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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(1) M. W. Duch and D. M. Grant, *Macromolecules*, **3**, 165 (1970).

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

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

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

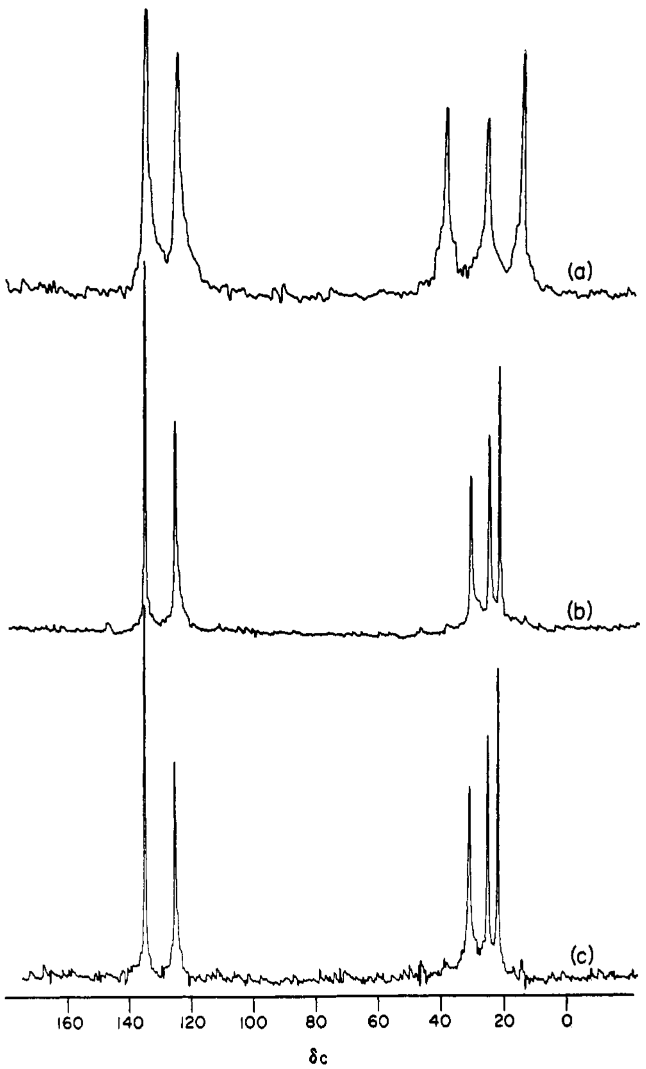

Figure 1. Fourier transforms of the noise-decoupled, natural-abundance ^{13}C free-induction decays of solid (a) natural *trans*-polyisoprene and (b) synthetic *cis*-polyisoprene. The free-induction decays were obtained by sampling the receiver output using 4096 channels of a time-averaging computer internally swept at a rate of 100 μsec/channel. The repetition time of the 90° pulse was 3 sec; 512 scans were accumulated for (a) and 128 scans for (b). The spectrum of *cis*-polyisoprene obtained under identical conditions to (b), except for the removal of all analog and digital filtering of the free induction decay, is shown in (c). Although the signal to noise ratio is reduced, there is no attenuation of the higher frequency lines.

the proton-coupled free-induction decay, and then performing a second transform. Except for the now unmodulated ^1H 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 Nicolet 1074. The ratio of the two integrals was used to determine the $^{13}C\text{-}\{^1H\}$ Overhauser enhancement. Overhauser enhancements of non-quaternary carbons were obtained by comparisons of integrated intensities in spin-decoupled spectra of both quaternary and non-quaternary carbons.

Nuclear Overhauser enhancements of both types of carbons were also measured by a transient technique.[5-7] By gating the ^1H rf decoupling frequency and waiting a variable delay time before triggering the ^{13}C pulse, a single-resonance spectrum is obtained whose integrated intensity is a function of the delay time. For very short delays (relative to spin-lattice relaxation times), the integrated intensity reflects almost the full Overhauser enhancements in contrast to what is observed for very long delays. A plot of the observed integrated intensity against the time delay in this experiment then yields an intercept and an asymptote which can be used to obtain the Overhauser enhancement. A possible advantage of such a graphical technique is the elimination of reliance upon the absolute values of just two measurements, the integrated intensities of the coupled and decoupled spectra, which, in general, do not cover the same spectral width. Also, information about proton and ^{13}C spin-lattice relaxation times sometimes can be extracted from this kind of experiment. (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.)

Selectively saturated Fourier transform spectra[8] were obtained by immediately preceding the usual sampling pulse with a relatively long burst of coherent, single-frequency power near the resonance frequency of one of the ^{13}C transitions. Depending on the cw power level and the length of the burst, any ^{13}C line can either be attenuated or completely removed from the transformed spectrum. This technique has a practical application in removing solvent, or other very intense lines which obscure nearby lines of interest. It can also be used to investigate the physics of relaxation processes, which was its purpose in this study. The cw ^{13}C rf was generated by a gated Hewlett-Packard 5105A-5110B frequency synthesizer and amplified by a Boonton 230A power amplifier. Power levels between 0.1 and 1.0 mW were used.

Samples of synthetic *cis*- and *trans*-polyisoprene $\text{+}CH_2CCH{=}CHCH_2\text{+}_x$, of a natural *trans*-polyisoprene, balata, and of a carbon black-filled *cis*-polyisoprene were obtained from Dr. Virgil Mochel, The Firestone Tire and Rubber Co., Akron, Ohio. The carbon-black-filled rubber was a standard, uncured tread stock containing 45-pph SAF black, as well as the usual assortment of other ingredients including sulfur, zinc oxide, oil, accelerators, and antioxidants in minor concentrations. A sample of *cis*-polyisoprene-*3-d*$_1$, $\text{+}CH_2CCH_3{=}CDCH_2\text{+}_x$, was supplied by Dr. Charles Wilkes, B. F. Goodrich Co., Brecksville, Ohio. Cylinders were cut from single pieces of these materials and fitted inside 13-mm Wilmad nmr tubes. The cylinders were greater in length than the receiver coil and fitted snugly into the sample tube. Air gaps between the sample and the sample tube were avoided.

In most of these experiments, a flux stabilizer provided the field stabilization. The internal, heteronuclear field-frequency stabilization of the spectrometer was not convenient to use with solids. Since the observed ^{13}C signals from all of the polyisoprenes were strong, spectra could be obtained in relatively short periods of times, thereby eliminating problems arising from long-term field drifts. When line widths of solids were to be measured, and especially narrow lines were expected, the free-induction decay was accumulated in a time limited to just a few seconds in order to avoid the possibility of line broadening resulting from field drift.

Results

(1) *cis*- and *trans*-Polyisoprenes. The ^{13}C nmr spectra of the synthetic *trans*- and *cis*-polyisoprenes at 40° and 22.6 MHz are shown in Figures 1a and 1b, respectively. The relative line positions agree with those reported previously.[1] For both polymers, the five lines in each spectrum are assigned to the quaternary vinyl carbon, the methine vinyl carbon, the methylene carbon adjacent to the quaternary carbon, the remaining methylene carbon, and the methyl carbon, in order of increasing magnetic field. These assignments have been documented before.[1]

Within each spectrum the integrated intensities of the five

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(5) K. F. Kuhlman, D. M. Grant, and R. K. Harris, *J. Chem. Phys.*, **52**, 3439 (1970).

(6) T. D. Alger, S. W. Collins, and D. M. Grant, *ibid.*, **54**, 2820 (1971).

(7) J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect," Academic Press, New York, N. Y., 1971, p 115.

(8) J. Schaefer, *J. Magn. Resonance*, **6**, 670 (1972).

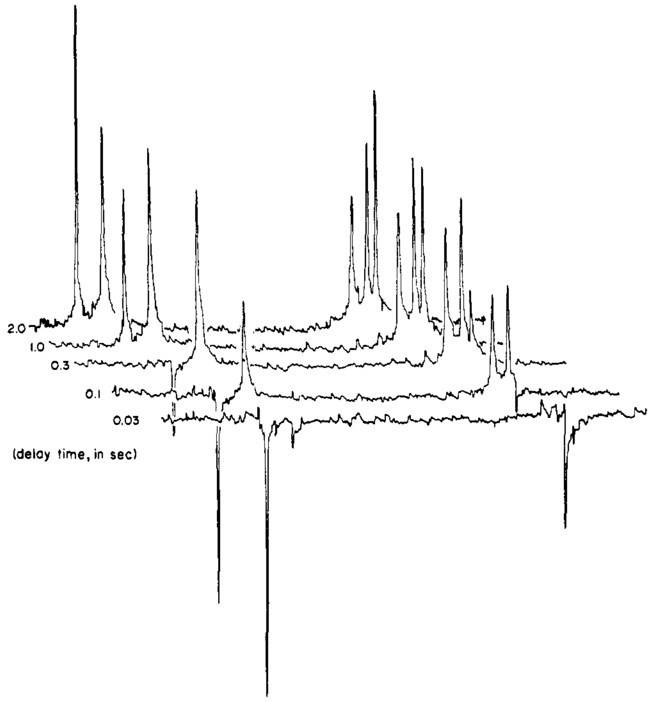

Figure 2. Partially relaxed Fourier transforms of the noise-decoupled, natural-abundance ^{13}C free-induction decays of solid, synthetic *cis*-polyisoprene at 40° and 22.6 MHz. The repetition time of the 180–t–90 pulse sequence was 4 sec. Delay times between the 180 and 90° pulses are given in the figure. The free-induction decays following the 90° pulse were accumulated as described in the caption to Figure 1c, except some analog filtering was used.

lines are the same. These measurements were performed on spectra in which the free-induction decay was not subjected to either significant active or passive analog filtering during accumulation or digital filtering after accumulation. The effect of analog filtering is often an attenuation at the high-frequency end of the spectrum, while the effect of digital filtering can be line broadening, varying from one line shape to another, and thereby altering relative integrated line intensities. Although a price is paid in sensitivity (Figure 1c), unfiltered, wide-frequency sweeps (corresponding, in the time domain, to narrow data-sampling windows) can yield reliable, accurate intensities in Fourier transformed spectra without digital correction schemes. The reliability of these intensities was confirmed from integrations of spectra of narrower frequency sweeps, again obtained with essentially no filtering in the bandwidth of interest.

