Carbon-13 Overhauser Effect in Polymer Solutions

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ABSTRACT: Carbon-13-{^{1}H} enhancements at 22.6 MHz have been found for a variety of polymers to be substantially less than the theoretical maximum, vary from one polymer type to another, and depend on the choice of solvent. They are not molecular weight or concentration dependent, but are influenced by the addition of paramagnetic species to the solution. For polystyrene, the Overhauser enhancements are not dependent on tacticity, within experimental error, and are the same for different types of carbons in or near the polymer main chain. All of these results are interpreted in terms of a nuclear relaxation mechanism dominated by dipolar interactions which are modulated by segmental motions, the correlation times of some of which do not satisfy the nmr extreme narrowing condition. This interpretation is consistent with ^{13}C spin–lattice relaxation (T_1) measurements performed on the same polymers at 22.6 MHz using partially relaxed Fourier transform techniques. In particular, the similarity of the reduced Overhauser enhancement for comparable carbons of solutions of both noncrystalline iso- and atactic polystyrene at room temperature can be related to their very similar spin–lattice relaxation times. These, in turn, are consistent with calculations of preferred conformations in polystyrene and the direct relationship between conformational populations and local segmental mobilities.

The development of ^{13}C nuclear magnetic resonance spectroscopy has been greatly facilitated by the application of double irradiation techniques involving both selective and random-noise proton decoupling.[2] In addition to spectral simplification, proton irradiation also gives rise to increased signal-to-noise ratios because of the operation of a ^{13}C-{^{1}H} Overhauser effect.[2b,3] However, for molecules having very low mobility in solution, the Overhauser enhancement can be substantially reduced by an amount determined, in part, by the details of the molecular motion.[3,4] The segmental mobilities of some polymers in solution have been characterized by ^{1}H nmr relaxation techniques.[5] They are, in fact, sufficiently low that, in general, only a fraction of the theoretical Overhauser enhancement can be expected in the ^{13}C nmr spectra of solutions of high polymers. Reduced Overhauser enhancements have already been reported for the quaternary carbons of both units of styrene–acetylonitrile copolymers in dimethyl sulfoxide.[6]

Reduced Overhauser enhancements which vary in a largely unpredictable way from one carbon to another could severely complicate the interpretation of the ^{13}C nmr spectra of polymers. In order to examine this possibility, we have measured the ^{13}C-{^{1}H} Overhauser enhancements (and spin–lattice relaxation times) of carbons in or near the polymer main chain for solutions of poly(ethylene oxide), polyacrylonitrile, and isotactic and atactic polystyrenes.

Theory

The Overhauser enhancement factor $[C_Z - C_0]/C_0$ for ^{13}C nuclei (C) due to proton (H) irradiation is given by[4]

$$\frac{C_Z - C_0}{C_0} = \rho_{\mathrm{CH}} S_{\mathrm{H}} \frac{\gamma_{\mathrm{H}}}{\gamma_{\mathrm{C}}} \frac{T_{1\mathrm{C}}(\mathrm{LH})}{T_{1\mathrm{CH}}} \tag{1}$$

where C_Z and C_0 are ^{13}C magnetizations with and without proton irradiation, respectively. (Nuclear Overhauser enhancements are often quoted as C_Z/C_0.) The ratio of gyromagnetic ratios, $\gamma_{\mathrm{H}}/\gamma_{\mathrm{C}}$, equals 3.976. The degree of saturation of proton absorption, S_{H}, is given by

$$S_{\mathrm{H}} = 1 - \frac{1}{1 + \gamma_{\mathrm{H}}^2 H_2^2 (T_1 T_2)_{\mathrm{H}}} \tag{2}$$

where γ_{H}, H_2, T_1, and T_2 are the gyromagnetic ratio, irradiation field intensity, and spin–lattice and spin–spin relaxation times, respectively, of the protons. Substitution of the condition[7]

$$\gamma_{\mathrm{H}}^2 H_2^2 \gg 4\pi^2 J_{\mathrm{CH}}^2 \tag{3}$$

for complete decoupling into eq 2 shows that decoupling always implies $S_{\mathrm{H}} = 1$ unless either J_{CH} or $(T_1T_2)_{\mathrm{H}}$ is very small. The nature and effectiveness of the dynamic coupling (usually dipolar) between the ^{13}C and ^{1}H spins is described by ρ_{CH}. The spin–lattice relaxation times of the ^{13}C nuclei due to all relaxation mechanisms and to ^{13}C–^{1}H coupling only are $T_{1\mathrm{C}}(\mathrm{LH})$ and $T_{1\mathrm{CH}}$, respectively. Relaxation mechanisms other than ^{13}C–^{1}H coupling may involve spin rotation, chemical shift anisotropy, and dipole, quadrupole, and scalar interactions with spins other than protons.[3] Such contributions to ^{13}C relaxation are included together in the ^{13}C lattice (L) relaxation time, $T_{1\mathrm{CL}}$, given by

$$\frac{1}{T_{1\mathrm{C}}(\mathrm{LH})} = \frac{1}{T_{1\mathrm{CH}}} + \frac{1}{T_{1\mathrm{CL}}} \tag{4}$$

Assuming purely dipolar intramolecular interactions between ^{13}C and ^{1}H, $T_{1\mathrm{CH}}$ can be approximated by[8]

$$\frac{1}{T_{1\mathrm{CH}}} = \frac{1}{10}\hbar^2 \gamma_{\mathrm{C}}^2 \gamma_{\mathrm{H}}^2 \sum_i r_i^{-6} [f(\omega_{\mathrm{H}} - \omega_{\mathrm{C}}) + 3f(\omega_{\mathrm{C}}) + 6f(\omega_{\mathrm{H}} + \omega_{\mathrm{C}})] \tag{5}$$

where

$$f(\omega) = \tau_{\mathrm{CH}}(1 + \omega^2 \tau_{\mathrm{CH}}^2)^{-1} \tag{6}$$

τ_{CH} is the single rotational correlation time for the ^{13}C–^{1}H coupling, and r_i is the distance between the ith proton and

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[1] (a) Monsanto Company; (b) University of Illinois.

[2] (a) R. R. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966); (b) D. M. Grant in "Magnetic Resonance," C. K. Coogan, *et al.*, Ed., Plenum Press, New York, N. Y., 1970, p 323.

[3] K. F. Kuhlmann, D. M. Grant, and R. K. Harris, *J. Chem. Phys.*, **52**, 3439 (1970).

[4] D. F. S. Natusch, R. E. Richards, and D. Taylor, *Mol. Phys.*, **11**, 421 (1966).

[5] See, for example, J. E. Anderson, K-J. Liu, and R. Ullman, *Discuss. Faraday Soc.*, No. **49**, 257 (1970).

[6] J. Schaefer, *Macromolecules*, **4**, 107 (1971).

[7] A. L. Bloom and J. N. Shoolery, *Phys. Rev.*, **97**, 1261 (1955).

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

the ^{13}C nucleus in question. The corresponding equation for $T_{2\mathrm{CH}}$ is

$$\frac{1}{T_{2\mathrm{CH}}} = \frac{1}{20}\hbar^2\gamma_{\mathrm{C}}^2\gamma_{\mathrm{H}}^2\sum_i r_i^{-6}\,[4\tau_{\mathrm{CH}} + f(\omega_{\mathrm{H}} - \omega_{\mathrm{C}}) + 3f(\omega_{\mathrm{C}}) + 6f(\omega_{\mathrm{H}}) + 6f(\omega_{\mathrm{H}} + \omega_{\mathrm{C}})] \quad (7)$$

The same assumptions give rise to[9]

$$\rho_{\mathrm{CH}} = \frac{-f(\omega_{\mathrm{H}} - \omega_{\mathrm{C}}) + 6f(\omega_{\mathrm{H}} + \omega_{\mathrm{C}})}{f(\omega_{\mathrm{H}} - \omega_{\mathrm{C}}) + 3f(\omega_{\mathrm{C}}) + 6f(\omega_{\mathrm{H}} + \omega_{\mathrm{C}})} \quad (8)$$

Figure 1 shows ρ_{CH} as a function of the product $\omega_{\mathrm{C}}\tau_{\mathrm{CH}}$.

Clearly, when $\omega_{\mathrm{C}}\tau_{\mathrm{CH}} \ll 1$, $\rho_{\mathrm{CH}} = {}^1/_2$, and the Overhauser enhancement factor depends only on the ratio $T_{1\mathrm{C}}(\mathrm{LH})/T_{1\mathrm{CH}}$. When the dipolar relaxation mechanism is dominant, the ratio $T_{1\mathrm{C}}(\mathrm{LH})/T_{1\mathrm{CH}}$ is unity, and the maximum theoretical Overhauser enhancement is obtained. This situation has been observed for a wide variety of systems by Allerhand, *et al.*[8,10,11]

In highly immobile systems, the extreme motional narrowing condition ($\omega_{\mathrm{C}}\tau_{\mathrm{CH}} \ll 1$) no longer holds and $\rho_{\mathrm{CH}} < {}^1/_2$. Under these circumstances the Overhauser enhancement depends both on the magnitude of ρ_{CH} and on the ratio $T_{1\mathrm{C}}(\mathrm{LH})/T_{1\mathrm{CH}}$.

Thus, provided that $S_{\mathrm{H}} = 1$, an Overhauser enhancement factor less than the maximum possible value of 1.976 can occur in three cases (shown by eq 9–11). Distinction among

$$T_{1\mathrm{C}}(\mathrm{LH})/T_{1\mathrm{CH}} < 1,\ \rho_{\mathrm{CH}} = 1/2,\ \omega_{\mathrm{C}}\tau_{\mathrm{CH}} \ll 1 \quad (9)$$

$$T_{1\mathrm{C}}(\mathrm{LH})/T_{1\mathrm{CH}} = 1,\ \rho_{\mathrm{CH}} < 1/2,\ \omega_{\mathrm{C}}\tau_{\mathrm{CH}} \sim 1 \quad (10)$$

$$T_{1\mathrm{C}}(\mathrm{LH})/T_{1\mathrm{CH}} < 1,\ \rho_{\mathrm{CH}} < 1/2,\ \omega_{\mathrm{C}}\tau_{\mathrm{CH}} \sim 1 \quad (11)$$

these three cases can be difficult even when experimental values of $T_{1\mathrm{C}}(\mathrm{LH})$ are available; however, cases 1 and 2 (eq 9 and 10, respectively) are distinguishable from their temperature or viscosity dependences. Thus, $(C_{\mathrm{Z}} - C_0)/C_0$ increases (or if spin rotation is unimportant, remains constant) with τ_{CH} in case 1 but decreases in case 2. Case 3 (eq 11) can give rise to a complicated temperature or viscosity dependence and it is only distinguishable if an independent value of τ_{CH} is available.

