Macromolecules 1980, *13*, 1121–1126

Carbon-13 $T_{1\rho}$ Experiments on Solid Glassy Polymers

Jacob Schaefer,* E. O. Stejskal, T. R. Steger, M. D. Sefcik, and R. A. McKay

Monsanto Company, Corporate Research Laboratories, St. Louis, Missouri 63166.
Received October 29, 1979

ABSTRACT: Experimental cross-polarization transfer rates, from protons in the local dipolar field to carbons in an applied radio-frequency field, can be used to determine quantitatively the relative contributions of spin–lattice and spin–spin processes to carbon $T_{1\rho}$ relaxation. We show that this procedure is to be preferred to determinations based either on various semiquantitative arguments, on the analysis of the H_1 dependence of $T_{1\rho}$, or on the use of theoretically calculated rigid-lattice spin–spin transfer rates. We find that average carbon $T_{1\rho}$'s (near 35 kHz) for a wide variety of glassy polymers at room temperature are predominantly spin–lattice (motional) in character.

In a recent review of ^{1}H NMR of solid polymers,[1] McCall pointed out that only T_2 or line-width measurements have proven to be generally useful. Interpretations of directly measured ^{1}H spin–lattice parameters (T_1 and $T_{1\rho}$) are complicated by spin-diffusion processes so that only averages of all side- and main-chain relaxation times are observed. Carbon-13 spin–lattice parameters are free from averaging arising from spin diffusion, at least for most natural-abundance experiments, and so are potentially useful. In fact, ^{13}C $T_{1\rho}$'s have been shown *qualitatively* to characterize the room-temperature mid-kHz main-chain motions of glassy polymers and have been empirically linked to the mechanical properties of the polymers which presumably depend on this motion.[2]

There is a complication in the use of ^{13}C $T_{1\rho}$'s however. The possibility exists[2] of static ^{1}H–^{13}C spin–spin interactions shortening $T_{1\rho}$ and so confusing its *quantitative* interpretation as a motional parameter. In order to evaluate such spin–spin contributions to ^{13}C $T_{1\rho}$'s, we have measured the ^{1}H and ^{13}C spin–spin and spin–lattice relaxation parameters of a wide variety of polymers. From an analysis of these measurements, we can show that at room temperature, for glassy polymers with ^{1}H line widths of about 5 G, ^{13}C $T_{1\rho}$'s (near 35 kHz) are indeed predominantly spin–lattice or motional and that a quantitative determination of the spin–spin or nonmotional contribution to the average $T_{1\rho}$(C) can be made.

Experiments

Carbon-13 cross-polarization NMR experiments were performed at 22.6 and 15.1 MHz with spectrometers constructed around 18-in. Bruker and 12-in. Varian electromagnets. Both spectrometers employed time-shared external ^{19}F field-frequency stabilization, routed quadrature detection,[3] spin-temperature alternation,[4] solid-state class-A transmitters, and double-tuned single-coil probes.[5] The magic-angle spinning results were obtained at 15.1 MHz by using a Beams–Andrew design rotor[6] (0.7-cm^3 sample volume) and spinning speeds of the order of 2 kHz. Spinning samples occupied approximately two-thirds of the volume of the coil. The 15.1-MHz spectrometer was also equipped with a software-controlled digital pulse programmer, which permitted automatic variation of pulse parameters coordinated with interleaved block-averaged data acquisition. This procedure eliminated possible systematic errors arising from slow drifts during prolonged $T_{1\rho}$ relaxation measurements.

The pulse sequences employed in these experiments are shown in Figure 1. In the first experiment, following a matched, spin-lock Hartmann–Hahn generation of a carbon polarization,[7] the proton radio-frequency field was turned off abruptly. After a 50-μs delay, measurement of the initial steady-state rate of decay of the total carbon magnetization held in its rotating field yielded $\langle T_{1\rho}(\mathrm{C})\rangle$, the average carbon spin-lock lifetime. (The full relaxation curve is designated $T_{1\rho}$(C).) The $T_{1\rho}$(C) experiment was performed on both stationary and rotating samples.