The spin–lattice relaxation times (T_1) at 40° were measured from partially relaxed Fourier transform spectra,[4] some examples of which are shown in Figure 2. The quaternary carbon has the longest spin–lattice relaxation time, and so its signal is inverted even with a relatively long delay time between 180 and 90° pulses. For a delay time on the order of 30 msec, the quaternary carbon magnetization vector has had no opportunity to relax from the effect of the inverting 180° pulse and so gives a negative absorption signal of full intensity following the 90° pulse. Relaxation times for the other carbons are presented in Table I. In general, the relaxation times of individual carbons of *trans*-polyisoprene are longer than those of the corresponding carbons of *cis*-polyisoprene at the same temperature. Measured relaxation times were the same, within experimental error, regardless of whether the irradiating pulse was offset to the high- or low-field side of the spectrum. This means that the spectral power distribution of the 36-μsec, 180° pulse was flat over the 3500 Hz of the observed ^{13}C nmr spectrum, within about 10%. Spin–lattice relaxation times were also the same, within experimental error, regardless of whether measured from plots of integrated intensities against delay times or from nulled intensities in experiments using 180–t–90 pulse sequences.[9]

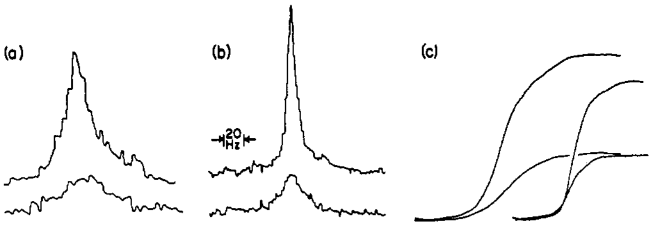

Figure 3. Fourier transforms of the spin-coupled (lower) and noise-decoupled (upper) natural-abundance ^{13}C free-induction decays of solid (a) *trans*-polyisoprene and (b) *cis*-polyisoprene. Only the spectra of the vinyl quaternary carbons are shown. The free-induction decay was obtained by sampling the receiver output immediately after the irradiating pulse using 1024 channels of a time-averaging computer internally swept at a rate of 1000 μsec per channel. The repetition time of the 90° pulse was 4 sec; 1024 scans were accumulated for (a) and 128 scans for (b). The integrated intensities of these spectra are shown in (c). The same relative intensities were measured from spectra obtained using faster data sampling rates. The horizontal scales are the same for (a), (b), and (c). The vertical scale of the two integrals of the spectra of (a) have been adjusted relative to those of (b) for display purposes.

TABLE I
PROTON-DECOUPLED CARBON-13 SPIN–LATTICE RELAXATION TIMES, OVERHAUSER ENHANCEMENT FACTORS, AND LINE WIDTHS FOR SOLID *cis*- AND *trans*-POLYISOPRENE AND *cis*-POLYISOPRENE-*3*-d_1 AT 40° AND 22.6 MHz

Polymer	Carbon[a]	T_1, msec[b]	$(C_Z - C_0)/C_0$[c]	Line width, Hz[d]
cis-Polyisoprene (synthetic, containing 9% defects)	α	700	1.2	7
	β	95	1.2	14
	γ	50	1.2	20
	δ	55	1.2	18
	ϵ	350	1.2	12
cis-Polyisoprene-*3*-d_1	α	840	1.2	7[e]
	β	420	0.9	11[e]
	γ	55	1.2	20[e]
	δ	60	1.2	18[e]
	ϵ	350	1.2	12[e]
trans-Polyisoprene (balata)	α	950	1.5	35
	β	160	1.5	40
	γ	85	1.5	50
	δ	85	1.5	50
	ϵ	450	1.5	35

[a] The numbering (following the line assignments in order of increasing magnetic field) is $-CH_2CCH_3{=}CHCH_2-$: γ, α, ϵ, β, δ. [b] Accuracy is ±10%. [c] Accuracy is ±0.1; C_Z and C_0 are enhanced and unenhanced signal intensities. Overhauser enhancements are sometimes reported as $1 + (C_Z - C_0)/C_0$. [d] Accuracy is ±10%; $T_2 = (\pi \times \text{line width})^{-1}$. The line width is full width at half height. [e] Measured in the presence of simultaneous ^{1}H and ^{2}H noise decoupling.

In addition to a longer relaxation time, the quaternary carbon of *trans*-polyisoprene also has a larger Overhauser enhancement than the quaternary carbon of *cis*-polyisoprene (Figure 3). Direct comparison of coupled and decoupled

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

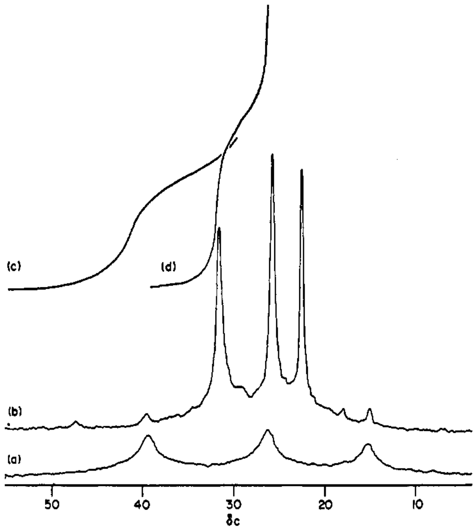

Figure 4. Fourier transforms of the noise-decoupled, natural-abundance ^{13}C free-induction decays of solid (a) *trans*-polyisoprene and (b) synthetic *cis*-polyisoprene. Only the spectra of the methylene and methyl carbons are shown. The free-induction decays were obtained by sampling the receiver output using 1024 channels of a time-averaging computer internally swept at a rate of 400 μsec per channel. The repetition time of the 90° pulse was 500 msec. This repetition rate is too fast to permit the methyl carbon (but not the methylene carbons) to completely relax between pulses, thereby producing a slightly attenuated methyl carbon line intensity. The additional weak lines shown in (b) arise from the structural and steric defects of the synthetic cis polymer. Both free-induction decays were the accumulations of 512 scans. The integrated intensities of the low-field methylene carbon lines of *trans*- and *cis*-polyisoprene are shown in (c) and (d), respectively.

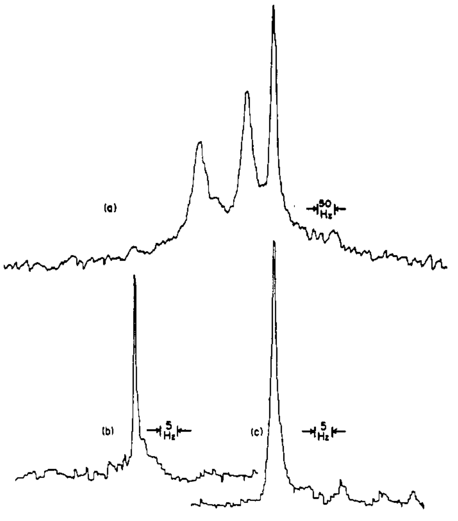

Figure 5. (a) A spectrum of solid *cis*- polyisoprene similar to that shown in Figure 4b, except the sample temperature is 5 rather than 40°. (b) Fourier transform of the noise-decoupled, natural-abundance ^{13}C free-induction decay of 2% chloroform solution of synthetic *cis*-polyisoprene. Only the vinyl quarternary carbon spectrum is shown. The free induction decay was obtained by sampling the receiver output using 1024 channels of a time-averaging computer internally swept at a rate of 1000 μsec per channel. The repetition time of the 90° pulse was 5 sec. The spectrum resulted from the accumulation of 8192 scans. (c) A spectrum of the vinyl methyl carbon of the same solution obtained as described for (b). Lines due to structural and steric defects in synthetic *cis*-polyisoprene are observed in the spectrum of (c) to the high-field side of the major line.

spectra of these quaternary carbons is possible without requiring integration over wide spectral ranges. The integrals obtained from these spectra are shown in Figure 3c. The Overhauser enhancement factor is $(C_Z - C_0)/C_0$, where C_Z and C_0 are the intensities of the enhanced and unenhanced lines, respectively.[10] The Overhauser enhancement factor for the trans isomer is 1.5 ± 0.1 (the ratio of integrated spin-decoupled to coupled intensities is 2.5) while that for the quaternary carbon of the cis isomer is 1.2 ± 0.1. These values are less than the theoretical maximum value[5] of 2.0, a situation which is characteristic of the behavior of polymers.[11] Other Overhauser enhancements were measured indirectly by comparisons of spin-decoupled line intensities and are given in Table I. The Overhauser enhancements were not changed when the ^1H decoupling power was increased by a factor of 2. In addition, the same Overhauser enhancements were obtained from comparisons of coupled and decoupled integrated line intensities as were obtained from comparisons of coupled line intensities measured as a function of the time delay from when the ^1H rf field was turned off to when the ^{13}C magnetization was sampled.

Not all of the carbons of the sample of *trans*-polyisoprene contribute to its observed ^{13}C nmr spectrum. Figure 4 shows the spectra of synthetic *cis*- and natural *trans*-polyisoprene obtained under identical conditions from samples of approximately the same size. Despite the greater Overhauser enhancement of the low-field methylene line of *trans*-polyisoprene, its integrated intensity is only about 60% of that from the corresponding carbon of synthetic *cis*-polyisoprene. (These spectra were obtained from pulse repetition times which were much greater than three times T_1 for each of the methylene carbons of the two polymers, so that direct comparison of the integrated intensities is possible.) This suggests that about 40% of *trans*-polyisoprene is crystalline at 40°, and that the carbons in these crystallites are sufficiently restricted, or immobilized, that they are unable to contribute to the high-resolution nmr signal.[1] This result is consistent with X-ray investigations of the crystalline content of *trans*-polyisoprene.[12]

The synthetic *cis*-polyisoprene used in most of these experiments contains about 9% structural and steric defects, and their presence is clearly visible in Figure 4b. In addition, the identification of some of these defects with trans placements, with essentially trans environments, resulting in lines at δ_c 15, 26, and 40, is quite likely by comparison with the corresponding spectra of the *trans*-polyisoprene.

The line widths of the signals from trans units in predominantly *cis*-polyisoprene chains, as well as cis units in predominantly *cis*-polyisoprene chains are less than half those of trans units in exclusively *trans*-polyisoprene chains at 40°. This can be seen in the expanded spectra of Figure 4. Line widths from spectra of synthetic *cis*-polyisoprene obtained under two other conditions are illustrated in Figure 5. At 5°, methylene and methyl carbon lines are, respectively, 50 and 25 Hz wide (Figure 5a), both twice as broad as they are at 40°. The corresponding lines of *trans*-polyisoprene are also similarly broadened at lower temperatures. Very narrow lines are observed in the spectrum of a 2% solution of *cis*-

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(10) Carbon-13 Overhauser enhancements are often reported as $1 + (C_z - C_0)/C_0$.

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

(12) L. Mandelkern, F. A. Quinn, and D. E. Roberts, *J. Amer. Chem. Soc.*, **78**, 926 (1956).