When case 2 operates and a single correlation time describes the motion, it is a simple matter to calculate a value of τ_{CH} from the observed Overhauser enhancement, if eq 6 and 8 are assumed. This enables either $T_{1\mathrm{CH}}$ or $\Sigma_i r_i^{-6}$ to be calculated from eq 5, if a value for the other quantity is available.

Molecular motion in systems of restricted mobility where case 2 operates is most likely to be anisotropic, and the assumption of eq 5 and 8 is not strictly valid. Nevertheless, relaxation studies in some motionally anisotropic systems indicate that the correlation functions for isotropic and anisotropic motion are not dissimilar[12,13] and that the simplified theory used here provides a reasonable qualitative description of intramolecular relaxation.

For most high polymers in solution, the many *segmental* motions of the chain (as opposed to the reorientational motion of the chain as a whole) are of primary importance in determining the spin–lattice relaxation and hence the Overhauser enhancement. When a simple isotropic description of segmental motion is clearly inadequate, the Overhauser enhancement of a given carbon may still be a much less sensitive function of the actual correlation times of the system than the spin–lattice relaxation times. For example, for a less restricted group such as a methyl group, the assumption of a single correlation time is inadequate. For such a carbon attached to a polymer main chain undergoing isotropic segmental motion (described by τ_{CH}), additional internal motion can be described by a correlation time τ_{int}. Then

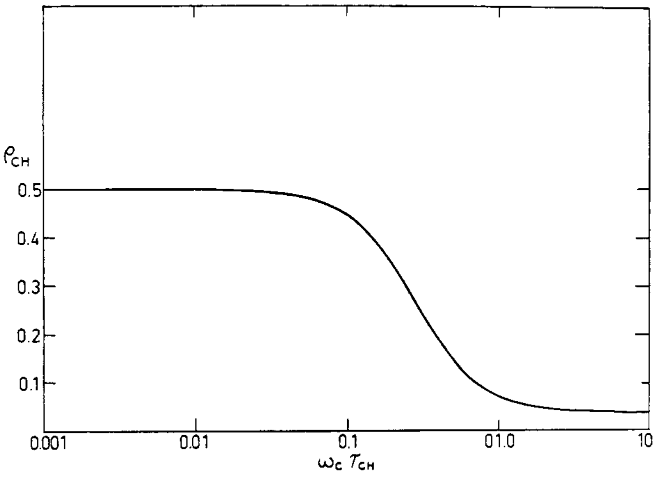

Figure 1. A plot of ρ_{CH}, a measure of the effectiveness of the dynamic dipolar coupling between C and H spins, as a function of the product of the ^{13}C frequency and correlation time, $\omega_{\mathrm{C}}\tau_{\mathrm{CH}}$ (see eq 8 in the text).

$$f(\omega) = \frac{A\tau_{\mathrm{CH}}}{1 + \omega^2\tau_{\mathrm{CH}}^2} + \frac{B\tau_{\mathrm{B}}}{1 + \omega^2\tau_{\mathrm{B}}^2} + \frac{D\tau_{\mathrm{D}}}{1 + \omega^2\tau_{\mathrm{D}}^2} \quad (12)$$

where

$$\tau_{\mathrm{B}}^{-1} = \tau_{\mathrm{CH}}^{-1} + (6\tau_{\mathrm{int}})^{-1} \quad (13)$$

$$\tau_{\mathrm{D}}^{-1} = \tau_{\mathrm{CH}}^{-1} + 2(3\tau_{\mathrm{int}})^{-1} \quad (14)$$

and A, B, and D are constants which depend on the geometry of the internal motion. When $\tau_{\mathrm{int}} \ll \tau_{\mathrm{CH}}$ and $\omega\tau_{\mathrm{CH}}$ is approximately 0.0–0.3, the first term on the right-hand side of eq 12 dominates and the ratio of terms, ρ_{CH}, becomes almost independent of the details of the internal motion. Thus, rapidly rotating methyl carbons and more slowly reorientating main-chain carbons can have similar reduced Overhauser enhancements even though the spin–lattice relaxation time of the methyl carbon is affected by internal motion. Doddrell, Glushko, and Allerhand[14] have treated the case of an Overhauser enhancement dependent on two correlation times in more detail and have generated numerical solutions to the problem in the form of plots. Their results confirm that in the region where $\omega\tau_{\mathrm{CH}}$ (of the slower, isotropic motion) is equal to 0.0–0.3, the Overhauser enhancement of a carbon having internal motion is insensitive to the internal motion (although T_1 can change by almost an order of magnitude). The enhancement is essentially independent of the internal motion if $\tau_{\mathrm{int}} \ll \tau_{\mathrm{CH}}$. This is not true if $\omega\tau_{\mathrm{CH}}$ exceeds about 0.5, in which case the Overhauser enhancement depends on the internal motion dramatically, as the main-chain motion now becomes inefficient in relaxation processes.

It has recently been demonstrated that the ^{13}C Overhauser effect can be reduced almost to zero by the addition of a

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suitable amount of an unreactive paramagnetic species to the sample.[15,16] This procedure sometimes enables the unenhanced intensities of ^{13}C resonances to be obtained. Furthermore, when $T_{1C}(\mathrm{LH})/T_{1CH} < 1$, it is possible to obtain values of $T_{1C}(\mathrm{LH})$, T_{1CH}, and T_{1CL}.[16] In the presence of a molar concentration, $[E]$, of a paramagnetic species, the ^{13}C Overhauser enhancement factor is given by

$$\frac{C_Z - C_0}{C_0} = \rho_{CH} S_H \frac{\gamma_H}{\gamma_C} \left[\frac{\dfrac{1}{T_{1CH}} + \alpha[E]}{\dfrac{1}{T_{1C}(\mathrm{LH})} + (k + \alpha)[E]} \right] \qquad (15)$$

where k and α describe the efficiency with which the paramagnetic species relaxes ^{13}C directly and *via* the protons, respectively.[4] In all cases studied to date,[17] $\alpha = 0$ and the Overhauser enhancement factor is reduced to zero when $1 + k[E]T_{1C}(\mathrm{LH}) \gg T_{1C}(\mathrm{LH})/T_{1CH}$. For the case where $T_{1C}(\mathrm{LH})/T_{1CH} = 1$, eq 15 reduces to

$$\frac{C_Z - C_0}{C_0} = \rho_{CH} S_H \frac{\gamma_H}{\gamma_C} \left[\frac{1}{1 + T_{1C}(\mathrm{LH})k[E]} \right] \qquad (16)$$

and only the product $kT_{1C}(\mathrm{LH})$ can be obtained from a plot of $(C_Z - C_0)/C_0$ *vs.* $[E]$.

In the presence of a paramagnetic species, eq 2 becomes

$$S_H = 1 - \frac{1}{1 + \gamma_H{}^2 H_2{}^2 T_{1H}{}^2 \left(\dfrac{1}{1 + pT_{1H}[E]} \right)^2} \qquad (17)$$

where p describes the efficiency with which the paramagnetic species relaxes the protons and $T_{1H} = T_{2H}$. Although S_H depends on $[E]$, it can be shown that normally $S_H = 1$ for values of $[E]$ less than required to produce line broadening, provided that the decoupling condition of eq 3 is fulfilled. This is not so, however, when J_{CH} is small ($\sim$5 Hz) or when T_{1H} is very short.[16] In such circumstances, the decoupled line is no longer a criterion for $S_H = 1$.

It should be remembered that the quantity $\gamma_H{}^2 H_2{}^2$ in eq 17 is a measure of the rf power which is effective in irradiating protons coupled to ^{13}C. Where random noise decoupling is employed, this power is only a fraction of the total given by

$$\gamma_H{}^2 H_2{}^2 = [\gamma_H{}^2 H_2{}^2]_{\mathrm{Total}} \frac{\delta\nu}{\Delta\nu} \qquad (18)$$

where $\Delta\nu$ is the total random noise bandwidth and $\delta\nu$ is the effective frequency bandwidth occupied by resonances arising from those protons coupled to the ^{13}C of interest.[2a] Where the chemical shifts of the irradiated protons differ widely, $\Delta\nu$ is necessarily large and the effective irradiation power may be insufficient to produce $S_H = 1$, especially as $[E]$ increases.

Experimental Section

High-resolution ^{1}H noise-decoupled, natural-abundance pulsed ^{13}C nmr spectra were obtained at 22.6 MHz using a Bruker spectrometer, some details of which have been described earlier.[18] The ^{13}C analytical channel was operated both in crossed-coil and single-coil modes. A 90° pulse required 120 μsec in the former mode and 18 μsec in the latter. Free-induction decays were accumulated in a Nicollet 1074 time-averaging computer. Fourier transforms were calculated by a Digital Equipment Corp. PDP-8/I computer interfaced to the 1074. Both amplitude spectra (the square root of the sum of the squares of the absorption and dispersion spectra) and pure absorption spectra were calculated, the latter calculation including a linear phase correction.

Only a wide data sampling window was used. The output of the receiver was sampled by the time-averaging computer, generally using 1024 channels (of the 4096 available) internally swept at a rate of 1 msec per channel. This corresponds to a narrow frequency domain of only 500 Hz. Frequency components greater than about 800 Hz were essentially removed from the free-induction decay by a low-pass analog filter between the receiver and the time-averaging computer. By sampling with a wide window in the time domain, a large enough number of data points can be used for each line in the spectrum to ensure a faithful transform.

No delay was introduced between the time of the irradiating pulse and the time the receiver was first sampled. In order to eliminate the possibility of any pulse leakage through the receiver and distortion of the accumulated free-induction decay, the contents of the first three data locations were erased. In our particular 1074 unit, the first few data locations do not contain valid data, so no useful information was lost by this procedure. No additional data manipulation preceded the Fourier transform. By avoiding digital filtering techniques which improve the signal to noise ratio and general appearance of transformed spectra, a less distorted Fourier transform is obtained. This, in turn, results in more reliable integrated intensities, which is of special importance in determining Overhauser enhancements.