In the second experiment illustrated in Figure 1, following a spin locking of the protons, the ^{1}H radio-frequency field was turned off in times of about 0.5 ms (long compared to proton T_2's), so that the order established by the spin lock was transferred to the local dipolar field.[8] This process is called an adiabatic demagnetization in the rotating frame (ADRF). Order in the dipolar field could be maintained for a characteristic time, $T_{1\mathrm{D}}$. Since $T_{1\mathrm{D}}$ was often short, the ADRF experiment was not a practical routine way to produce a large carbon polarization. Nevertheless, an estimate of the initial rate of nontransient polarization transfer from the local field to the ^{13}C radio-frequency field, $(\mathrm{d}S/\mathrm{d}t)_{t=0}$, was always possible. The time $t = 0$ is defined as the end of the transient and is generally taken as 50 μs after the turnon of the carbon radio-frequency field. From $(\mathrm{d}S/\mathrm{d}t)_{t=0}$ the average ADRF cross-polarization time constant, $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$, was derived.[9] (This time constant also characterizes the extent of a spin–spin carbon-to-proton S–I polarization transfer during a $T_{1\rho}$(C) experiment.[9]) Subsequent measurement of polarization transfer for longer contact times yielded $S(t)$, the evolution of the carbon signal, S, during the ADRF contact time. These measurements were performed on stationary (nonspinning) samples to avoid perturbing the orientation of the ^{1}H–^{1}H internuclear vectors relative to the applied static magnetic field, shortening the proton $T_{1\mathrm{D}}$[10] and, in some cases, altering the sign of the polarization transferred to the carbon radio-frequency field.

Determinations of proton T_2's were made by observation of a solid echo, using a $(\pi/2)_x$–t–$(\pi/2)_y$ sequence,[11] and determinations of proton $T_{1\mathrm{D}}$'s by introducing a delay time before a fixed-length ADRF contact in the cross-polarization experiment described above.

All of the polymers used in these experiments were commercially available with the exception of the *o,p*-bisphenol-A polycarbonate, which was the kind gift of Dr. Don LeGrand, General Electric Co., Schenectady, NY. Poly(ethylene terephthalate) was examined both as a noncrystalline glass, formed by quenching in ice water a $^1/_8$-in. sheet mold containing the polymer at 250 °C, and as a part-crystalline biaxially oriented (Mylar) film. Thin strips of the film were wound on a mandrel and inserted into the rotor for magic-angle experiments. The spinning axis was therefore parallel to one of the draw directions of the film. The other polymers in this study were examined as noncrystalline powders or compression-molded glasses, the preparations for which have been given earlier.[2]

Results

A. $T_{1\rho}$(C). Matched spin-lock, cross-polarization ^{13}C NMR spectra of normal polycarbonate and the *o,p*-isomer of polycarbonate are shown in Figure 2. The magic-angle spectrum of the latter clearly shows the nonequivalence of the methyl carbons. The spectra of both nonspinning polymers are similar for long contact times, with differences apparent when short contact times (30 μs) are used. In the latter situation, only a fraction of the protonated aromatic carbons (low field) and methyl carbons (high field) are significantly polarized. Using this short contact time to prepare the carbon spin system permits the $T_{1\rho}$(C) of the protonated aromatic carbons of both nonspinning polycarbonates to be determined from integrals of the corresponding low-field regions. The $\langle T_{1\rho}(\mathrm{C})\rangle$'s of the two

0024-9297/80/2213-1121$01.00/0

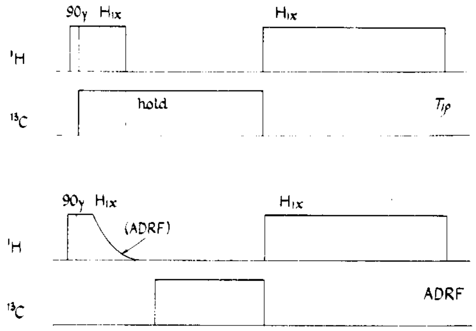

Figure 1. Pulse sequences for two cross-polarization experiments.

