weight poly(propylene oxides) prepared from different catalysts. Some spectra are shown in Figure 7. The polymer of Figure 7a has no structural defects,[13] while that of Figure 7b has structural defects[14]

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(11) S. Seely, "Radio Electronics," McGraw-Hill, New York, N. Y., 1956, p 384.

(12) P. J. Green and E. B. Whipple, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **12**, 354 (1971).

(13) As determined by chromatographic analysis of the products of ozone degradation reported by C. C. Price and R. Spector, *J. Amer. Chem. Soc.*, **87**, 2069 (1965). The polymer was a high molecular weight material prepared using a zinc hexacyanoferrate catalyst. The sample and its chromatographic analysis were supplied by R. J. Herold, General Tire and Rubber Co., Akron, Ohio. The same kind of analysis also indicates that the low molecular weight poly(propylene oxide) of Figures 3 and 5 is free of structural defects.

(14) Although not in as high a concentration as the 40% concentration reported by Price for amorphous poly(propylene oxides) produced by catalysts similar to the diethylzinc–water used to make this polymer. This sample was also supplied by R. J. Herold, General Tire and Rubber Co., Akron, Ohio.

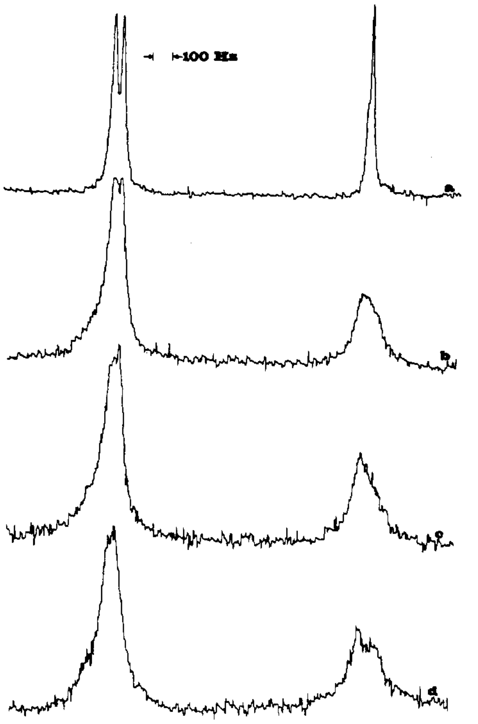

Figure 6. The noise-modulated partially decoupled ^{13}C nmr spectra of a high molecular weight solid poly(propylene oxide) for approximate values of the decoupling field intensity, $\gamma H_2/2\pi$, of (a) 2500, (b) 250, (c) 75, and (d) 25 Hz. A component of the high-field line of the low-field pair appears to remain unbroadened in the noise-modulated partially decoupled spectra of (b) and (c).

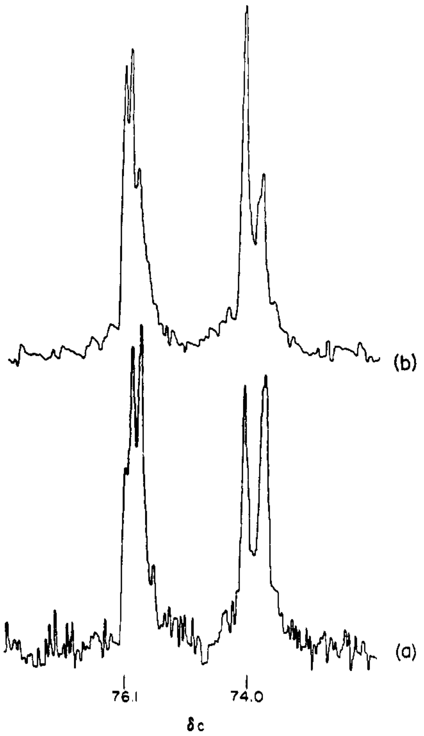

Figure 7. The ^{1}H decoupled ^{13}C nmr spectra of the main-chain carbons of 5% (weight/volume) *o*-dichlorobenzene solutions of high molecular weight poly(propylene oxides) prepared using (a) a zinc hexacyanoferrate catalyst and (b) a diethylzinc–water catalyst. Data accumulation for (b) was four times that for (a). The reference is tetramethylsilane. Spectra of the extremely viscous solutions were obtained at 40°. Chromatographic analysis of the products of degradative ozonalysis suggests that the polymer of (b) has fewer steric but more structural defects than that of (a). The chemical shift of the lowest field major line of (b) matches that of the low-field shoulder of (a).

but a reduced steric-defect content.[15] In the spectra of both of these polymers, all of the major lines in the high-field grouping have the same spin–lattice relaxation time which is shorter by a factor of 1.3 than the single spin–lattice relaxation common to all of the major lines of the low-field grouping. The spin–lattice relaxation times were obtained from straight-line plots similar to those shown in Figure 3. Noise-modulated partial-decoupling experiments on solutions of both of these polymers indicate that all of the major lines in the high-field grouping arise from methylene carbons, while all of those in the low-field grouping arise from methine carbons.[16] This is consistent with the equal integrated intensities of the two regions and with earlier assignments based on model systems.[17] (The fact that two major methylene-carbon lines are observed in the spectrum of the structurally regular polymer shows that the influence on the chemical shift of the steric environment is responsible for this splitting rather than the influence of the structural environment. This is opposite to the earlier assignment based on model systems.[17])

Noise-modulated partial-decoupling experiments on solutions of polystyrene, polyacrylonitrile, and poly(vinyl chloride) have also been performed and can be used to distinguish methine- from methylene-carbon lines. For each of these particular polymers, the assignments are in agreement with those based on spin–lattice relaxation times, the latter not being complicated by the effects of pronounced anisotropy in the segmental motion of the chain.

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(15) This is a spectrum of the whole polymer. The isotactic structurally regular, crystalline fraction constituted about 30% of the sample.

(16) The observed, opposite β and γ shielding effects, measured by Green and Whipple (ref 12) for ethylene oxide–propylene oxide copolymers, would predict the chemical shift of a methylene carbon in a tail-to-tail propylene oxide dyad in poly(propylene oxide) to be about the same as that observed for a methine carbon in a head-to-tail propylene oxide dyad. However, no major line has ever been observed in the lower field main-chain region of a spectrum of poly(propylene oxide) which can definitely be attributed to a methylene carbon. Thus, either the shielding effects measured for propylene oxide copolymers are not transferrable to the homopolymer, or, what is more likely, the concentration of structural defects in these chains is less than indicated by degradative ozonolysis.

(17) J. Schaefer, *Macromolecules*, 2, 533 (1969).