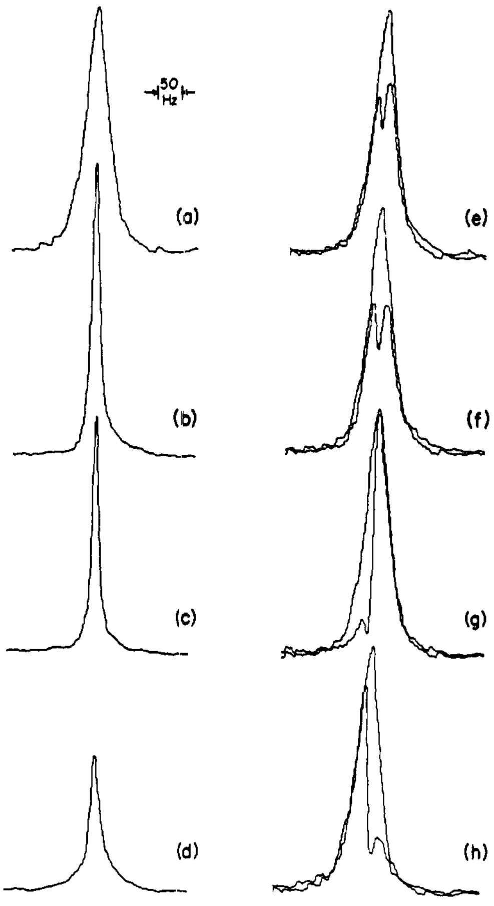

Figure 6. (a) An inhomogeneously broadened, proton-decoupled ^{13}C nmr line due to the vinyl carbon of *cis*-polybutadiene observed by Fourier transform techniques. (b) The unbroadened version of the same line. (c) The unbroadened version of the same line observed the same way except that preceding the usual irradiating pulse a 1-sec, 1-mW burst of ^{13}C rf, about 10 Hz off resonance, has been introduced. (d) The same line observed in a similar two-part experiment except the ^{13}C rf burst is closer to being on resonance. (e–h) A series of experiments showing the effect of a preceding 1-sec, 1-mW ^{13}C rf burst on the inhomogeneously broadened line. The center frequency of the ^{13}C rf burst is varied for the four spectra, which are shown superimposed on the original line. The width of the hole burned into the inhomogeneously broadened line depends on the natural dipolar line width.

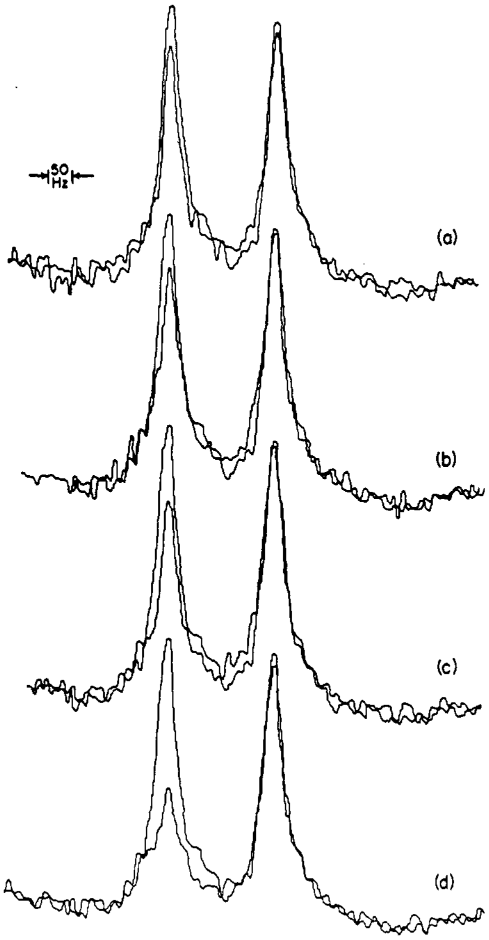

Figure 7. Selective saturation Fourier transform ^{13}C nmr spectra of the two vinyl carbons of *trans*-polyisoprene. The prepulse 500-msec ^{13}C rf burst is on resonance relative to the low-field carbon. The burst power, in mW, is approximately (a) 0.1, (b) 0.2, (c) 0.4, and (d) 1.0. The selectively saturated spectra are shown superimposed on a spectrum obtained in the usual fashion. For all of these spectra, the delay between repetitive 90° pulses has been chosen to produce equal intensities for the two vinyl carbon lines in the absence of any prepulse irradiation. The uniformity of the selectively saturated spectra indicate that the line widths of *trans*-polyisoprene are homogeneous line widths.

polyisoprene in $CHCl_3$. The quaternary carbon linewidth is 0.7 Hz while that of the methine vinyl carbon is 2.0 Hz. The ratio of widths for these two lines in dilute solution is thus about 3, compared to 2 in the solid. Defect lines are also observable in the solution spectrum of the methine vinyl carbon (Figure 5c) but not of the quaternary carbon (Figure 5b). Values for carbon line widths of the solids are given in Table I. These values, obtained at 22.6 MHz, appear to be slightly less than values for similar polyisoprenes obtained by cw techniques at 15.1 MHz.[1]

The use of selective saturation Fourier transform techniques to establish natural line widths[13] is illustrated in Figure 6. An artificially inhomogeneously broadened line is shown in Figure 6a. The broadening was created by altering the usual gradients of the homogeneity coils. The natural line width (of the ^{1}H noise-decoupled vinyl carbon of *cis*-polybutadiene) is shown in Figure 6b. This line can be attenuated by 1-sec, 1-mW off-resonance ^{13}C rf bursts without affecting its peak position or general symmetry (Figures 6c–d). When the same experiment is performed on the inhomogeneously broadened line, an asymmetric pattern is observed (Figures 6e–h). In effect, only a part of the inhomogeneously broadened line is saturated by a long, single-frequency rf burst. The width of the hole burned into the broad line depends on the natural dipolar line width.

The spectra of Figure 7 arise from slective saturation Fourier transform experiments performed on solid, *trans*-polyisoprene. Only the spectra of the two vinyl carbons are shown. A 500-msec, variable power burst preceded the usual pulse sequence, and, depending on the power, produced reductions in intensity of one of the two vinyl carbon lines without significantly altering line shape. In fact, Figure 7a shows that the reduced line has the same center and the same width at half-height even though the cw rf had only a minor effect on line intensity. Similar results were obtained when using 100- and 1000-msec prepulse bursts, and when using higher power off-resonance rf bursts. Similar results were also obtained for *cis*-polyisoprene.

(13) This experiment was suggested to the author by Dr. K. J. Packer, University of East Anglia, Norwich.

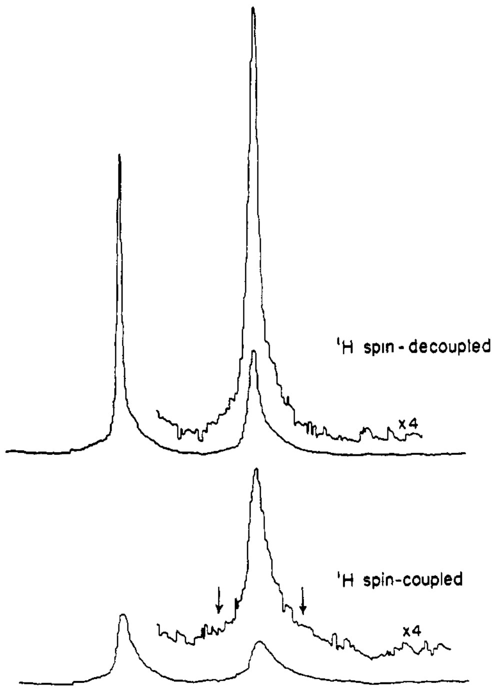

Figure 8. Spectra of the vinyl carbon region of *cis*-polyisoprene-*3*-d_1. The spectra were obtained by methods similar to those described in the caption to Figure 3. The arrows are 150 Hz apart and indicate the approximate positions of the spin multiplet of the residual protonated methine carbon. This multiplet is not detectable above the noise.

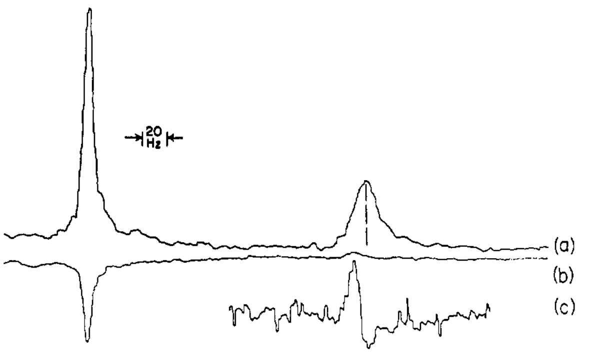

Figure 9. Partially relaxed Fourier transforms of the ¹H spin-decoupled natural-abundance ^{13}C free-induction decays of the vinyl carbons of *cis*-polyisoprene-*3*-d_1 for a delay time of (a) 2 sec and (b) 300 msec. The repetition time of the 180–t–90 pulse sequence was 5 sec. For both spectra, 64 scans were accumulated. The insert (c) was taken from a spectrum similar to (b) except that, in a separate experiment, four times as many scans were accumulated, and the gain of the display scale has been increased. The residual protonated methine carbon of the deuterated polymer can be seen in the partially relaxed Fourier transform spectra of (b) and (c). This resonance is shifted downfield from the major line.

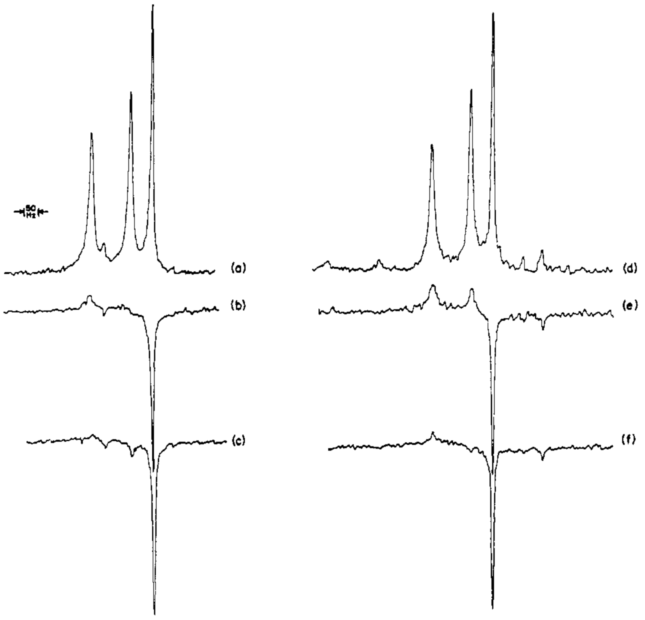

Figure 10. Partially relaxed Fourier transforms of the ¹H spin-decoupled natural-abundance ^{13}C free-induction decays of the methylene and methyl carbon regions of *cis*-polyisoprene-*3*-d_1 for a delay time of (a) 1 sec, (b) 40 msec, and (c) 35 msec. The repetition time of the 180–t–90 pulse sequence was 3 sec. The free-induction decays following the 90° pulse were accumulated as described in the caption to Figure 4. (This provides greater accuracy in the measurement of T_1 than accumulating a free-induction decay corresponding to a 5000-Hz frequency spectrum.) Spectra obtained under identical conditions of normal *cis*-polyisoprene are shown in (**d–f**). While a delay of 40 msec between the 180 and 90° pulses is sufficient to null the middle, methylene carbon line of the deuterated polymer, it is incapable of doing this to the corresponding line of normal *cis*-polyisoprene. The high-field methyl carbon lines behave the same in both sets of spectra.