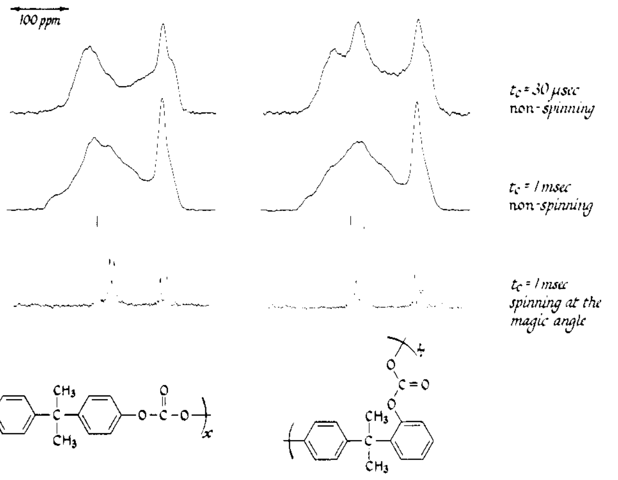

Figure 2. Cross-polarization ^{13}C NMR spectra of *p,p*-polycarbonate (left) and *o,p*-polycarbonate (right) under a variety of conditions. The protonated aromatic carbon lines of the former are the second and third lowest field lines and of the latter, the third lowest field line of the magic-angle spinning spectra (bottom). Methyl carbon lines appear at highest field for both polymers.

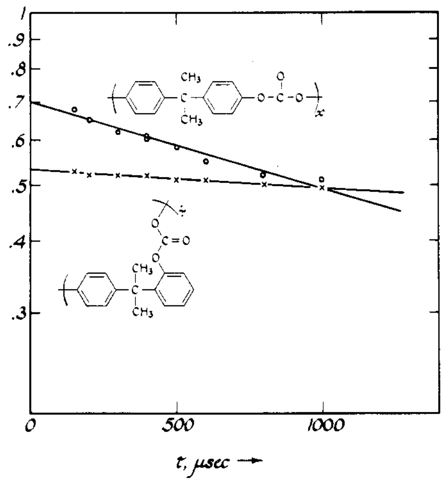

Figure 3. Carbon-13 $T_{1\rho}$ plots (28 kHz) for the protonated aromatic carbon of two polycarbonates. The carbon polarization was prepared as described in Figure 2 (top). Contributions due to cross-polarization transfers from dipolar order within the proton spin system were removed as described in the text.

polymers, evaluated as the slope of the semilog $T_{1\rho}(C)$ decay curve between 0.150 and 1.000 ms, differ by a factor of about 5 (Figure 3). Contributions to $T_{1\rho}(C)$, due to a transfer from ^1H to ^{13}C arising from dipolar order established among the protons during their spin lock, were determined by $T_{1\rho}(C)$ experiments in which the spin-locked carbon–proton contact was omitted.[9] These ("ADRF") contributions were small for both polymers. This result is due in part to relatively weak static ^1H–^1H interactions for the two polymers (the room-temperature proton T_2's are 25 and 15 μs for *p,p*- and *o,p*-polycarbonates, respectively). Because high-speed spinning destroys the dipolar order within the proton system,[10] no significant ADRF polarization transfer from protons to carbons occurs in magic-angle $T_{1\rho}(C)$ experiments employing carbon spin-lock hold times of 100 μs or more.