The 90-MHz ^{1}H rf was produced by a Hewlett-Packard 5105A-5110B frequency synthesizer and amplified by a Boonton 230A rf power amplifier driving an Instruments for Industry Model 5000 power amplifier. This combination was capable of producing a 15-W cw rf signal. Enough of this output was coupled into the probe to produce a decoupling field intensity $\gamma H_2/2\pi$, equal to 2600 Hz under standard operating conditions with a maximum available field intensity of 3300 Hz. The decoupling field intensity was measured by observing the residual splitting of the dimethyl sulfoxide methyl carbon quartet when the single-frequency coherent ^{1}H rf was offset 200 Hz. The effective decoupling power level heated the 13-mm o.d. nmr sample tube to about 40°.

Modulation of the ^{1}H rf was achieved in two ways. First, the frequency synthesizer was phase modulated by the output of a Hewlett-Packard 3722A noise generator. The clock period and output amplitude of the noise generator were chosen to produce a 1-kHz ^{1}H rf bandwidth which was measured as about 1100 Hz using a spectrum analyzer. The decoupling bandwidth was reduced to values as low as 100 Hz by suitable changes of the noise generator. Second, the output of the frequency synthesizer was connected to one input port of a Hewlett-Packard 10534A double-balanced mixer and the audio output of a swept waveform generator to the other input port. The balanced mixer suppressed the center-band frequency and created two first-order rf side bands separated by twice the audio frequency. These side bands were themselves frequency swept at a rate small compared to the modulation frequency. This kind of decoupling scheme is useful when the maximum available rf power is desired over two widely separated, fairly narrow regions of the ^{1}H spectrum.

Nuclear Overhauser enhancements were measured directly by accumulating a proton-decoupled free-induction decay, performing the Fourier transform, storing the transformed spectrum in one of the unused quarters of the 1074 memory, offsetting the ^{1}H rf by 50 kHz, collecting the proton-coupled free-induction decay, and then performing a second transform. Except for the ^{1}H rf offset, the two spectra were obtained consecutively under identical conditions. They were then integrated also under identical conditions using the wired integration program of the Nicollet 1074. The ratio of the two integrals was used to determine the ^{13}C-$\{^1$H$\}$ Overhauser enhancement. Direct Overhauser enhancements were also measured when the single resonance spectrum was obtained with a ^{1}H rf offset of 5 MHz, and with the ^{1}H rf completely removed from the experiment.

The most reliable Overhauser enhancements are measured when the same narrow spectral range is integrated for both coupled and decoupled spectra. For the systems studied here, this was possible

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(15) G. N. La Mar, *J. Amer. Chem. Soc.*, **93**, 1040 (1971).
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(17) G. N. La Mar, private communication.
(18) J. Schaefer, *Macromolecules*, **4**, 98 (1971).

for at least one carbon of each polymer. The Overhauser enhancements of the other carbons of the polymer were then obtained from comparisons of decoupled spectra, obtained under identical conditions.

Nuclear Overhauser enhancements were also measured using a transient technique. By gating the ^1H decoupling channel, and waiting a variable time after the decoupler had been turned off before triggering the irradiating pulse and accumulating the free-induction decay, a single-resonance spectrum was obtained whose integrated intensity is a function of the delay time.[3,19,20] For short delays, almost normal Overhauser enhancements were observed until finally, after a sufficiently long delay, no enhancement was observed. A semilog plot of the observed integrated intensity against the delay time has an intercept which is the normal enhanced integrated intensity ($t = 0$) and an asymptote which is the single-resonance integrated intensity. Information about both proton and carbon spin–lattice relaxation times can sometimes be extracted from this experiment.[3,19,20] (For polymers with very short relaxation times, on the order of a millisecond, the companion experiment of measuring the intensity of the decoupled line as a function of the delay after the decoupler has been turned on is complicated by the finite time required for the cw transmitter to reach full power.)

Spin–lattice relaxation times were measured from partially relaxed Fourier transform spectra[8] obtained from 180–t–90 sequences. The sequence timing for the 180 and 90° pulses, as well as the external trigger for the time-averaging computer, were provided by a crystal-controlled, Ortec two-channel pulse generator.

Poly(ethylene oxide) was obtained from Union Carbide. Samples were low molecular weight liquids (molecular weight $\sim 10^3$). Polyacrylonitrile and atactic polystyrene were obtained from Monsanto and are commercial, high molecular weight materials (molecular weight $\sim 10^5$). Isotactic polystyrene was also obtained from Monsanto (Springfield, Mass.) and used in the form of the whole polymer characterized as being 2% methyl ethyl ketone soluble. This polymer was a high molecular weight material (molecular weight $\sim 10^6$), but not highly crystalline. A 5% solution in *o*-dichlorobenzene could be maintained at 40°.

Since polymer relaxation times are generally much less than 1 sec, there was no need to remove oxygen from any of the polymer solutions.

Results

(1) Nuclear Overhauser Enhancements. The observed nuclear Overhauser enhancement factor, $(C_Z - C_0)/C_0$, for the methylene carbon of poly(ethylene oxide), $-\!\!\left(CH_2CH_2O\right)\!\!-_x$, is 1.7 ± 0.1, close to the theroetical maximum of 1.988 (Figure 2a–c). The same value is obtained for the neat liquid as for a 10% solution of the polymer in methylene chloride. A slightly larger value of 1.9 ± 0.1 is obtained for the neat liquid when amplitude rather than absorption spectra are used (Figure 2d–f). In general, intensity measurements from absorption spectra are more accurate than those from amplitude spectra since the latter contain contributions from the wings of the dispersion mode spectra. For broad polymer lines, however, these wings have often disappeared in the noise, and the advantage of using absorption spectra is reduced. This is especially true when the spectra are relatively simple and spectral wings do not overlap. The reasonable agreement between the integrals of the two kinds of spectra means that systematic data manipulative errors, resulting either from imperfect phase corrections or from the improper removal of invalid data in the first few locations of the time-averaging computer, have been avoided. Such errors, if present, would have affected the phasing and base lines of absorption spectra differently from those of amplitude spectra, making unlikely the observed agreement.

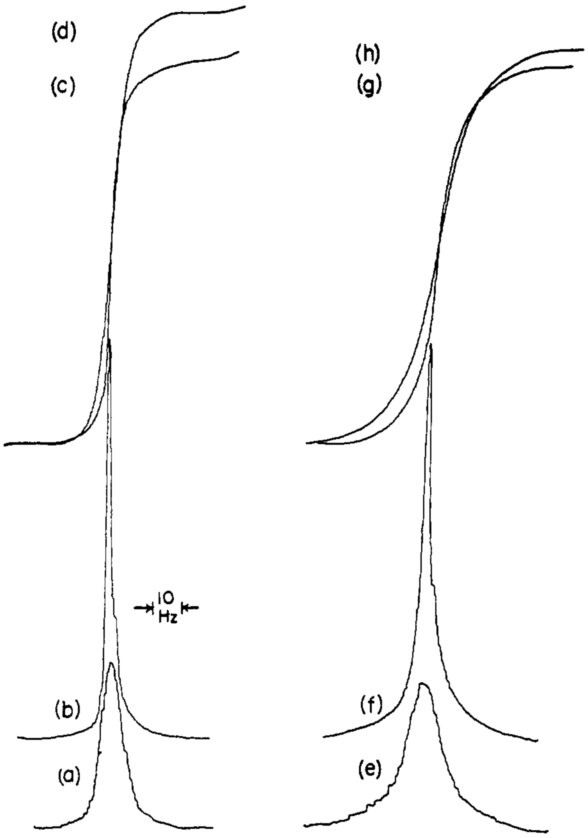

Figure 2. Fourier transforms of the natural-abundance ^{13}C free-induction decays of a neat solution of poly(ethylene oxide) with (a) no spin decoupling and (b) spin decoupling. In (a) only the central line of the spin-coupled methylene triplet is shown. Ninety-six scans were accumulated for (a) and sixteen, or one-sixth as many, for (b). Details of the accumulations of the free-induction decays are given in the text; 90° pulses were used with 1.5-sec spacings. The integrated intensities of (a) and (b) are shown in (d) and (c), respectively. If a theoretical maximum Overhauser effect of $C_Z/C_0 = 3.0$ were operating, the decoupled line intensity would be equal to six times the integrated intensity of the central line of the triplet. The observed decoupled line intensity is only about 90% of six times the intensity of the spin-coupled line, leading to an Overhauser enhancement factor, $(C_Z - C_0)/C_0$, of 1.7. The amplitude spectra corresponding to the absorption spectra of (a) and (b) are shown in (e) and (f) and their integrals in (h) and (g), respectively.

Both amplitude and absorption spectra give a value of 1.2 ± 0.1 for the Overhauser enhancement factor of the nitrile carbon of a dimethyl sulfoxide solution of polyacrylonitrile, $-\!\!\left(CH_2CHCN\right)\!\!-_x$. Because only long-range spin coupling is involved, the single- and double-resonance spectra cover essentially the same spectral region. The nitrile carbon is completely decoupled from the influence of the ^{14}N quadrupole.[21] Enhancements for the methine and methylene carbons of polyacrylonitrile were obtained from comparisons of decoupled spectra and are presented in Table I.