(2) *cis*-Polyisoprene-3-d_1. The ^{13}C nmr spectra of *cis*-polyisoprene-*3*-d_1 are significantly different from those of the normal polymer. The spectra show that the catalyst used to prepare the deuterated polyisoprene produced relatively few structural or steric defects. The resonance of the simultaneously ¹H and ²H decoupled deuterated vinyl methine carbon is somewhat reduced in intensity and shifted upfield about 0.5 ppm from its usual position.[14] In addition, this carbon has an observed spin–lattice relaxation time of 420 msec, about four times as long as normal. The large difference in spin–lattice relaxation times can be used in a determination of the concentration of residual methine protons in the deuterated polymer. This can be done by an experiment involving resolution enhancement using partially relaxed Fourier transform techniques.[9] Although the polymer lines are too broad to see directly the methine proton spin-coupled doublet in the spectrum of *cis*-polyisoprene-*3*-d_1 (Figure 8), the deuterated methine carbon line can be nulled by an appropriate choice of delay time in a 180–t–90 pulse sequence without substantially affecting the protonated methine carbon line. This line appears at slightly lower magnetic field (Figure 9). The solid polymer is estimated to be 97% deuterated in the 3 position.

Replacing the vinyl proton with a deuterium also increases the spin–lattice relaxation times of adjacent carbons. The quaternary carbon relaxation time is increased about 20%, while those of the nearby methylene carbons appear to be increased by about 5–10%. Figure 10 illustrates this point. Delay times in 180–t–90 pulse sequences which are short enough to null the methylene carbon resonances of *cis*-polyisoprene-*3*-d_1 do not completely null the resonances of the corresponding carbons of the normal *cis*-polyisoprene. Slightly longer methylene carbon spin–lattice relaxation times for *cis*-polyisoprene-*3*-d_1 relative to the normal polymer were also obtained from the slopes of semilog plots of integrated intensity as a function of delay times between 180 and 90° pulses. Values for all the spin–lattice relaxation times and

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(14) For a review of isotope effects on chemical shifts, see H. Batiz-Hernandez and R. A. Bernheim, *Progr. Nucl. Magn. Resonance Spectrosc.*, 3, 63 (1967).

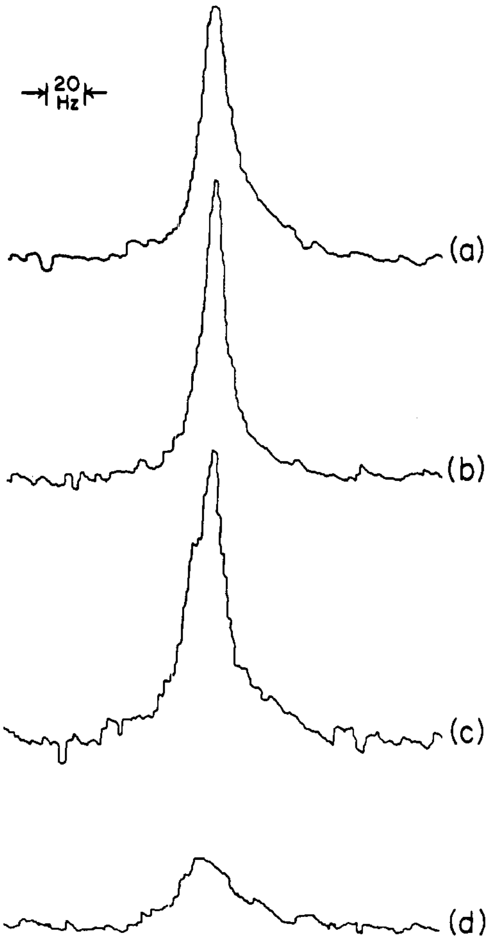

Figure 11. (a) The ^{1}H spin-decoupled methine carbon line of a *cis*-polyisoprene, containing 9% defects. (b) The ^{1}H and ^{2}H spin-decoupled methine carbon line of *cis*-polyisoprene-*3-d*$_1$. (c) The ^{1}H spin-decoupled methine carbon line of *cis*-polyisoprene-*3-d*$_1$, vertical gain increased by a factor of 2. (d) The spin-coupled methine carbon line of *cis*-poly-isoprene-*3-d*$_1$. Selective deuteration does not have a major line-narrowing effect.

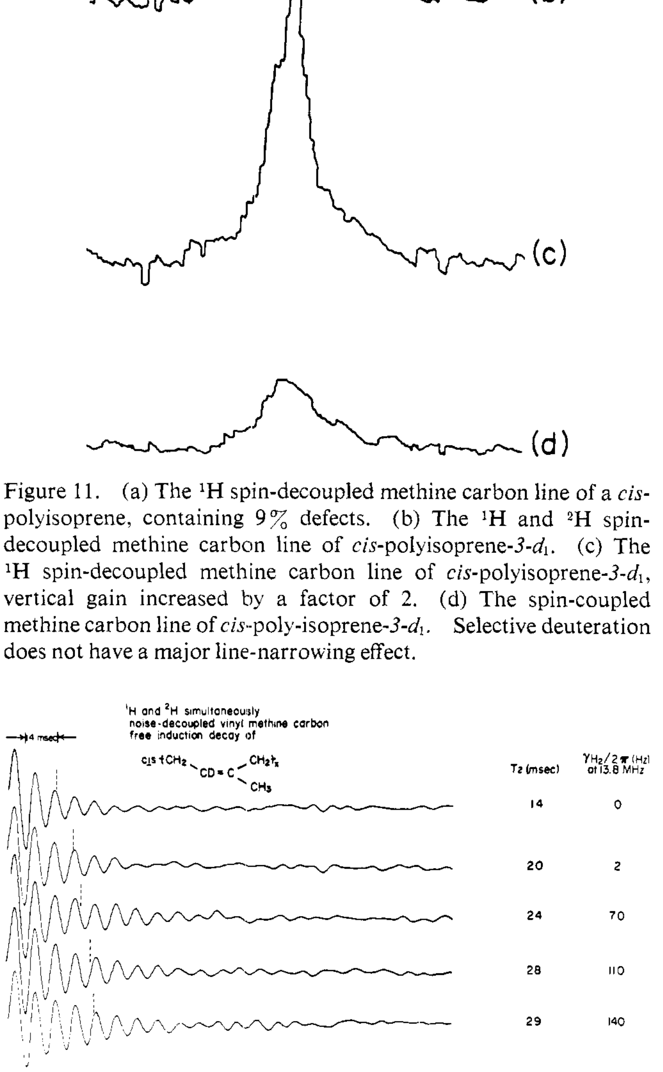

Figure 12. A display of some free-induction decays of the methine carbon of *cis*-polyisoprene-*3-d*$_1$ as a function of the ^{2}H decoupling field. Signals from the other carbons have been removed by heavy analog filtering. The dotted lines indicate the times at which the free-induction decays have decayed to 0.368 of the values measured from the left-hand arrow.

Overhauser enhancements for *cis*-polyisoprene-*3-d*$_1$ are presented in Table I.

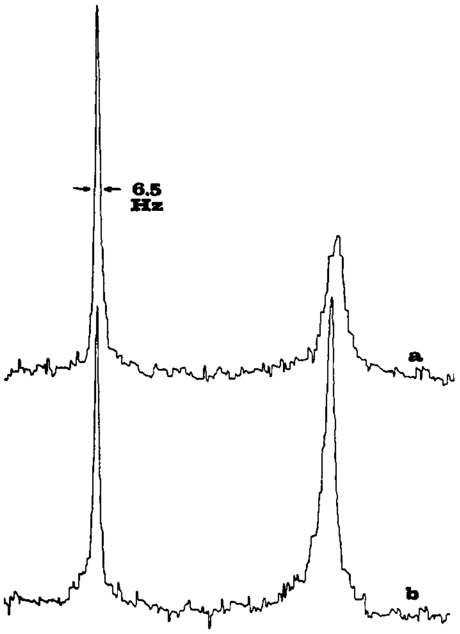

Figure 13. Spectra of the vinyl carbon regions of (a) *cis*-polyisoprene-*3-d*$_1$ and (b) a synthetic *cis*-polyisoprene (containing 1% defects). The spectra were obtained as described in the caption to Figure 4, except that only 64 scans were accumulated in a little over 30 sec. The short spacing between 90° pulses has affected the intensities of the nonprotonated carbons. The low-field, quaternary carbon line widths of both normal and deuterated polymers are the same.

Only one line width of the deuterated polyisoprene is noticeably different from its usual value. The deuterated vinyl methine carbon line width has been reduced by about 20%, relative to its usual value (Figure 11). (However, compared to the vinyl methine carbon line width of a normal synthetic *cis*-polyisoprene containing only 1% defects, the reduction is virtually nil.) The effect of the small C–D coupling on the line width has been removed by noise decoupling (with a noise bandwidth of about 100 Hz) at 13.8 MHz as established by a series of experiments in which the decoupling field intensity was varied (Figure 12). Within experimental error, the same line width is obtained for all $\gamma H_2/2\pi$ greater than about 100 Hz.[14a] These decoupling field intensities were measured by single-frequency off-resonance decoupling experiments on dimethyl-*d*$_6$ sulfoxide. Because of the much smaller quadrupole moment, the deuterium nuclei are more involved in effective scaler coupling to directly bonded and nearby carbons in *cis*-polyisoprene-*3-d*$_1$ than are the ^{14}N nuclei in polyacrylonitrile.[15]

Other line widths in *cis*-polyisoprene-*3-d*$_1$ are close to their normal values, including the quaternary carbon line

(14a) NOTE ADDED IN PROOF. In a private communication, H. Sternlicht (Bell Laboratories, Murray Hill, N. J.) has pointed out that there may still be a small scalar contribution to the methine carbon line of *cis*-polyisoprene-*3-d*$_1$. This is due to the fact that the methine-carbon line width actually depends on the deuterium $(\pi T_2)^{-1}$, J_{CD}, and $\gamma_{\mathrm{H}_2}/2\pi$ at 13.8 MHz, all of which are comparable. Thus completely removing the small observed C–D scalar coupling of a few hertz in the deuterated polymer may still require a decoupling field large compared to the full J_{CD}, which is on the order of 35 Hz. In order to obtain an estimate of the residual scalar contribution to the deuterated carbon line width, we observed the broadening of the quaternary carbon line of normal *cis*-polyisoprene, when a noise-modulated ^{1}H $\gamma_{\mathrm{H}_2}/2\pi$ of 100 Hz was used. This experiment matches the situation for the ^{2}H decoupling experiment on *cis*-polyisoprene-*3-d*$_1$. That is, the decoupling field is larger than, but comparable to, the scalar interactions present, and smaller than, but comparable to, the line width of the spin being irradiated. The observed quaternary carbon line width was 10 Hz compared to a completely decoupled value of 7 Hz and a single resonance value of 23 Hz. Thus, it is reasonable to conclude that the residual scalar contribution to the methine-carbon line of *cis*-polyisoprene-*3-d*$_1$ is, at most, a few hertz.