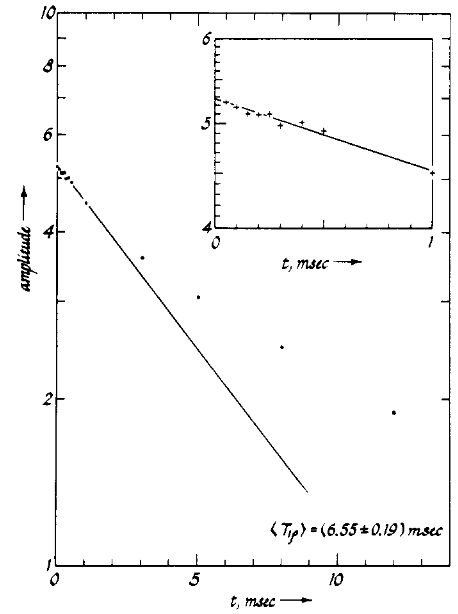

Figure 4. Carbon-13 $T_{1\rho}$ plot (28 kHz) for the protonated carbons of *p,p*-polycarbonate under magic-angle spinning conditions. The carbon polarization was prepared as described in Figure 2 (bottom). Signal amplitude is based on peak heights.

Table I
$\langle T_{1\rho}(C)\rangle$ for Protonated Aromatic Carbons of *p,p*-Polycarbonate (T = 26 °C) Spinning at the Magic Angle at 2 kHz

$H_1(C)$, kHz	$\langle T_{1\rho}(C)\rangle$,[a] ms	$H_1(C)$, kHz	$\langle T_{1\rho}(C)\rangle$,[a] ms
20	5.2	44	8.2
28	6.6	60	8.6
37	7.4		

[a] Least-squares straight-line fit to relaxation data (such as shown in Figure 4); t = 0.050–1.000 ms after turnoff of the proton H_1.

The $T_{1\rho}(C)$ curve at 28 kHz for the protonated aromatic carbon of *p,p*-polycarbonate is shown in Figure 4. The decay curve is monotonically decreasing for all t; that is, there are no transient oscillations. Similarly, no transient oscillations were observed for the corresponding decay curve for *o,p*-polycarbonate.

The relaxation decay curve in Figure 4 is not represented by a single time constant. Thus, the value of $\langle T_{1\rho}(C)\rangle$ depends upon how much of the relaxation curve is used to determine the initial slope. If $\langle T_{1\rho}(C)\rangle$ for *p,p*-polycarbonate is determined from an initial slope measured between 0.050 and 0.150 ms, a value of about 3 ms is obtained, half that shown by the plotted straight line and reported in Table I. Shorter $\langle T_{1\rho}(C)\rangle$'s are determined for still shorter sampling times. When a 1-ms spin-lock preparation is used, protonated main-chain magic-angle $\langle T_{1\rho}(C)\rangle$'s for *p,p*-polycarbonate are observed to be some 3 times *shorter* than the magic-angle $\langle T_{1\rho}(C)\rangle$'s of *o,p*-polycarbonate when evaluated between 0.050 and 1.000 ms and 5 times shorter when evaluated between 0.025 and 0.100 ms.

Table II
Relaxation Parameters for Methylene Carbons of Poly(ethylene terephthalate) at 26 °C

sample	H_1(C), kHz	$\langle T_{IS}(\mathrm{ADRF})\rangle$,[a] ms	$\langle T_{1\rho}(\mathrm{C})\rangle$,[b] ms
quenched disk	28	100	2.1
	37	>100	3.5
	44	>100	7.0
oriented film	28	18	4.9
	37	53	18
	44	125	50

[a] Stationary sample; average value obtained as described in Results (eq 3), using relaxation data collected from t_c(ADRF) = 0.300 to t_c(ADRF) = 0.800 ms with ϵ = 0.75 and average methylene-proton local fields for the quenched glass and partially crystalline film of 5 and 10 kHz, respectively. The latter were estimated from T_2(H)'s. (See I. M. Ward, *Trans. Faraday Soc.*, 56, 648 (1960)). [b] Sample spinning at 2.1 kHz at the magic angle; average value is least-squares straight-line fit to relaxation data collected from t = 0.300 to t = 0.800 ms. Carbon polarization was prepared by a 1-ms matched spin-lock cross-polarization transfer.

The $\langle T_{1\rho}(\mathrm{C})\rangle$ of *p,p*-polycarbonate, as evaluated between 0.050 and 1.000 ms, is almost independent of H_1(C), changing by less than a factor of 2 between 20 and 60 kHz (Table I). The $\langle T_{1\rho}(\mathrm{C})\rangle$ as evaluated between 0.050 and 0.150 ms is similarly almost independent of H_1(C).