For poly(ethylene oxide), a residual enhancement of the single-resonance integrated intensity of about 5–10% was observed for an ^1H rf offset of 50 kHz relative to the value measured when the ^1H rf was completely removed. Virtually all of this residual enhancement disappeared, however, if in addition to the 50-kHz ^1H offset, the noise modulation of the ^1H rf was also eliminated. A similar residual enhancement

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TABLE I
CARBON-13 POLYMER OVERHAUSER ENHANCEMENT FACTORS AND CORRELATION TIMES MEASURED AT 22.6 MHZ AND 40°

Polymer	Solvent	Carbon	$(C_Z - C_0)/C_0$[a]	ρ[b]	τ_{CH}, sec × 10^9 [b]
Poly(ethylene oxide)	Neat liquid	Methylene	1.7	0.43	
Polyacrylonitrile	DMSO	Methine	1.2	0.30	1.7
		Methylene	1.2	0.30	1.7
Polystyrene (isotactic)	*o*-Dichlorobenzene	Quaternary	0.8	0.20	2.7
		Methine	0.8	0.20	2.7
		Methylene	0.8	0.20	2.7
Polystyrene (atactic)	*o*-Dichlorobenzene	Quaternary	0.8	0.20	2.7
		Methine	0.8	0.20	2.7
		Methylene	0.8	0.20	2.7
	$CDCl_3$	Quaternary	1.1	0.27	1.9
		Methine	1.1	0.27	1.9
		Methylene	1.1	0.27	1.9
	Tetrachloroethylene	Methine	1.0	0.25	2.1
		Methylene	1.0	0.25	2.1
	$CHCl_3$	Quaternary	1.1	0.27	1.9
	CCl_4	Quaternary	1.0	0.25	2.1
	Tetrachlororethane	Quaternary	1.0	0.25	2.1
	1,2,4-Trichlorobenzene	Quaternary	0.5	0.12	4.1

[a] Accuracy is ±0.1. Overhauser enhancements are sometimes reported as C_Z/C_0, where C_Z and C_0 are enhanced and unenhanced signal intensities. [b] Obtained from eq 1, 6, and 8 and experimental Overhauser enhancements.

for the quaternary carbon of polyacrylonitrile was not outside experimental error. The integrated intensity of the single-resonance spectrum of the nitrile quaternary carbon was the same for an unmodulated ^{1}H rf offset of 5 MHz as for 50 kHz, within experimental error. Furthermore, nuclear Overhauser enhancements for poly(ethylene oxide) and polyacrylonitrile extracted from a semilog plot of observed intensity of the single-resonance spectrum as a function of the delay from the time when the ^{1}H rf was gated off to when the free induction decay was obtained were in agreement (±10%) with those obtained from comparisons of decoupled to coupled spectra.

The Overhauser enhancement factors were determined for three carbons of a dilute, *o*-dichlorobenzene solution of isotactic polystyrene, $-(CH_2CHC_6H_5)-_x$. The aromatic, quaternary carbon enhancement was determined directly by comparison of the integrated intensities of decoupled and coupled spectra. Examples of the absorption spectra and their integrals (obtained under a variety of conditions) are shown in Figure 3. The observed Overhauser enhancement factor is 0.8 ± 0.1, less than half of the theoretical maximum. Since the spin-decoupled spectrum of the methine and methylene carbons covers a spectral range only about three times as large as that of the spin-coupled quaternary carbon, a direct comparison of the integrated intensities of these three lines is acceptable (Figure 4), and indicates the same Overhauser enhancement for the methine and methylene carbons as for the quaternary carbon.

The Overhauser enhancements for polystyrene are not dependent on tacticity, within experimental error. Spectra of the quaternary carbon of isotactic and atactic polystyrene in *o*-dichlorobenzene are shown in Figure 5. The ratios of integrated intensities of spin-coupled and -decoupled amplitude spectra for both kinds of polystyrene are the same and lead to a value for the enhancement factor of 0.8 ± 0.1, in agreement with values obtained from absorption spectra. The enhancement factors for polystyrene are dependent, however, on solvent. Values as large as 1.1 are observed when chloroform is used as a solvent (Figure 6), and as small as 0.5 for solutions of polystyrene in 1,2,4-trichlorobenzene. These differences are independent of polystyrene concentration and were observed for molecular weight fractions ranging from 4000 to 1.6×10^6. Within a given class of solvent (for example, chlorobenzene, dichlorobenzene, trichlorobenzene), the Overhauser enhancement decreases with increasing solvent viscosity. Values for a variety of solvents are presented in Table I.

In addition to a dependence on solvent, the polystyrene Overhauser enhancements also depend on the concentration of any stable free radical in solution. In the presence of an 0.26 *M* chloroform solution of *p*-hydroxy di-*tert*-butyl nitroxide,[22] the Overhauser enhancement factor for the quaternary carbon of polystyrene has been reduced from 1.1 to 0.7, without a significant effect on line shape (Figure 7). As the free radical concentration is increased to 0.65 *M*, the Overhauser enhancement factor is further reduced to 0.4, although now somewhat broader lines and reduced resolution are observed. A plot of the enhancement factor for a chloroform solution of atactic polystyrene as a function of free radical concentration is presented in Figure 8. The experimental values, indicated by the circles and error bars, are in agreement with the theoretical predictions, indicated by the solid curve, calculated from eq 16 assuming $\alpha = 0$ and $kT_{1C}(LH) = 2.24$ l. mole^{-1}.

Although it is possible to remove completely the spin–spin interactions of the polystyrene quaternary carbon with only a fraction of the available ^{1}H rf power (Figure 9), this becomes progressively more difficult as the free radical reaches molar concentrations owing to the drastically reduced proton spin–lattice relaxation time. Complete decoupling, leading to the largest possible observed Overhauser enhancement, can still be ensured in these circumstances by restricting the ^{1}H rf to only those two regions of the spectrum containing polystyrene resonances. This was done for polystyrene solutions containing more than 0.3 *M* free radical, using the balanced mixed decoupling technique described in the Experimental Section.

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(22) This is structure II in O. H. Griffith and A. S. Waggoner, *Accounts Chem. Res.*, 2, 17 (1969).

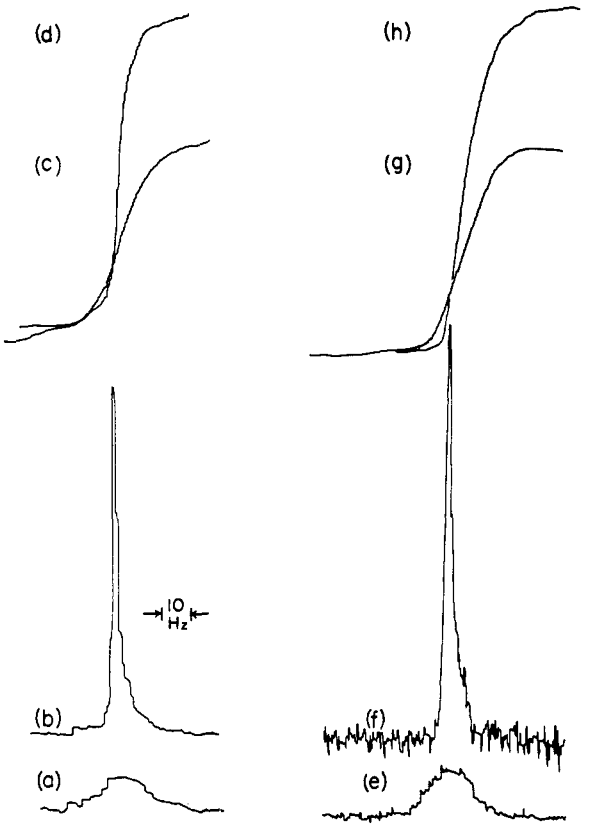

Figure 3. Fourier transforms of the natural-abundance ^{13}C free-induction decay of a 5% (by weight) *o*-dichlorobenzene solution of isotactic polystyrene with (a) no spin decoupling and (b) spin decoupling. These are absorption spectra of the aromatic quaternary carbon region. Both spectra resulted from the accumulations of 4096 free-induction decays, details of which are given in the text; 90° pulses were used with 3-sec spacings. The integrals of (a) and (b) are given in (c) and (d), respectively. Similar absorption spectra are shown in (e) and (f), except that four times as much computer memory capacity was used to digitize the free-induction decay. In addition, 8192 scans were accumulated for (e) and only one-third as many for (f); the vertical display scale for (f) is three times that used for (e). The integrals of (e) and (f) are given in (g) and (h), respectively. For all of these spectra, and for all spectra used in Overhauser enhancement measurements, no digital manipulation of the data followed the accumulation of the free-induction decay prior to the Fourier transform.

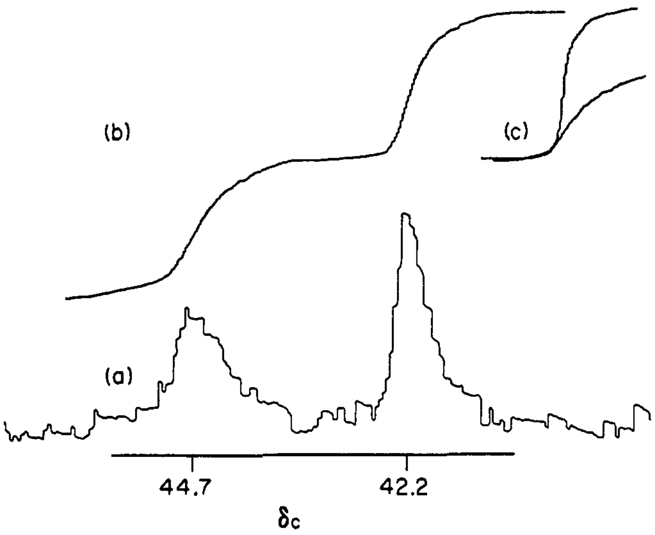

Figure 4. (a) Fourier transform of the spin-decoupled, natural-abundance ^{13}C free-induction decay of a 5% (by weight) *o*-dichlorobenzene solution of isotactic polystyrene. This is an absorption spectrum of the methylene (lower field) and methine carbons. The spectrum was obtained by the same method used to obtain the quaternary carbon spectrum of Figure 3b. The integral of (a) is shown in (b) and compared to the integrals of the spin-coupled and -decoupled spectra of the quaternary carbon of isotactic polystyrene in (c). The reference is tetramethylsilane.

Table II
Proton-Decoupled Carbon-13 Polymer Spin–Lattice Relaxation Times Measured at 22.6 MHz and 40°

Polymer	Solvent	Carbon	T_1, msec[a]
Poly(ethylene oxide)	Neat liquid	Methylene	265
Polyacrylonitrile	DMSO	Methine	115
		Methylene	60
Polystyrene (isotactic)	*o*-Dichlorobenzene	Quaternary	550
		Methine	65
		Methylene	32
Polystyrene (atactic)	*o*-Dichlorobenzene	Quaternary	550
		Methine	60
		Methylene	30
	$CDCl_3$	Quaternary	650
		Methine	85
		Methylene	45
	Tetrachloroethylene	Methine	80
		Methylene	40

[a] Accuracy is ±10%.