(15) J. Schaefer, *Macromolecules*, **4**, 105 (1971).

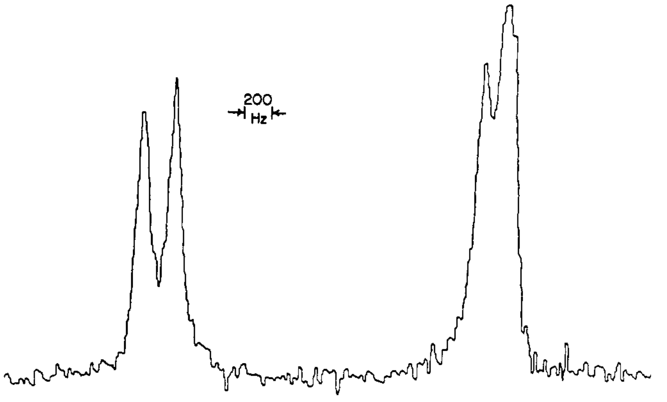

Figure 14. A spectrum of a carbon-black-filled *cis*-polyisoprene. The spectrum was obtained as described in the caption to Figure 1a except only 256 scans were accumulated. The carbon black had a SAF designation and was present at a concentration of 45 pph. The broadness of the lines prevents resolution of the high-field methylene and methyl carbon lines.

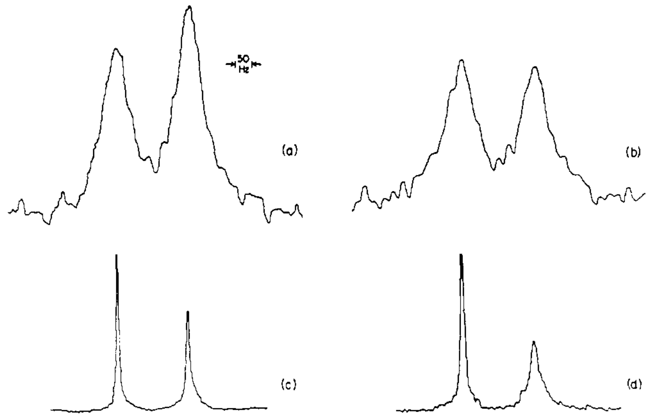

Figure 15. Spectra of the vinyl carbon region of the carbon-black-filled *cis*-polyisoprene at (a) 40 and (b) 5°; similar spectra of normal *cis*-polyisoprene at (c) 40° and (d) 5°. All the horizontal frequency scales are the same. The spectra were obtained by methods similar to those described in the caption to Figure 4, except the repetition time between pulses was 3 sec and only 128 scans were accumulated for each spectrum.

width (Figure 13), even though a substantial change was observed in the quaternary carbon spin–lattice relaxation time as a result of the deuteration. As with the normal polymer, narrow lines were observed in the spectra of dilute chloroform solutions of *cis*-polyisoprene-*3*-d_1. Values for all the solid line widths are presented in Table I.

(3) Carbon-Black-Filled *cis*-Polyisoprene. The ^{13}C nmr spectrum of a carbon-black-filled *cis*-polyisoprene is shown in Figure 14. The line widths are all on the order of 100 Hz, and this prevents the resolution of the high-field methylene and methyl carbon lines. For the quaternary carbon line, this represents a broadening, by the filler, of an order of magnitude. The carbon black used as filler had a SAF designation,[16] indicating a fairly high surface area. Spectra were also obtained of *cis*-polyisoprene filled with carbon blacks of lesser surface areas. Somewhat narrower lines were observed in these ^{13}C nmr spectra. In particular, with an HAF carbon-black filler, the quaternary carbon line width is noticeably less than that of the methine carbon, unlike the situation for the SAF-black-filled *cis*-polyisoprene.

Table II

Proton-Decoupled Carbon-13 Line Widths for Solid *cis*-Polyisoprene and Carbon-Black-Filled *cis*-Polyisoprene at 22.6 MHz

Polymer	Carbon	Temp, °C	Line width,[a] (Hz)	Line width ratio[b]
cis-Polyisoprene (synthetic, 1% defects)	Quaternary	40	7	
		5	12	1.7
	Methine	40	14	
		5	30	2.1
Carbon-black-[c] filled *cis*-polyisoprene	Quaternary	40	100	
		5	125	1.3
	Methine	40	85	
		5	125	1.5

[a] Accuracy is ±10%. Line widths are full width at half-height. [b] Ratio of vinyl carbon line widths at 40 and 5°. [c] 45-pph SAF black.

The possibility of line broadening resulting from macroscopic iron impurities carried into the polymer by the filler or subsequent mechanical manipulation can be ignored. As determined by X-ray analysis, the iron content of the sample was three orders of magnitude less than the zinc content, present as ZnO (2 pph). Furthermore, similar to the results for *trans*-polyisoprene, the center of the quaternary carbon line and its symmetry were unchanged when the line was reduced in intensity in a series of selective saturation experiments, even using burst length comparable to T_2.

The spin–lattice relaxation time of the quaternary carbon of the carbon-black-filled *cis*-polyisoprene was 750 msec, the same value observed for the unfilled polymer, within experimental error. Since a reduced T_1 is not observed in the bulk polymer of the filled system, it is unlikely that the known presence[16] of free radicals on the surface of the carbon black plays a significant role in determining the nmr parameters of the polyisoprene, at least away from the immediate vicinity of the filler surface. Spin–lattice relaxation times for the four other carbons of the filled system were not measured.

The temperature dependence of the ^{13}C nmr spectra of the vinyl carbons of both filled and unfilled *cis*-polyisoprene are similar (Figure 15). The widths of both the quaternary and methine carbon lines are greater at 5 than at 40°, but the increase is proportionally less for the quaternary-carbon line. This is true for both ordinary *cis*-polyisoprene and carbon-black-filled *cis*-polyisoprene. Values for these line widths are presented in Table II.

Discussion

(1) Spin–Lattice Relaxation Times. The spin–lattice relaxation times of the methine carbons of both *cis*- and *trans*-polyisoprenes are, within experimental error, twice those of the methylene carbons. Since the relaxation times are inversely proportional to the number of directly bonded protons, the dominant relaxation mechanism must be dipolar for these two carbons in both kinds of chains.[5] The longer relaxation times for the carbons of *trans*- compared to *cis*-polyisoprene are consistent with the greater freedom of the extended trans configuration,[17] and the known dependence of polymer spin–lattice relaxation times on the segmental

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(16) The nature of a variety of carbon blacks are described in G. Kraus, *Advan. Polym. Sci.*, **8**, 155 (1971).

(17) See, for example, P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969, p 198.

motions, particularly rotational motions,[18] associated with this freedom. This difference in segmental motion resulting from a difference in geometry is far more pronounced for the *cis-* and *trans*-polyisoprenes than any corresponding difference resulting from variations in stereochemistry for solutions of more rigid chains such as polystyrene and polyacrylonitrile.[11] In the latter two systems, the spin–lattice relaxation times for corresponding carbons in different tactic units were indistinguishable.

The foregoing interpretations are implicitly based on the assumption of a spin–lattice relaxation model for these high polymers in which dipolar interactions are modulated by isotropic segmental motion of the polymer chains. (Motion of the chain as a whole can be ignored.) The justification for such an assumption is based on evidence which 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 effective or average correlation time.[11,19,20] Thus, for the polyisoprenes, the simple isotropic model appears to be a reasonable description, at least to first order. Deviations from the predictions of the simple model do occur, however, and the effects of a breakdown of the isotropic model are discussed later.

Despite the presence of three directly bonded protons, the methyl carbon spin–lattice relaxation times of both *cis-* and *trans*-polyisoprene are fairly long. This is consistent with the known internal freedom of the methyl group. The internal rotational freedom of the methyl group reduces the effectiveness of dipolar coupling to directly bonded protons, thereby increasing its spin–lattice relaxation time relative to other carbons with directly bonded protons.[9]

The fact that substantially different spin–lattice relaxation times are observed for chemically different carbons in the same solid polymer demonstrates that spin diffusion is not a complicating feature of these relaxation measurements. Carbon-13 nuclei are isolated from one another by their low natural abundance. In addition, they do not efficiently exchange energy *via* spin diffusion with protons (in nonrotating frame experiments[21]) because of the difference in resonance frequencies. This situation is unlike that for ^{1}H nmr experiments on solid polymers such as polyisoprene. In ^{1}H nmr experiments frequently only a single proton spin-lattice relaxation time is observed.[22] The slowly relaxing protons of a solid polymer can efficiently exchange energy by spin diffusion with more rapidly relaxing protons, thereby creating a single, averaged proton spin-lattice relaxation time.[23] The net result of this averaging in the ^{1}H experiment is the loss of information concerning the details of the segmental motions of the polymer.

Although the dipolar interactions of the proton-bearing carbons with their directly bonded protons are the most important in determining the ^{13}C spin–lattice relaxation times, nonbonded interactions are still significant. Thus, the spin-lattice relaxation time of the methine carbon of *cis*-polyisoprene-*3-d*$_1$ is not increased by a factor of about 16 (as expected theoretically) by replacing the directly bonded proton with a deuterium (with its smaller magnetogyric ratio), but only by a factor of about 4. In other words, to a good approximation for the methine carbon

$$\frac{1}{T_1(\text{nonbonded})} = \frac{1}{T_1(\text{obsd})} - \frac{1}{T_1(\text{bonded})}$$

$$= \frac{1}{420\ \text{msec}} - \frac{\gamma_D{}^2 S_D(S_D + 1)}{\gamma_H{}^2 S_H(S_H + 1)} \frac{1}{T_1(\text{bonded})}$$

for the deuterated polymer and

$$= \frac{1}{95\ \text{msec}} - \frac{1}{T_1(\text{bonded})}$$

for the normal polymer, where $\gamma_H = 2.6752 \times 10^4$ rads G^{-1} sec^{-1}, $\gamma_D = 0.4106 \times 10^4$ rads G^{-1} sec^{-1}, $S_D = 1$, and $S_H = {}^1/_2$. Thus, T_1 (nonbonded) = 475 msec. Since the protonated methine carbon spin–lattice relaxation time is only 95 msec, the nonbonded contribution to this value must be about 20%. Furthermore, by comparing the methylene carbon spin–lattice relaxation times of *cis*-polyisoprene with the increased values of *cis*-polyisoprene-*3-d*$_1$, it appears that the methine proton may account for as much as about 5–10% of the methylene carbon spin–lattice relaxation time of normal *cis*-polyisoprene despite the presence of two directly bonded protons. By a similar comparison, it is experimentally even more clear that the methine proton contributes about 20% to the spin–lattice relaxation time of the quaternary carbon of *cis*-polyisoprene even though, within the monomer unit, it is on the order of 2.3 Å distant, or more than two C–H bond lengths. A separation this size suggests a nonbonded contribution of the order of $({}^{1.1}/_{2.3})^6$, or ${}^1/_{80}$ of (95 msec)$^{-1}$ rather than the observed 20%, or ${}^1/_5$ of (700 msec)$^{-1}$. These nonbonded contributions are most likely dipolar in nature (*cf.* the discussion of the Overhauser enhancements later). Thus, these results lead to the conclusion that at least part (although a fairly small part) of the nonbonded dipolar contributions to relaxation are intermolecular in origin, or possibly intramolecular if the chain is assumed to fold back upon itself.