B. T_{IS}(ADRF). For the ADRF experiment of Figure 1, the carbon polarization is given by[9]

$$S = S_i e^{-t/T_{1\rho}(\mathrm{C})} + S_0/T_{IS}(\mathrm{ADRF})\left\{\frac{e^{-t/T_{1D}} - e^{-t/T_{1\rho}(\mathrm{C})}}{1/T_{1\rho}(\mathrm{C}) - 1/T_{1D}}\right\} \quad (1)$$

where S_i is the transient carbon polarization developed immediately following the turnon of the carbon radiofrequency field, T_{1D} is the proton dipolar lifetime, and

$$S_0 \approx S_M(\gamma_S H_1(\mathrm{C})/\gamma_I H_L)\epsilon \quad (2)$$

In eq 2, γ_S and γ_I are the gyromagnetic ratios of S and I spins, respectively, and S_0 is the total carbon polarization available in an experiment with no dissipative relaxation processes. The latter is evaluated from, first, S_M, the matched spin-lock carbon polarization, second, H_L (equal to $(M_2^{\mathrm{II}}/3)^{1/2}$, where M_2^{II} is the proton second moment obtained from T_2(H)), and, third, ϵ, the average net efficiency of the proton ADRF process. (For our experiments, ϵ was determined[9] to be 0.75.) The rate of relaxation, represented by $[T_{1\rho}(\mathrm{C})]^{-1}$ in eq 1, is actually the sum of a spin-lattice relaxation component and a spin-spin component, the latter given by $[T_{IS}(\mathrm{ADRF})]^{-1}$. If there is no spin-lattice contribution, $T_{1\rho}$(C) equals T_{IS}(ADRF). The percentage spin-spin contribution to $T_{1\rho}$(C) is determined by the ratio of $T_{1\rho}$(C) to T_{IS}(ADRF).

For polymers, $T_{1\rho}$(C) and T_{IS}(ADRF) of eq 1 are replaced by suitable distributions of relaxation times[9] or represented by average values. In this situation, from eq 1

$$(\mathrm{d}S/\mathrm{d}t)_{t=0} = S_0/\langle T_{IS}(\mathrm{ADRF})\rangle - S_i/\langle T_{1\rho}(\mathrm{C})\rangle \quad (3)$$

That is, $\langle T_{IS}(\mathrm{ADRF})\rangle$ can be evaluated from the initial rate of polarization transfer following the transient, with a (usually) small correction term involving the size of the polarization transfer during the transient. Values for $\langle T_{IS}(\mathrm{ADRF})\rangle$ for the methylene carbons of two poly(ethylene terephthalate) samples, a quenched amorphous poly(ethylene terephthalate) and an oriented film, determined this way are given in Table II, along with the corresponding $\langle T_{1\rho}(\mathrm{C})\rangle$'s. For both polymers, $\langle T_{1\rho}(\mathrm{C})\rangle$'s are shorter than $\langle T_{IS}(\mathrm{ADRF})\rangle$'s for all H_1(C)'s. We observe that, for these H_1's, main-chain carbon $\langle T_{1\rho}(\mathrm{C})\rangle$'s are about the same in both 2-kHz spinning and nonspinning experiments, the latter corrected for any effects of dipolar order among the protons (cf. above). Of course, to avoid interfering with local dipolar order, we must measure $\langle T_{IS}(\mathrm{ADRF})\rangle$ only on nonspinning samples. In general, even with overlapping chemical shift anisotropies, individual $\langle T_{IS}(\mathrm{ADRF})\rangle$'s can be determined separately for protonated aromatic, aliphatic, and methyl carbons.