(2) Spin–Lattice Relaxation Times. Partially relaxed Fourier transform spectra[6,23,24] of both polyacrylonitrile and polystyrene were obtained using 180–*t*–90 pulse sequences. Typical spectra of polyacrylonitrile are shown in Figure 10, and relaxation times presented in Table II. The integrated intensities of the quaternary carbon of an *o*-dichlorobenzene solution of isotactic polystyrene corresponding to a variety of delay times between the 180 and 90° pulses are shown in Figure 11. For a delay time of 50 msec, the magnetization vector of the quaternary carbon has had no chance to recover from the inverting 180° pulse, so that the Fourier transform of the free-induction decay obtained following the 90° pulse produces an inverted line of full intensity. The spin–lattice relaxation time can be obtained from the slope of a plot of integrated intensity against delay time, and an example is shown in Figure 12. Values for the relaxation times obtained from these plots agree with those obtained from nulled spectra to better than ±10%. Just as for the Overhauser enhancements, the spin–lattice relaxation times of the quaternary carbons of iso- and atactic polystyrene are the same, within experimental error. Values are presented in Table II.

As with polyacrylonitrile, the spin–lattice relaxation times of the methine and methylene carbons of isotactic polystyrene in *o*-dichlorobenzene differ by a factor of 2 (Table II). Moreover, the relaxation times of these carbons in isotactic polystyrene are the same as those of the corresponding carbons of atactic polystyrene, in the same solvent. Typical partially relaxed Fourier transform spectra are shown in Figure 13a,b. Although tacticity is not critical in determining the spin–

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(23) A. Allerhand, O. Doddrell, V. Glushko, D. N. Cochran, E. Wenkert, P. J. Lawson, and F. R. N. Gurd, *J. Amer. Chem. Soc.*, **93**, 544 (1971).

(24) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR," Academic Press, New York, N. Y., 1971, p 82.

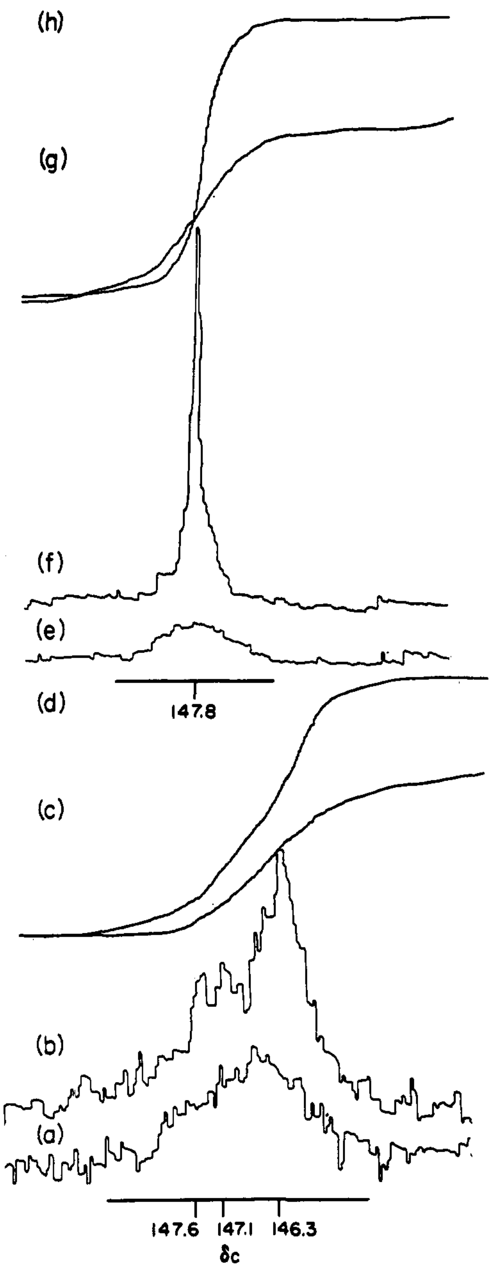

Figure 5. Fourier transforms of the natural-abundance ^{13}C free-induction decays of a 20% (by weight) *o*-dichlorobenzene solution of atactic polystyrene with (a) no spin decoupling and (b) spin decoupling. These are amplitude spectra of the aromatic quaternary carbon region. Both spectra resulted from the accumulations of 2048 free-induction decays, details of which are given in the text; 90° pulses were used with 3-sec spacings. The integrals of (a) and (b) are given in (c) and (d), respectively. The corresponding amplitude spectra and their integrals of the *o*-dichlorobenzene solution of isotactic polystyrene, obtained under identical conditions, are given in (e)–(h), respectively. The Overhauser enhancement factors resulting from these integrals are the same for both atactic and isotactic polystyrene, and the same as obtained from integrals of absorption spectra.

lattice relaxation time, the choice of solvent is important. Figure 13c shows partially relaxed Fourier transform spectra of a tetrachloroethylene solution of atactic polystyrene. While a 50-msec delay between pulses has more than completely nulled the high-field methine carbon signal of this polystyrene solution, it has not done so for an *o*-dichlorobenzene solution of the same polymer. Thus, the spin–lattice relaxation times of polystyrene in tetrachloroethylene are about 20% longer than those in *o*-dichlorobenzene. Values for spin–lattice relaxation times in several solvents are given in Table II.

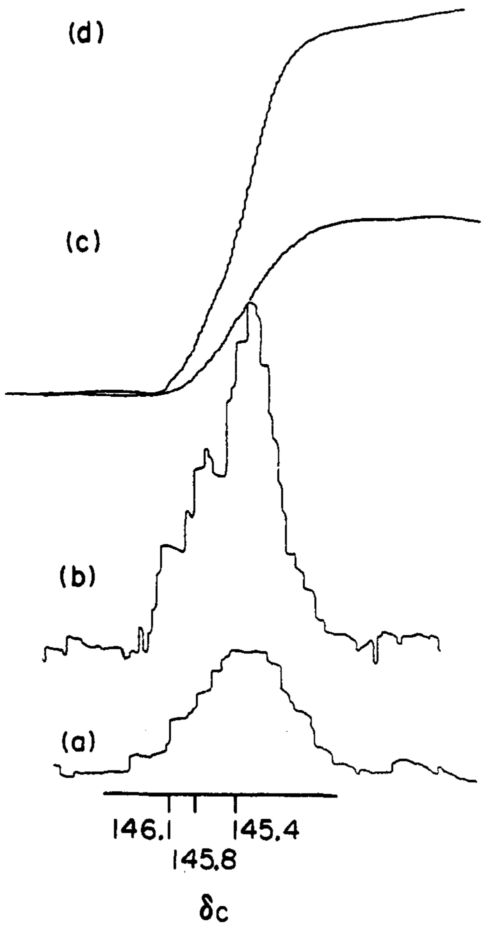

Figure 6. Fourier transforms of the natural-abundance ^{13}C free-induction decays of a 20% (by weight) chloroform solution of atactic polystyrene with (a) no spin decoupling and (b) spin decoupling. These are absorption spectra of the aromatic quaternary carbon region. Both spectra resulted from the accumulations of 2048 free-induction decays, details of which are given in the text; 90° pulses were used with 3-sec spacings. The integrals of (a) and (b) are given in (c) and (d), respectively.

Discussion

(1) Spin–Lattice Relaxation Times and ^{13}C Overhauser Enhancement Factors. The spin–lattice relaxation times for the methine and methylene carbons of polyacrylonitrile and polystyrene in a variety of solvents differ from one another by a factor of 2. This result establishes the likely operation of a purely carbon–proton dipolar relaxation mechanism for these two kinds of carbons.[3] Furthermore, the equality of the methine, methylene, and quaternary carbon Overhauser enhancements for both polymers suggests a purely dipolar relaxation mechanism for all three types of nuclei. In general, if other relaxation mechanisms were important for the quarternary carbon, its Overhauser enhancement would be expected to be smaller than the methine and methylene carbon enhancement.[3]

The absence of nondipolar relaxation means that $T_{1C}(LH)/T_{1CH} = 1$, and that the observed deviations of the Overhauser enhancements from the theoretical maximum are due to deviations of ρ from the maximum value of $^1/_2$. In other words, the Overhauser enhancements are small because the correlation times of the polymeric segmental motions, impor-

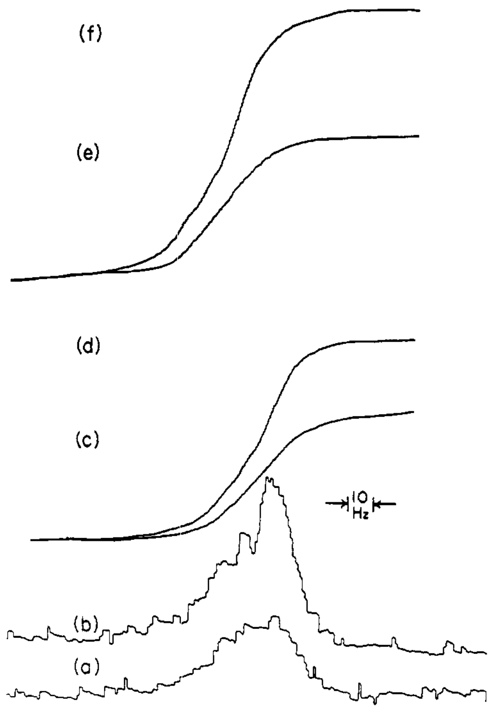

Figure 7. Fourier transforms of the natural-abundance ^{13}C free-induction decays of a 20% (by weight) deuteriochloroform solution of atactic polystyrene containing 0.26 *M* nitroxide free radical with (a) no spin decoupling and (b) spin decoupling. These are amplitude spectra of the aromatic quaternary carbon region. Both spectra resulted from the accumulations of 2048 free-induction decays, details of which are given in the text; 90° pulses were used with 3-sec spacings. The integrals of (a) and (b) are given in (c) and (d), respectively, and compared to integrals of spectra obtained under identical conditions in the absence of the free radical in (e) and (f). The enhanced line intensity is less in the system containing the free radical.