The methine vinyl carbon of *cis*-polyisoprene-*3-d*$_1$ has a relaxation time which is twice as short as that of the quaternary carbon. Since neither carbon has a directly bonded proton, one might have expected the two carbons to have more nearly equal spin–lattice relaxation times. At least three factors can contribute to the difference. First, dipolar coupling of the methine carbon to its *directly bonded* ^{2}H is still capable of making a contribution of about 25% to the observed methine carbon T_1. This accounts for about half of the difference. Second, the methyl group attached to the quaternary carbon can act as a steric block to the approach of nonbonded protons, thereby reducing the effectiveness of their dipolar coupling. Although this blocking effect is completely absent for the methine carbon, it is still difficult to estimate its relative importance. If, for example, nonbonded contributions to the spin–lattice relaxation times of the quaternary and methine carbons by methylene protons from distant monomer units in the same chain are important in *cis*-polyisoprene, then such steric interactions will also be important, and perhaps more important than if the origin of the nonbonded contributions were *inter*molecular. (Contributions from distant units in the same chain are known to be important in the spin–lattice relaxation of the quaternary carbon of polystyrene in dilute solution,[11] although in this case the quaternary carbon is not in the main chain.) Finally, it is unlikely that the segmental motion of *cis*-polyisoprene is actually isotropic. This means both that its segmental mo-

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(18) D. W. McCall, D. C. Douglass, V. J. McBrierty, and M. J. R. Hoch, *Discuss. Faraday Soc.*, No. 48, 205 (1969).

(19) L. A. McLachlan, D. F. S. Natusch, and R. H. Newman, *J. Magn. Resonance*, 4, 358 (1971).

(20) R. Kimmich and F. Noack, *Z. Naturforsch. A*, 25, 299 (1970).

(21) F. M. Lurie and C. P. Slichter, *Phys. Rev. A*, 133, 1108 (1964).

(22) For a recent review, see D. W. McCall, *Accounts Chem. Res.*, 4, 223 (1971).

(23) D. C. Douglass and G. P. Jones, *J. Chem. Phys.*, 45, 956 (1964).

tion is not necessarily well described by a single main-chain correlation time and also that the average distance to nonbonded methylene protons need not be the same for the two vinyl carbons. Accordingly, their spin–lattice relaxation times need not be identical.

Indeed, ^{13}C spin–lattice relaxation measurements on some solid, rubbery polymers, such as poly(propylene oxide) and *cis*-polybutadiene, indicate that substantial deviations from the predictions of a single-correlation time, isotropic model of segmental motion are rather common.[24] This eliminates any simple relationship between the observed spin–lattice relaxation times and the number of directly bonded and nearby protons. For these systems, methine and methylene carbon spin–lattice relaxation times do not differ by a factor of 2.0, but by a factor of about 1.2.[24] Furthermore, spin–lattice relaxation measurements on partially deuterated *cis*-polybutadiene suggest that the methine protons are more important in the relaxation of the methylene carbons than the methylene protons are in the relaxation of the methine carbon, even though there are only half as many methine protons.[24] (However, this contribution to the methylene carbon T_1 is less than 10%.) An asymmetry in nonbonded dipolar interactions such as this is presumably related to differences in distances of closest approach for neighboring spins which vary for different carbons.

For more rigid polymers, such as polystyrene, even in solution, the complications of the effects of apparent anisotropic segmental motion on both bonded and nonbonded dipolar interactions are absent.[11] It appears that *cis*-polyisoprene is an intermediate case. The discrepancies resulting from a description of motion based on an isotropic model are larger than for solutions of polystyrene, but smaller than for poly(propylene oxide) and polybutadiene. Nevertheless, the lack of symmetry in the geometry and segmental motion of *cis*-polyisoprene helps to explain the difference between spin–lattice relaxation times of the vinyl carbons of *cis*-polyisoprene-*3*-d_1, and also provides a rationale for other anomalies such as the small difference between the observed spin–lattice relaxation times of the two methylene carbons in both normal and deuterated polyisoprenes.

(2) Carbon-13 Overhauser Enhancements. Carbon-13 Overhauser enhancement factors $(C_Z - C_0)/C_Z$, are often less than the theoretical maximum of 2.0 for polymers since many of the segmental modes of motion, important in relaxation processes, have correlation times, τ, whose inverses are comparable to observing radio frequencies, ω, used in the nmr experiment.[11] For these motions, the extreme narrowing condition, $\omega\tau \ll 1$, fails, and the Overhauser enhancement is correspondingly reduced.[5,11] This is the situation for both of the polyisoprenes. The Overhauser enhancement factors of the five carbons of *trans*-polyisoprene are all the same, a value of 1.5, substantially different from the value of 1.1 for each of the five carbons of *cis*-polyisoprene. Both values are less than the theoretical maximum. The fact that a single Overhauser enhancement is observed for each polymer supports the conclusion based on T_1 measurements that for every carbon, including the quaternary carbon, the dominant spin–lattice relaxation mechanism is dipolar, modulated by essentially the same segmental motion of the chain. If other relaxation mechanisms (such as chemical shift anisotropy) were important, they would presumably be more important for some carbons than for others, leading to differences in the observed, reduced enhancements. (Because of the sizable experimental error in the Overhauser enhancement the possibility of small, nondipolar contributions to relaxation cannot be eliminated.)

The larger Overhauser enhancement for *trans*-polyisoprene is consistent with the ^{13}C spin–lattice relaxation measurements showing that the trans main chain has the greater flexibility. Thus, more of its segmental motions satisfy the extreme narrowing condition, leading to a larger Overhauser enhancement. In terms of a description of relaxation based on a single correlation time, the greater freedom of the trans chain results in a shorter *average* correlation time which more nearly satisfies the extreme narrowing condition. This leads to a larger enhancement for *trans*-polyisoprene than for *cis*-polyisoprene.

The deviation of an observed Overhauser enhancement factor from the theoretical maximum can sometimes be used to extract an effective spin–lattice correlation time, if an isotropic, dipolar relaxation model is assumed. This has been successfully done, for example, for ^{13}C measurements on solutions of polystyrene.[11] Such a procedure is possible but less useful for the polyisoprenes because the assumptions of symmetry and isotropic, segmental motion described by a single correlation time (as opposed to a distribution of correlation times) are not particularly good ones. In addition, the Overhauser enhancement factor is not sensitive to the small differences that result from a comparison of a detailed description of motion of the polyisoprenes with simple, isotropic description, using a single correlation time. Thus, it appears that anisotropies in segmental motion need not produce large differences in main-chain Overhauser enhancements. This means that the Overhauser enhancements are not always good sources of information concerning main-chain segmental correlation times. These qualifications are true as long as the theoretical description of the segmental motion and of the Overhauser enhancement are not complicated by close proximity to the T_1 minimum.[11,25] (That is, as long as the polymers are "liquid-like" and not "solid-like."[26])

For much the same reasons, it is not possible to extract information about the rapid, internal freedom of the methyl group of the polyisoprenes from Overhauser enhancement measurements. The methyl carbon Overhauser enhancement can be shown to be almost independent of the details of rapid internal rotation and determined primarily by the much slower segmental reorientation of the polyisoprene main chain.[11,25] This explains why the intensity of the resonance of the rapidly rotating methyl carbon is the same, within experimental error, as those of the main-chain carbons.

The spin–lattice relaxation time of the deuterated carbon of *cis*-polyisoprene-*3*-d_1 was suggested earlier to be determined primarily by dipolar interactions with nonbonded protons. This is consistent with the observation of about the same Overhauser enhancement factor for the deuterated carbon as for the nondeuterated carbons. Although the presence of a third-spin species can result in a substantial reduction of the observed Overhauser enhancement, this will not occur if the third spin is not important in relaxation processes affecting the observed spin.[5]

(3) Line Widths. The segmental motions in polymers which dominate the spin–lattice relaxation time and Overhauser enhancement are not, in general, the same motions which determine the nmr line width. For polymers, T_1 is

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[24] J. Schaefer, manuscript in preparation.

[25] D. Doddrell, V. Glushko, and A. Allerhand, *J. Chem. Phys.*, **56**, 3683 (1972).

[26] If $\omega\tau$ of the main-chain motion is between zero and 0.3, the descriptions of the Overhauser enhancements and spin–lattice relaxation times are still qualitatively simple, just as for liquids; see ref 11.

generally greater than T_2, and this difference can be, in part, a consequence of those slower modes of polymer motion, characterized by long correlation times, which are unable to contribute effectively to $(T_1)^{-1}$, but can contribute to $(T_2)^{-1}$.[27] For the polyisoprenes, the ^{13}C T_1/T_2 ratio is on the order of 5 to 10 even though T_1 is not near its minimum.

Once past the level of such generalities, the observed ^{13}C nmr line widths for the polyisoprenes are not simple to interpret. Ratios of individual carbon line widths are not equal to ratios of the corresponding spin–lattice relaxation times. The line widths do not show any obvious trend with either an inverse sixth- or inverse third-power dependence on proton distances. Thus, the quaternary carbon line always appears to be unusually broad relative to the other carbon line widths. In fact, for balata, the natural, defect-free *trans*-polyisoprene, the line widths of carbons in the amorphous region (carbons within the crystalline regions are not contributing to the high-resolution signal) are very nearly all equal. For the carbon-black-filled *cis*-polyisoprene, the line widths are all equal, within 10%, and are greater than in the unfilled polymer by factors of 5–10. In addition, contrary to expectations, substituting a deuterium for a proton in *cis*-polyisoprene-*3-d*$_1$ makes very little difference in any of the line widths, although it makes a large difference in some of the spin–lattice relaxation times.

Several explanations, or partial explanations, of the unusual ^{13}C nmr line widths of the polyisoprenes, although plausible, can still be dismissed with reasonable confidence. We will present four such explanations and point out their inconsistencies. We will then present our own explanation which we suggest is consistent with existing observations.

I. Four Explanations of the Line Widths

(a) The Line Widths Are Determined by Defects in the Polymer Chain. The possible broadening of the quaternary carbon line of synthetic *cis*-polyisoprene, resulting from chemical shift differences between various structural and steric irregularities in the chain, may be of some importance in the ^{13}C nmr spectra of the dilute solutions of the polymer (compare Figures 5b and 5c). However, this source of broadening is not nearly large enough to account for the similarities in the much greater line widths observed in the spectra of the solid. The concentrations of defects in the polyisoprenes range from zero for the natural polymers to only 9% for the synthetic polymers. Furthermore, defects which might be associated with cross-links (and hence have a more profound effect on line width, *cf.* below) are known to be absent.[28]

(b) The Line Widths Are Determined by Microscopic Inhomogeneities. A description of nmr line widths of polymers using a model of a microscopically inhomogeneous system has been suggested[29] (although not necessarily for solid polyisoprenes). The model is based on evidence of large concentration fluctuations in polymer solutions available from light-scattering experiments.[29] It is possible that these fluctuations are not completely averaged in an nmr experiment, can influence resonance frequencies, give rise to an effective distribution of chemical shifts, and hence lead to line broadening. This model has been used to describe the unusual T_1/T_2 ratios observed in proton nmr experiments on concentrated benzene solutions of poly(methyl methacrylate).[29] It is a special example of the general theory of nuclear spin relaxation in multiphase systems[30] in which each phase can have separate chemical shift and exchange between phases is of a slow to intermediate rate. (Rapid exchange is unlikely in immobile systems.)

Such models are not applicable to a description of the ^{13}C nmr line widths of the polyisoprenes. The results of the selectively saturated experiments showed that the observed line widths of *cis*- and *trans*-polyisoprene (as well as of carbon-black-filled *cis*-polyisoprene) are homogeneous line widths. They are not caused by inhomogeneous broadening resulting from equivalent nuclei being subject to differing local magnetic fields, which, in effect, produce a distribution of apparent chemical shifts. Conceivably, the presence of filler particles (either crystallites or carbon black) in the two-phase systems could have led to a broadening of the observed nmr line widths either by the production of microscopic regions of differing magnetic susceptibility, or perhaps by the production of apparent chemical shifts resulting from local, slowly varying, fluctuations in density, which influence the chemical shift much like a solvent effect. However, if either of these mechanisms had been operating, the long prepulse rf burst in the selective saturation experiment would have produced an irregular nmr line as a function of offset, since only a fraction of the sample would have been in a resonance condition for any given offset. The broad line would have had a narrow hole burned in it, with the width of the hole determined, in part, by the natural dipolar line width.[31] This was not observed. In fact, the results of the selective saturation experiment eliminate any explanation of the polyisoprene line widths based on a distribution of resonances having different Larmor frequencies. (This also includes, for example, distributions generated by chemical shift anisotropies which have not been isotropically averaged.) Furthermore, since holes cannot be burned into the ^{13}C lines, the ^{13}C spins must be coupled to the ^{1}H spins only through the lattice.

(c) The Line Widths Are Determined by the Motion of the Bulk Polymer as a Quasi-Lattice. A description of the polyisoprene ^{13}C line widths has been suggested based on the assumption of a very slow, anisotropic tumbling of the solid polymer as a quasi-lattice.[32] Such motions, theoretically, can give rise to narrow lines for highly restricted systems under certain circumstances.[33,34] Presumably, the anisotropic motions would be such as to produce the observed differences in line widths for different kinds of carbons. This description has been used to interpret the ^{13}C nmr spectra of amino acids bound to rigid exchange resins.[32] We feel that such descriptions are not applicable to the polyisoprenes. The ^{13}C nmr signals from the polyisoprenes arise from the amorphous parts of the polymers which, at 40°, are on the order of 100° above their glass transitions.[35] These solids are almost liquids, and while they may have some long-range order, they have no well-defined rigid lattice. Relatively coherent tumbling motions of the polymer as a whole are therefore unlikely. Furthermore, a prediction of the quasi-lattice model is a specific, well-defined dependence of the line width on the carbon–proton internuclear distance[32,33] and on the sizes of the carbon and proton nuclear magnetic mo-

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

(28) All of the unfilled polyisoprenes were completely soluble in solvents such as methylene chloride.

(29) J. E. Anderson and K-J. Liu, *J. Chem. Phys.*, **49,** 2850 (1968).

(30) For a recent review, see K. J. Packer, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3,** 87 (1967).

(31) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73,** 679 (1948).

(32) H. Sternlicht, G. L. Kenyon, E. L. Packer, and J. Sinclair, *J. Amer. Chem. Soc.*, **93,** 199 (1971).

(33) D. E. Woessner, *J. Phys. Chem.*, **70,** 1217 (1966).

(34) D. E. Woessner, *J. Chem. Phys.*, **36,** 1 (1962).

(35) W. A. Lee and G. J. Knight in "Polymer Handbook," J. Brandrup and E. H. Immergut, Ed., Interscience, New York, N. Y., 1966.

ments. This naturally leads to the expectation of a significantly reduced (by at least a factor of 3) line width for the deuterated carbon of *cis*-polyisoprene-*3-d*$_1$ because of the relatively small magnetic moment of deuterium. A substantially reduced line width, however, was not observed.

(d) The Line Widths Are Determined by Pronounced Differences between the Correlation Times for Different Carbons in the Main Chain. Analysis of the ^{13}C spin-lattice relaxation times of *cis*-polyisoprene suggests some anisotropies in the main-chain segmental motions. Presumably, those anisotropies could be more pronounced for those (primarily) lower frequency segmental motions most important in determining the line width. Thus, individual carbons in the same monomer unit in the main chain would be assigned different correlation times. Since the dominant relaxation mechanism modulated by the segmental motion of the chain is dipolar, and since the dipolar interactions for quaternary carbons are different from those of methine or methylene carbons, it is conceivable that the effective correlation times of the various carbons could be different in just such a way as to compensate for the differences in the strengths of the dipolar interactions. The net result could be comparable line widths for substantially different types of carbons. For the filled polyisoprene systems, broadening of individual carbon lines would occur to the extent that the filler could produce an increase in the effective correlation time of each carbon. That is, the effect of the filler on the rate of segmental motion influencing a given carbon line width would be analogous to the effect of an increase in local viscosity, or a decrease in temperature. Since even the broadened lines are fairly narrow ($T_2 \sim 5$ msec), the effective or average correlation times involved must still be short.

We feel such descriptions are not applicable to the polyisoprenes. One of the most obvious peculiarities of the ^{13}C nmr spectra of the polyisoprenes is that while the ratio of line widths of the two vinyl carbons is close to two, the ratio of spin-relaxation times is about seven. Since these are directly bonded carbons (connected by a relatively inflexible double bond in the polymer main chain), and since the flanking groups for both are chemically very similar, it seems unreasonable to expect one of these particular two carbons to be significantly more free than the other, as required by a description based on differences between correlation times. Furthermore, since the methine vinyl carbon is sterically less hindered than the methyl-substituted quaternary vinyl carbon, any dipolar coupling with nonbonded, distant methylene protons should be stronger for the methine carbon than for the quaternary carbon. This would lead to a narrower quaternary carbon line than otherwise expected, opposite to what is observed.

In addition to these speculative arguments against a description based on differences between correlation times, there are also firm experimental results which do not support such a model. For example, the model is incompatible with the observation of no pronounced line narrowing resulting from deuteration of the methine carbon of *cis*-polyisoprene. Since substitution of ^{2}H for ^{1}H has little effect on rotational correlation times, but does drastically affect the nuclear magnetic dipole important to dipolar coupling, the result of deuteration should be pronounced line narrowing, contrary to experiment. In addition, the temperature dependence of the line widths of the two vinyl carbons in filled and unfilled *cis*-polyisoprene does not support a description based on differences in correlation times. Above the glass-transition temperature, the temperature dependence of the correlation time associated with a dipolar line width will be of the form $\tau_c = \tau_0 \exp(-\Delta E/kT)$, where ΔE is some sort of an average barrier to thermal, rotational jumps.[27] The average is taken over the whole distribution of barriers corresponding to the distribution of segmental motions important to T_2. The temperature dependences for the vinyl carbon lines of filled and unfilled *cis*-polyisoprene are essentially the same (Table II). Thus, in a model of polyisoprene line widths based on differences in correlation times, the broadened line of the carbon-black-filled *cis*-polyisoprene must be primarily the result of a decreased effective correlation time, τ_0. One is therefore led to the implausible conclusion that while the filler can strongly influence (or discriminate against) some segmental motions and correlation times which contribute to τ_0, it has little effect on the energy barrier presumably averaged over values now associated with the substantially altered distribution of correlation times.

II. An Explanation of the Line Widths in Terms of Incomplete Motional Narrowing

We suggest that the observations of ^{13}C nmr line widths of the polyisoprenes can be explained if it is assumed that not all the spatial orientations of the polymer chain are readily accessible as a result of its segmental motions, and that the observed nmr lines are therefore subject to rapid but incomplete motional narrowing. One probable source of the restriction in ordinary *cis*-polyisoprene is chain entanglement. For the crystallite and carbon-black-filled polymers, the filler itself acts as an additional cross-linking source of entanglements, thereby producing increased line widths. When the entanglements are made less likely (as, for example, in experiments on dilute solutions), individual carbon line widths are now not only much narrower but their ratios are proportional, or closer to proportional, to the corresponding ratios of spin-lattice relaxation times. Since entanglements probably determine both the filled and unfilled polyisoprene line widths, it seems reasonable that these line widths have a similar temperature dependence.

The ^{13}C line widths of the polyisoprenes are narrow lines, and only slight restrictions are required to produce broadening of about an order of magnitude. Excluding the magnetization vectors from solid sectors of only a few degrees is sufficient.[36] Furthermore, the broadening of individual carbon lines, which varies from carbon to carbon, will depend (and in certain circumstances may reveal) the details of how the restrictions destroy the symmetry of the motional narrowing. Thus, a carbon line width may be influenced to an even greater extent by, *e.g.*, intramolecular interactions with several, nearby, nonbonded protons (which are not being isotropically, motionally averaged) than it is by interactions with one or two directly bonded protons. Such a rationale is consistent with the observations of similar line widths for both quaternary and methylene carbons in the filled systems, and of the absence of a pronounced narrowing of any of the lines resulting from partial deuteration of *cis*-polyisoprene. Finally, the fact that a partially motionally narrowed line can be expected to behave in a selective saturation experiment as a single, dipolar-broadened nmr line[37] is also consistent with observation.