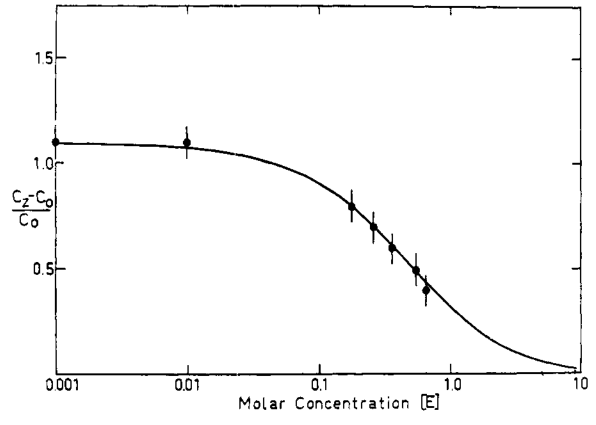

Figure 8. A plot of the Overhauser enhancement factor for the aromatic quaternary carbon of a deuteriochloroform solution of atactic polystyrene as a function of the nitroxide free radical concentration of the solution. Experimental values are given by points and error bars. The solid curve gives the theoretical dependence (see the text for details).

tant to relaxation, are long enough that at the nmr observing frequency of 22 MHz the extreme narrowing condition does not apply, relations 10 do apply, and the efficiency of the dynamic coupling between carbons and protons is reduced.

This situation is not unexpected for polymer solutions. Liu and Ullman[25] have estimated that appoximately 5–10% of

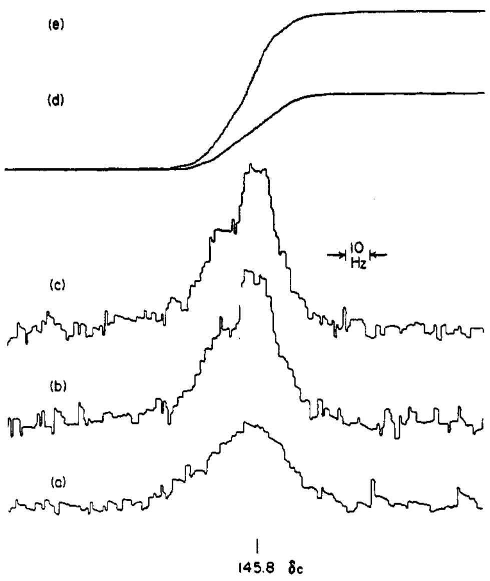

Figure 9. Fourier transforms of the natural-abundance ^{13}C free-induction decays of a 20% (by weight) tetrachloroethane solution of atactic polystyrene with (a) no spin decoupling, (b) spin decoupling using a field intensity $\gamma H_2/2\pi$ = 300 Hz, and (c) spin decoupling using a field intensity $\gamma H_2/2\pi$ = 3000 Hz. All three spectra are amplitude spectra of the aromatic quaternary carbon region and resulted from the accumulations of 2048-free-induction decays, details of which are given in the text; 90° pulses were used with 3-sec spacings. The integrals of (a) and (b) are given in (d) and (e), respectively. The enhanced integrated line intensity is the same for both weak and strong ^1H decoupling fields.

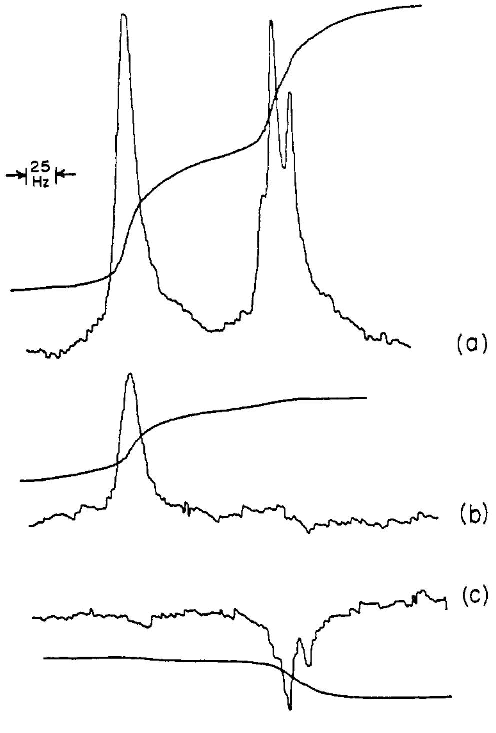

Figure 10. Partially relaxed Fourier transforms of the spin-decoupled natural-abundance ^{13}C free-induction decays of the methylene and methine carbon regions of a dimethyl-d_6 sulfoxide solution of polyacrylonitrile for a delay time of (a) 600, (b) 80, and (c) 40 msec. The repetition time of the 180°-t-90° pulse sequence was 2 sec. The free-induction decays following the 90° pulse were obtained by sampling the receiver output using 1024 channels of a time-averaging computer internally swept at a rate of 400 μsec per channel. The high-field methine carbon line is nulled for a delay time twice that required to null the low-field methylene carbon line.

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(25) K-J Liu and R. Ullman, *J. Chem. Phys.*, **48**, 1158 (1968).

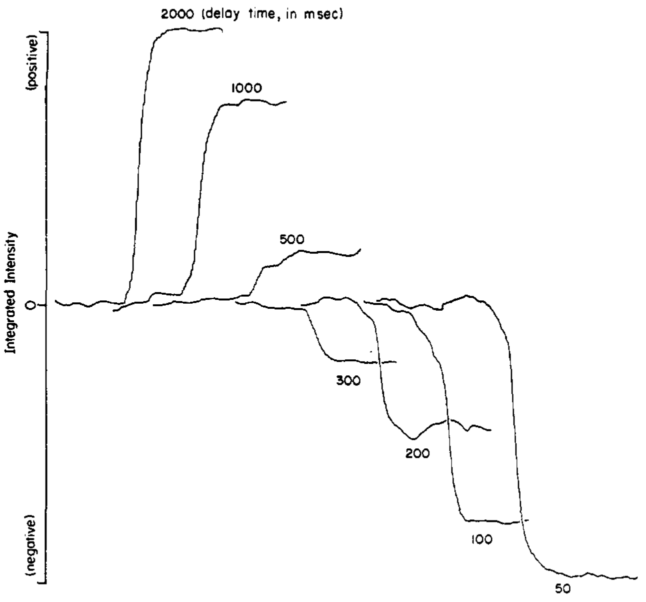

Figure 11. A display of integrated intensities of the spin-decoupled absorption spectrum of the aromatic quaternary carbon of a 5% (by weight) *o*-dichlorobenzene solution of isotactic polystyrene. The intensities were obtained from a series of partially relaxed Fourier transform experiments. The repetition time of the 180°-t-90° pulse sequence was 5 sec. The delay times between the 180 and 90° pulses are indicated in the figure. The same procedure was used as for the spectrum of Figure 3b except that each spectrum resulted from the accumulation of 512 free-induction decays.

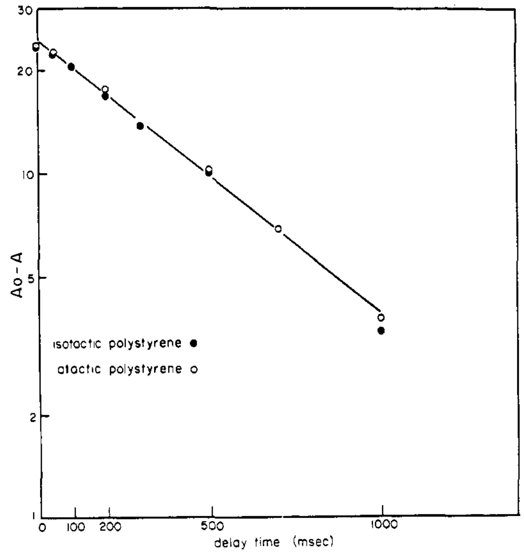

Figure 12. A plot of integrated intensities of the spin-decoupled aromatic quaternary carbon line of *o*-dichlorobenzene solutions of iso- and of atactic polystyrene as a function of the delay time, t, in a partially relaxed Fourier transform experiment. The observed integrated intensity is A, and the 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 $A = A_0[1 - 2\exp(-t/T_1)]$.

the segmental motions which contribute to dipolar proton spin-lattice relaxation of poly(ethylene oxide) at 60 MHz do not satisfy the extreme narrowing condition. One would therefore expect $\rho_{CH} < {}^1/_2$ for ^{13}C nmr spectra obtained at 22 MHz provided that similar segmental motions modulate the ^{13}C-^1H coupling. Furthermore, one would expect

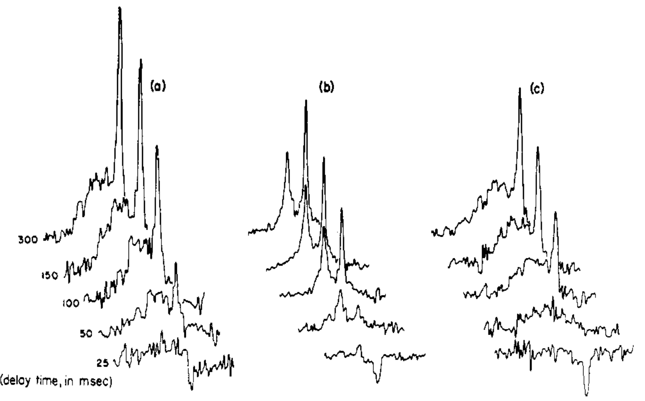

Figure 13. Partially relaxed Fourier transforms of the spin-decoupled, natural-abundance ^{13}C free-induction decays of (a) an *o*-dichlorobenzene solution of atactic polystyrene, (b) an *o*-dichlorbenzene solution of isotactic polystyrene, and (c) a tetrachloroethylene solution of atactic polystyrene. Only the methylene and methine carbon regions are shown. The repetition time of the 180°-t-90° pulse sequence was 1 sec. Delay times between pulses are given in the figure. The free-induction decays following the 90° pulse were obtained by sampling the receiver output using 1024 channels of a time-averaging computer internally swept at a rate of 400 μsec per channel. Only 512 scans were accumulated for each free-induction decay. *The 1K of data were transformed into a 2K absorption* spectrum using digital filtering techniques. (This kind of data manipulation was avoided in the Overhauser enhancement measurements.) Just as for the quaternary carbon of polystyrene, differences in tacticity have less effect on the spin-lattice relaxation times of the methylene and methine carbons than differences in solvent (see text for discussion of this point).

polymer chains more hindered than poly(ethylene oxide) to have even larger numbers of segmental motions with still longer correlation times which fail to satisfy the extreme narrowing condition, resulting in even greater deviations of ρ from ${}^1/_2$, and hence smaller Overhauser enhancements. This is consistent with the results of Table I, which show smaller Overhauser enhancements for polyacrylonitrile and polystyrene than for poly(ethylene oxide). In terms of a description of relaxation based on a single correlation time, the greater freedom of poly(ethylene oxide) relative to polystyrene or polyacrylonitrile results in a shorter *average* correlation time which more nearly satisfies the extreme narrowing condition. This leads to the larger Overhauser enhancement for the flexible poly(ethylene oxide).