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(36) S. Kaufman, W. P. Slichter, and D. D. Davis, *J. Polym. Sci., Part A-2*, 9, 829 (1971).

(37) However, the line need no longer be Lorentzian-like. Furthermore, if the broadening is excessive (unlike the present situation) the line can be asymmetric.

The immediately preceding discussion has been necessarily qualitative. It seems clear that the potential exists for a detailed structural analysis of the observed line widths (and spin–lattice relaxation times) of the individual carbons of solid polymers and their selectively deuterated analogs. Such an analysis might separate, for example, the contributions to the line widths from short-range, segmental restrictions as opposed to long-range chain entanglements and packing. However, this has not yet been attempted. The development of ^{13}C nmr as a genuinely useful tool for the characterization of solid, amorphous polymers depends upon the utilization of appropriate theoretical models and methods. Most of the basic techniques already exist. The problem involves combining statistical descriptions of chain configurations with classical mechanical descriptions of restricted, anisotropic, segmental motions (or perhaps distributions of motions), all of this complicated by chain–chain interactions. Obviously, this is not a simple problem. The motivation for attempting to do this theory, emphasizing nmr relaxation processes for the carbons of the backbones of polymers, is the wealth of new, detailed data the ^{13}C experiment can produce. The data may be detailed enough to provide guides for the theory which were not previously available. Within the framework of an appropriate theoretical description, this data could be transformed into fundamental information and insight.

In addition to the ^{13}C line-width arguments presented here, a variety of examples provide definitive evidence for line broadening resulting from partial, anisotropic motional narrowing of nmr lines. These include studies of apparently homogeneous systems of crystals[38] and polymers[39] as well as studies of obviously heterogeneous systems such as the mixed lamellar and cubic phases of potassium laurate–water,[40] and the combination of a micellar liquid with a crystallite.[7]

The line broadening resulting from rapid but partial motional narrowing is distinct from the broadening resulting from isotropic rotational motions and diffusion at a rate not quite fast enough to average anisotropic, dipolar interactions to small values in a time T_2.[41] An argument based in part on the temperature dependence of the vinyl carbon line widths, for why the latter is not likely to be the correct explanation for the broadened lines of the carbon-black-filled *cis*-polyisoprene, has been given earlier in this discussion. However, the distinction between the two sources of line broadening can experimentally often be made unambiguously. If a solid polyisoprene sample is rotated at a rate rapid compared to the line width and on an axis which makes an angle of 54° 44′ with the applied magnetic filed,[42] then line narrowing may be observed if the line width is due to only partial motional narrowing, but will not be observed if it is due to isotropic motion at a slightly reduced rate. The basis for expecting differences is that the frequency spectrum associated with the random, isotropic part of a segmental motion of slightly reduced rate will still cover frequencies on the order of the inverse of the correlation time of the motion. For a solid, rubbery polymer having narrow lines this would be on the order of 10^6 Hz. Clearly in this case, sample rotation at the experimentally accessible frequencies of 10^2–10^4 Hz, and at the magic angle, will have no influence, since the line width is determined by frequencies several orders of magnitude greater. In the event of line broadening due to partial motional narrowing, however, the line width may be determined, in effect, by motion the spectral density of which lies primarily at zero or low frequency. (Thus, partial motional narrowing has a greater influence on T_2 than T_1.) This motion, described by long correlation times, can be identified with the residual dipole remaining from the incomplete spatial average. The details of the anisotropy of the average determined whether the motion is low frequency (0–10^4 Hz) or higher frequency (10^5–10^6 Hz). Now, sample rotation at the magic angle at frequencies comparable to the broadened line can result in narrowing. The extent of line narrowing depends on the actual spectral distribution of the residual dipolar interactions, relative to the spinning frequency.[41, 42a]

Results from proton nmr studies of both solid *cis*- and *trans*-polyisoprenes and similar rubbers have been in the literature for 15 years.[43, 44] At room temperature, line widths on the order of 200 Hz at 20 MHz (for *cis*-polyisoprene, *e.g.*) prevent individual proton resonances from being detected and a single composite ^{1}H nmr line is observed. The broad lines, relative to the ^{13}C nmr lines, are apparently due to greater intermolecular and long-range (in the sense of through bonds but not through space) intramolecular interactions. Although ^{13}C and ^{1}H spin–lattice relaxation times (obtained at the same frequency) for polymers and polymer solutions are comparable,[45] the ^{13}C nmr line widths are, in general, much less than the ^{1}H nmr line widths. The ^{13}C nmr line widths are less even for those carbon bearing directly bonded protons, when both spectra are obtained under the same conditions. This is true not only for solid rubbers[1] and gels,[2] but also for concentrated solutions at 40° of isotactic poly(methyl methacrylate) and isotactic polystyrene. The difference between the ^{13}C and ^{1}H line widths is much greater than can be attributed to the less efficient transverse relaxation resulting from the coupling of unlike spins (^{13}C to ^{1}H) compared to the coupling of like spins (^{1}H to ^{1}H).[46] In addition, the noise-modulated ^{1}H decoupling fields used in the ^{13}C experiments are not strong enough to remove the ^{1}H–^{13}C and ^{1}H–^{1}H dipolar coupling and hence narrow the ^{13}C lines.[47] It seems reasonable to suppose that, in all of these systems, as a result of chain folding and entanglement low-frequency segmental motions produce intermolecular and long-range (through bond) intramolecular dipolar interactions

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(38) H. Kessemeier and R. E. Norberg, *Phys. Rev.*, **155**, 321 (1967).

(39) I. J. Lowe, *Phys. Rev. Lett.*, **2**, 285 (1959).

(40) J. Charvolin and P. Rigny, *J. Magn. Resonance*, **4**, 40 (1971). This reference also contains a description of a pulsed experiment which is the equivalent of the combined pulsed-cw selectively saturated Fourier transform experiment described in this paper.

(41) See, for example, E. R. Andrew, *Progr. Nucl. Magn. Resonance Spectrosc.*, **8**, 1 (1971).

(42) The so-called "magic angle," which makes the factor (3 cos^2 θ − 1) of dipolar interactions equal to zero; θ is the angle between the direction of the axis of specimen rotation and the direction of the laboratory magnetic field.

(42a) NOTE ADDED IN PROOF. Magic-angle spinning at 1 kHz results in line narrowing by a factor of 4 for a vulcanized, carbon-black-filled *cis*-polyisoprene: J. Schaefer, S. H. Chin, and S. I. Weissman (submitted for publication in *Macromolecules*).

(43) H. S. Gutowsky, A. Saika, M. Takeda, and D. E. Woessner, *J. Chem. Phys.*, **27**, 534 (1957).

(44) W. P. Slichter and D. D. Davis, *J. Appl. Phys.*, **34**, 98 (1964).

(45) For example, ^{1}H spin–lattice relaxation times at 30 MHz and 40° for *cis*-polyisoprene and *cis*-polybutadiene are about 45 and 300 msec, respectively: W. P. Slichter and D. D. Davis, *J. Appl. Phys.*, **35**, 3103 (1964). The corresponding spin–lattice relaxation times for methylene carbons of the same polymers are 50 and 400 msec, at 22.6 MHz (ref 24).

(46) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 297.

(47) F. Bloch, *Phys. Rev.*, **111**, 841 (1958). Decoupling fields in the experiments reported here were made just large enough that the residual scalar-coupling contribution to the line width was small compared to the dipolar-coupling contribution. There is evidence suggesting that some dipolar-broadened ^{13}C lines in filled systems can be narrowed by even modest decoupling fields. This will be discussed elsewhere.

which are more efficient for peripheral protons than for protected main-chain carbons. This is especially true when conditions of solvent, concentration, or temperature are not carefully chosen to minimize such interactions. The result is relatively shorter proton T_2 values and so relatively broader lines.

A 30-MHz ^{1}H nmr study of rubber–carbon black interaction has been reported recently by Kaufman, Slichter, and Davis.[36] These authors conclude that the carbon black, in addition to severely immobilizing rubber chains in the immediate vicinity, also imposes temperature-independent restrictions on the segmental motions of polymer chains farther away. They further conclude that the result of these restrictions is that the ^{1}H nmr line width is subject to only partial motional narrowing, and that this causes line broadening. This kind of description is essentially the same used to interpret the ^{13}C nmr line widths. There is a distinction to be made, however. The ^{13}C line-broadening effect is not temperature independent. The isolation of the ^{13}C spins allows them to avoid some of the more obscuring, intermolecular dipolar interactions which results in narrow lines and thereby permits the detection of the small but important temperature dependence of the line width. The fact that in both experiments the line widths of the filled system are about five times greater than in the unfilled system suggests a comparable spatial factor over which the motional narrowing is incomplete, with the ^{1}H nmr lines broader in an absolute sense because of the smaller average distance to a nearby spin.

Conclusion

The use of ^{13}C nmr to characterize the amorphous region of a solid polymer above the glass-transition temperature is aided by two factors, both of which are absent in ^{1}H nmr experiments: narrow line widths and the absence of spin diffusion. These two factors permit the measurement of individual T_1 and T_2 values for individual carbons, and the interpretation of the differences in terms of structure. The origin of both factors can be traced to the isolation of the ^{13}C spins.

As applied to the analysis of the polyisoprenes, the ability to measure individual T_1 and T_2 values for individual carbons results in the identification of the relative ease of high-frequency segmental motion of the trans chain due to its extended configuration, as well as the difficulty of low-frequency segmental motion of both cis and trans filled polyisoprenes due to spatial restrictions imposed on the bulk polymer by the filler. Comparisons of individual relaxation times also indicate differences between similar carbons in the same chain, and these can be related to deviations from perfect, isotropic behavior for both high- and low-frequency segmental mitoins.

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Methylene Proton Magnetic Resonance of Some Partially Deuterated Polypropylenes

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ABSTRACT: Several partially deuterated propylene polymers have been studied by pmr. A partial assignment of the methylene hexad proton resonances is tentatively proposed. The high stereoregularity of the *n*-heptane-insoluble fraction of isotactic polypropylene prepared using the HRA $TiCl_3–Al(C_2H_5)_2I$ catalyst system and also the methylene proton tetrad resonance assignment have been confirmed.

The use of recent developments in proton magnetic resonance techniques has given much information about the microstructure of poly(α-olefins).[1–17] Detailed information about microstructure is particularly useful in an understanding of the properties of the polymers and the polymerization stereochemistry. This paper describes the results we have obtained by proton magnetic resonance studies of partially deuterated propylene polymers. In particular, we have focused our attention on the methylene resonances of some polypropylenes having different steric regularities and have tried to correlate them with the hexad composition of the polymers. Our results led us to also reconsider the steric regularity of isotactic polypropylene and the previous tetrad assignment.[1,2]

Results

Tetrad Assignment. A complete tetrad methylene assignment was made as shown in Table I in a previous paper.[2]

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