Liu and Anderson[26] have also shown that proton spin-lattice relaxation times of polymer solutions depend on the choice of solvent. Qualitatively, for a given solvent class, as the solvent viscosity increases, the local polymer microviscosity increases, the segmental correlation time increases, and this, in turn affects the proton T_1. Assuming that the dipolar model outlined earlier offers an acceptable description of ^{13}C relaxation in these polymer solutions, an increase in local microviscosity will also decrease ρ_{CH}, and hence the Overhauser enhancement. The results in Table I are consistent with this interpretation. The large Overhauser enhancements for polystyrene were observed for the less viscous members of a solvent class. For example, the enhancement in dichlorobenzene is greater than in trichlorobenzene, and greater in chloroform than in carbon tetrachloride. It should be noted that local microviscosity depends qualitatively on the viscosity of the *solvent* rather than that of the solution and

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(26) K-J Liu and J. E. Anderson, *Macromolecules*, **3**, 163 (1970).

that the correlation only applies within a given solvent class.

The ^{13}C spin–lattice relaxation times are solvent dependent. The fact that the polystyrene quaternary carbon Overhauser enhancement has the same solvent dependence as its spin–lattice relaxation time, and the same dependence as the solvent dependence of the Overhauser enhancements and relaxation times of the methine and methylene carbons of polystyrene, supports the conclusion that all of the carbons of polystyrene are dominated by the same dipolar relaxation mechanism.

The foregoing interpretations are based, for the most part, on the assumption of a model in which dipolar interactions are modulated by isotropic segmental motion of the polymer chains. Clearly, such motion is unlikely to be isotropic. However, the evidence suggests that the unknown correlation function describing the actual motion (or distribution of motions) may not differ greatly from that due to isotropic motion described by a single average correlation time τ_{CH}.[12,13] This suggests that eq 1, 5, and 8 can reasonably be used to obtain values of ρ_{CH} and thus τ_{CH} from observed Overhauser enhancement factors. These values are listed in Table I. Generally, $\omega_C\tau_{CH} < 0.3$. Furthermore, by utilizing the values of τ_{CH} obtained, eq 5 can be used to predict the frequency dependence of $T_{1C}(LH)$, since $T_{1C}(LH) = T_{1CH}$. Thus, on the basis of spin–lattice relaxation times and Overhauser enhancement factors measured at 22.6 MHz (Table II), the corresponding values for the methine and methylene carbons of polystyrene in tetrachloroethylene at 15.1 MHz are calculated to be 31 and 62 msec, respectively. These are in excellent agreement with experimental[11] values of 32 and 63 msec.[26a] This further supports the assumption that the simplified model of isotropic segmental motion and a single correlation time can be used to describe the main features of ^{13}C spin–lattice relaxation in solutions of polymers, or at least of nonelastomeric polymers.

The assumption is unlikely to be useful in describing the segmental motion of flexible polymers, such as poly(ethylene oxide), or the closely related poly(propylene oxide), as well as solid rubbers such as polybutadiene. In fact, for poly(propylene oxide) it can be shown that the spin–lattice relaxation times of the methine and methylene carbons differ by only 20% even though the dominant relaxation mechanism is dipolar, and even though the Overhauser enhancements are the same for all carbons.[27] The anisotropy or asymmetry of the segmental motion prevents an adequate description in terms of a single correlation time, even for carbons located in the main chain, and so prevents extracting correlation times from Overhauser enhancement measurements. (For this reason, a calculated correlation time for poly(ethylene oxide) has been omitted from Table I.) For solid polymers such as *cis*-polybutadiene, the distribution of motions is such that a single correlation time is sometimes an inadequate description and a distribution of correlation times is required.[27] Despite this complication, the Overhauser enhancements for different carbons in polybutadiene, while smaller than the maximum theoretical value, are all equal, within experimental error. Thus, even though a simple, isotropic description of relaxation and the ^{13}C Overhauser enhancement is obviously inadequate, the enhancement itself does not necessarily complicate the interpretation or analysis of the spectra of these polymers. This conclusion is discussed in more detail in the next paragraph.

(2) Some Implications of the ^{13}C T_1 and Overhauser Enhancement Measurements for Other ^{13}C Nmr Measurements of Polymers. The equality of the observed Overhauser enhancements of different carbons in the same polymer in solution (for a variety of systems) has the important consequence that the integrated intensities, at any frequency, of ^{13}C nmr lines of a given polymer in solution can, in general, be expected to be directly related to the number of carbons contributing to each resonance. Thus, there is no loss of ^{13}C spectral information even though significant (but less than maximum) Overhauser effects operate. Exceptions can be expected only if all the carbons in a polymer do not somehow comparably share in about the same kind of main-chain segmental motion. For example, complications in comparing ^{13}C intensities might be expected for relatively long, flexible side chains connected to more rigid main chains. As indicated in the theoretical section, complications might also be expected interpreting intensities in spectra of polymers which have anisotropic main-chain segmental motions, the correlation times for many of which satisfy $\omega\tau_{CH} > 0.5$, or $\tau_{CH} \approx \tau_{int}$. However, this situation is not likely for *solutions* of most polymers. In the majority of cases, especially for synthetic polymers, it will be possible to use the integrated intensities of a ^{13}C nmr spectrum of a given polymer solution obtained at any presently available frequency to count the number of carbons contributing to the signal to obtain both structural and steric information.

For example, since the Overhauser enhancements of the various carbons of polystyrene are independent of tacticity, within experimental error, the measurement of quantities such as the concentration of steric defects is straightforward. This is also true even for polymers whose glass-transition temperatures (and so, presumably, some details of their segmental motions) depend on stereoregularity. Thus, there is no obvious dependence of integrated ^{13}C nmr line intensities on tacticity for polymers such as poly(methyl methacrylate)[18,28] and poly(vinyl chloride).[29] In each of these cases, the ^{13}C nmr measurement of the tacticity of an atactic material compared to a more stereoregular version of the same polymer[30] was in agreement with comparable measurements using other physical techniques, such as ^{1}H nmr and ir spectroscopy.

(3) Some Chemical Implications of the ^{13}C T_1 and Overhauser Enhancement Measurements. The quaternary carbon of polystyrene has a relaxation time about eight times longer than the methine carbon. Nevertheless, this relaxation time is still shorter, by about a factor of 4, than is predicted. The prediction is based on eq 5, the correlation time in Table I (obtained from the Overhauser enhancement measurements), and published values for proton–carbon distances within the monomer unit (the smallest of which, the distance to the two ortho protons, is 2.15 Å, or twice an average C–H bond distance). This discrepancy exists despite the fact that using the same procedure, calculated values for the relaxation times of both the main-chain methine and methylene carbons, as well as the side-chain aromatic meta and para carbons are in good agreement with experiment,[11] results which make

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(26a) NOTE ADDED IN PROOF. Values of 38 and 73 msec (at 15.1 MHz) have now been reported for the two main-chain spin–lattice relaxation times of a polystyrene of molecular weight about 200,000 in tetrachloroethylene (A. Allerhand and R. K. Hailstone, *J. Chem. Phys.*, **56**, 3718 (1972)). These values are in poorer agreement with our calculated values at 15.1 MHz than were the earlier experimental values. However, the recent measurements are reported to be at a somewhat higher temperature and are claimed to be no more accurate than ±15–30%.

(27) J. Schaefer, manuscript in preparation.

(28) Y. Inoue, A. Nishioka, and R. Chûjô, *Polym. J.*, **4**, 535 (1971).

(29) J. Schaefer, reported at the 13th Eastern Analytical Symposium, New York, N. Y., Nov 1971.

(30) The poly(vinyl chloride) of increased syndiotacticity was prepared according to C. Mazzolini and F. Denti, U. S. Patent 3,388,201 (1968).

unlikely possible pronounced anisotropies in the motion of the phenyl side group relative to the main chain. The discrepancy cannot be attributed to additional nondipolar contributions to the quaternary carbon spin–lattice relaxation time, since this is inconsistent with the observed Overhauser enhancements and their solvent dependence discussed earlier. Spin diffusion[31] is not effective in these experiments in equalizing ^{13}C spin–lattice relaxation times (and so lowering the quaternary carbon T_1) because the ^{13}C nuclei are isolated from one another by their low natural abundance. In addition, the carbon nuclei do not efficiently exchange energy *via* spin diffusion with intervening protons. For two species of nuclei whose resonance frequencies are greatly different, heteronuclear spin diffusion can become important in determining spin–lattice relaxation times only in rotating frame or spin-locking nmr experiments.[32,33]

The apparent discrepancy arises because the spin–lattice relaxation time of the quaternary carbon results from dipolar coupling with many protons, including those of nearest-neighbor monomer units in the chain. For example, an estimate[34] of the distance of the quaternary carbon to the closest methine proton in a nearest-neighbor monomer unit in crystalline polystyrene is comparable to estimates of the shortest quaternary carbon–proton distances within the monomer. In addition, space-filling molecular models of both iso- and syndiotactic polystyrene point to this proton as being particularly close to the aromatic quaternary carbon. Considering protons of the same monomer unit, as well as protons of nearest- and next-nearest-neighbor monomer units, there are some six to ten protons which, in solution, are probably within 2.0–2.5 Å of a given quaternary carbon. All of these protons are capable of making a significant dipolar contribution to the quarternary carbon T_1.

Because of the likely importance of dipolar interactions with protons of nearest-neighbor monomer units, the similarities of relaxation times and Overhauser enhancements for the quaternary carbons of both iso- and atactic polystyrene in solution require that the average distance between a quaternary carbon and its nearest-neighbor protons be about the same for the two polymers. Furthermore, these protons and carbons in both polymers must be involved in about the same kind of segmental motion. This is consistent with calculations by Fujiwara and Flory of conformational populations in polystyrene.[35] These calculations show that the very few, highly preferred conformations of iso- and syndiotactic polystyrene dominate all other contributors (some of which have more strained geometries and less normal internuclear distances), and that as a result, the average distance between a quaternary carbon and its nearest-neighbor protons is about the same for both iso- and syndiotactic placements. Furthermore, in each of the preferred conformations, the phenyl group is constrained by about the same steric interactions of its ortho protons and carbons with various main-chain protons.[35] The physics of the steric interactions of the phenyl group is of primary importance for polystyrene. Thus, while different chemical environments can give rise to different ^{13}C chemical shifts, the dominant physical interactions controlling the segmental motions for the different preferred conformations are similar, and this leads to similar relaxation times and Overhauser enhancements.

Of course, the probabilities for the preferred conformations are not identical for both iso- and syndiotactic placements. They are even slightly different for syndiotactic placements in predominantly isotactic chains compared to syndiotactic placements in predominantly syndiotactic chains. The preferred conformations themselves are not identical and do not have identical steric interactions. These differences have led to the suggestion that the *proton* nmr resonance due to a syndiotactic placement in an isotactic chain may be broad and difficult to detect because of a wide variety of long-range, configurationally dependent chemical shifts.[36] This would permit isotactic polymers to have high concentrations of steric defects which would remain undetected in proton nmr spectra, conditions attributed to both isotactic polypropylene[37] and polystyrene.[35] Regardless of their effects on proton nmr spectra, these differences are not large enough to cause complications in ^{13}C nmr spectra. The integrated intensities of the quaternary and methine carbon lines of isotactic polystyrene are the same even though the dependence on the steric configuration of the chemical shift of the quaternary carbon is more than an order of magnitude greater than that of the methine carbon. Thus, if long-range steric configurational effects were important, steric defects would cause a spread of quaternary carbon lines, thereby resulting in an apparent loss of intensity of the major line. This is not observed. The only effect of steric defects (which must be present in a concentration of less than 5%) on the noncrystalline, isotactic polystyrene quaternary carbon spectrum is a slight shoulder on the high-field side of the resonance. This shoulder is not even enough, however, to affect significantly the quaternary carbon line width. The ratios of widths of the quaternary, methine, and methylene lines (2:12:24 Hz, respectively) are about the same as the ratios of spin–lattice relaxation times of the three carbons.[38]

(4) The Addition of Paramagnetic Species to Polymer Solutions. Regardless of the details of any segmental motions, a method for obtaining absolute intensities from proton-decoupled ^{13}C nmr spectra of polymers is to eliminate completely the Overhauser enhancement by addition of a paramagnetic species. The quaternary carbon of polystyrene is particularly amenable to an investigation of the effectiveness of this technique because its undecoupled intensity is easily measured. The results depicted in Figure 8 indicate that addition of approximately 1 *M* nitroxide free radical to atactic polystyrene in $CDCl_3$ does, indeed, reduce the Overhauser enhancement factor of the quaternary carbon to about zero. For polystyrene, it has been demonstrated that $T_{1C}(LH)/T_{1CH} = 1$, so it is not possible to extract independent values of $T_{1C}(LH)$, T_{1CH}, k, and α from the data in Figure 9 using eq 15. However, the solid line in Figure 9 is calculated from eq 16, assuming $\alpha = 0$ and the product $kT_{1C}(LH) = 2.24$ l. mol^{-1}. (It has been established that $S_H = 1$ for all radical concentrations reported here.) The radical used is capable of forming

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(31) Problems associated with spin diffusion affecting proton spin-lattice relaxation measurements in polymer solutions are discussed in J. E. Anderson and K-J Liu, *J. Chem. Phys.*, **49**, 2850 (1968).

(32) S. R. Hartmann and E. L. Hahn, *Phys. Rev.*, **128**, 2042 (1962).

(33) F. M. Lurie and C. P. Slichter, *ibid., A*, **133**, 1108 (1964).

(34) Based on coordinates in G. Natta, P. Corradini, and I. W. Bassi, *Nuovo Cimento, Suppl.*, **15**, 68 (1960).

(35) Y. Fujiwara and P. J. Flory, *Macromolecules*, **3**, 43 (1970).

(36) P J. Flory and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **88**, 2873 (1966).

(37) P. J. Flory, *Macromolecules*, **3**, 613 (1970).

(38) Note that these widths, or T_2 values, are not well described by eq 7 and the average correlation time which, with the isotropic model and eq 5, does adequately describe the various T_1 values for polystyrene. The reason for this is the T_2 is sensitive to those slower modes of motion which do not contribute effectively to T_1. Most segmental motions in polymers and polymer solutions can be considered distributions of motions, associated with distributions of correlation times. Since, in effect, T_1 and T_2 sample different parts of the distribution of motions, a different average correlation time is involved for each.

dimers by hydrogen bonding through the hydroxyl groups.[39] If it is assumed that all the radical is present in the form of dimers, kT_{1C}(LH) = 4.48 l. mol^{-1}. A more rigorous analysis based on the assumption of fast exchange between radical monomers and dimers and incomplete dimerization results in a slightly better description of the data. However, the errors in $(C_Z - C_0)/C_0$ are too large to distinguish the number of radical species actually present. A noticeably worse fit is obtained if $\alpha/(k + \alpha) \geq 0.05$. To date no systems have been found in which α is demonstrably greater than zero.

(39) As detected by ir techniques described in A. Ens and F. E. Murray, *Can. J. Chem.*, **35**, 170 (1957).

Comparisons of the Carbon-13 Nuclear Magnetic Resonance Spectra of Some Solid *cis*- and *trans*-Polyisoprenes

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ABSTRACT: Fourier transforms have been obtained of the ^{1}H and ^{2}H simultaneously noise-decoupled, natural-abundance, 22.6-MHz ^{13}C free-induction decays of solid *cis*- and *trans*-polyisoprene, *cis*-polyisoprene-*3*-d_1, and carbon-black-filled *cis*-polyisoprene. Carbon-13 line widths and Overhauser enhancements have been measured from the phase-corrected normal and selectively saturated absorption spectra, and spin–lattice relaxation times measured from partially relaxed Fourier transform absorption spectra. The spin–lattice relaxation times and Overhauser enhancements of the individual carbons of the amorphous part of *trans*-polyisoprene are all greater than those of the corresponding carbons of *cis*-polyisoprene, and, excluding the deuterated carbon, of *cis*-polyisoprene-*3*-d_1. These spin–lattice relaxation times are interpreted in terms of a dipolar relaxation mechanism modulated by the segmental motion of the chain. The greater relative segmental flexibility of the *trans*-polyisoprene chain leads to longer spin–lattice relaxation times. The flexibility of the trans chain also permits more of its segmental motions to satisfy the extreme narrowing conditions, and this leads to the larger observed Overhauser enhancement. The various spin–lattice relaxation times of the individual carbons of *cis*-polyisoprene are not noticeably affected by the addition of carbon black. However, the ^{13}C line widths are affected by the filler. The line widths of individual carbons of the carbon-black-filled *cis*-polyisoprene are greater than those of ordinary *cis*-polyisoprene by factors of 5–10. The broadening is different for different carbons. These results are interpreted in terms of the exclusion by the filler of the polymer from some spatial orientations leading to only partial motional narrowing of the nmr lines. Even in the absence of a filler, factors such as chain entanglements can prevent total isotropic motional narrowing of the lines. This effect can be used to explain the absence of any pronounced line narrowing upon selective deuteration of *cis*-polyisoprene, even though large differences in spin–lattice relaxation times result. The ^{13}C line widths of all of these solid, rubbery polymers are as much as a factor of 20 less than the ^{1}H nmr line widths of the same polymers. The narrow lines are attributed to the isolation of the ^{13}C spins from dipolar interactions with each other and with most protons.

Narrow lines are observed in the ^{13}C nmr spectra of solid polymers if the temperature at which the experiment is performed is above the glass-transition temperature of the solid. This is true for solid elastomers,[1] or rubbery polymers, as well as more rigid polymers in solid gels.[2] The lines are more than an order of magnitude narrower than ^{1}H nmr lines of the same systems and are sufficiently narrow to permit resolution of the resonances of individual carbons. In addition, for rubbers such as the polyisoprenes, the ^{13}C line widths vary from one type of a carbon to another in a generally unexpected way. In order to gain some understanding of the origin and significance of these narrow lines, we have compared the ^{13}C nmr spectra of solid *cis*- and *trans*-polyisoprene, *cis*-polyisoprene-*3*-d_1, and carbon-black-filled *cis*-polyisoprene. The interpretation of the differences observed in the spectra of these polymers (including differences not only in line widths but also in spin–lattice relaxation times and Overhauser enhancements) suggests that ^{13}C nmr may be especially sensitive to the structure of the amorphous regions of many solid polymers above the glass-transition temperature, especially filled polymers, and may therefore constitute a new approach to the characterization of such systems.

Experimental Section

High-resolution, natural-abundance pulsed ^{13}C nmr spectra were obtained at 22.6 MHz using a Bruker spectrometer, some details of which have been described earlier.[3] The ^{13}C nmr spectra were obtained with only ^{1}H or with simultaneous ^{1}H and ^{2}H noise decoupling, the latter to simplify the spectra of partially deuterated materials. The ^{13}C analytical channel was operated in a single coil mode with a 90° pulse requiring 18 μsec. Free-induction decays were accumulated in a Nicolet 1074 time-averaging computer, and Fourier transforms were calculated by a Digital Equipment Corp. PDP-8/I computer. The calculation of the pure absorption spectra included a linear phase correction.

Spin–lattice relaxation times were measured from partially relaxed Fourier transform spectra[4] obtained from 180–*t*–90 sequences. The sequence timing for the 180 and 90° pulses, as well as the external trigger for the time-averaging computer, were provided by a crystal-controlled, Ortec two-channel pulse generator.

Nuclear Overhauser enhancements of the quaternary carbons of the polyisoprenes were directly measured by accumulating a proton-decoupled free-induction decay, performing the Fourier transform, storing the transformed spectrum in the 1074 memory, offsetting the ^{1}H rf by 50 kHz, turning off the ^{1}H noise modulation, collecting

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(2) J. Schaefer, *ibid.*, **4**, 110 (1971).
(3) J. Schaefer, *ibid.*, **4**, 98 (1971).
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