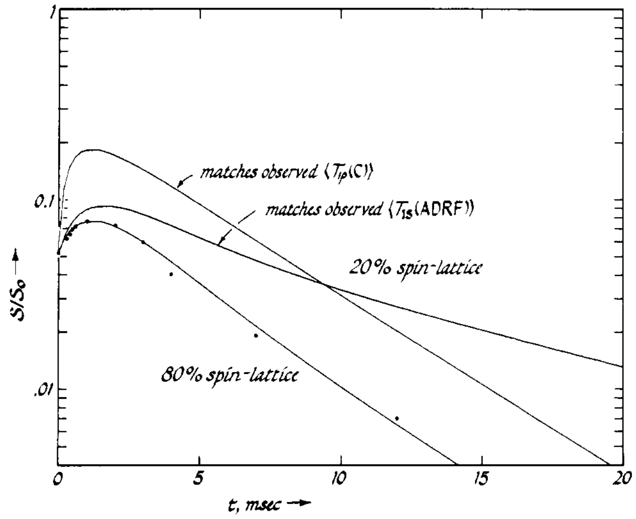

Figure 5. Main-chain carbon polarization of a nonspinning polystyrene sample observed (solid circles) in a 36-kHz ADRF cross-polarization experiment and calculated (solid lines) under various assumptions for relaxation mechanisms.

It is also possible to obtain $\langle T_{IS}(\mathrm{ADRF})\rangle$'s from a fit of $S(t)$ in an ADRF experiment with long cross-polarization contact times.[9] For the aliphatic main-chain carbons of polystyrene, for example, a fit to the observed $S(t)$ is possible with $\langle T_{1\rho}(\mathrm{C})\rangle$ = 3 ms, $\langle T_{IS}(\mathrm{ADRF})\rangle$ = 15 ms, and T_{1D} = 1.2 ms (Figure 5, 80% spin-lattice). The values of $S(t)$ were measured[9] on a nonspinning sample having a vertical height slightly greater than that of the receiver coil. The $\langle T_{1\rho}(\mathrm{C})\rangle$ of 3 ms was determined in a separate experiment on the same nonspinning sample, using data from 0.050 to 0.500 ms after removal of the proton radio-frequency, with a nominal H_1(C) = 36 kHz. The T_{1D} of 1.2 ms (more than an order of magnitude shorter than $\langle T_{IS}(\mathrm{ADRF})\rangle$) was also measured on the same sample. An advantage in determining $\langle T_{IS}(\mathrm{ADRF})\rangle$ from an overall fit to $S(t)$ is that this procedure is less sensitive to errors in S_0. Further details of the fitting procedure are described in ref 9.

If one assumes $\langle T_{1\rho}(\mathrm{C})\rangle$ is only 20% spin-lattice in character and then matches either the initial or final slopes of $S(t)$, poorer overall fits to $S(t)$ are obtained (Figure 5, top two solid curves). For $\langle T_{1\rho}(\mathrm{C})\rangle$ = 12 ms and $\langle T_{IS}(\mathrm{ADRF})\rangle$ = 15 ms, the initial slope of $S(t)$ is matched but the long-term behavior is incorrectly predicted, while for $\langle T_{1\rho}(\mathrm{C})\rangle$ = 3 ms and $\langle T_{IS}(\mathrm{ADRF})\rangle$ = 3.8 ms, the reverse is true. For both pairs of numbers, the ratio of $\langle T_{1\rho}(\mathrm{C})\rangle$ to $\langle T_{IS}(\mathrm{ADRF})\rangle$ is 0.8, corresponding to 80% spin-spin contributions to $\langle T_{1\rho}(\mathrm{C})\rangle$.

If a truncated polystyrene sample is used (approximately two-thirds the vertical height of the receiver coil), we find that $\langle T_{IS}(\mathrm{ADRF})\rangle$ = 30 ms with $\langle T_{1\rho}(\mathrm{C})\rangle$ = 5 ms (measured from 0.050 to 0.500 ms) and $\langle T_{1\rho}(\mathrm{C})\rangle$ = 8 ms (measured from 0.050 to 1.000 ms). The more uniform, larger effective H_1(C) over the truncated sample presumably accounts for the increases in relaxation times. Except for the results reported in the preceding two paragraphs,

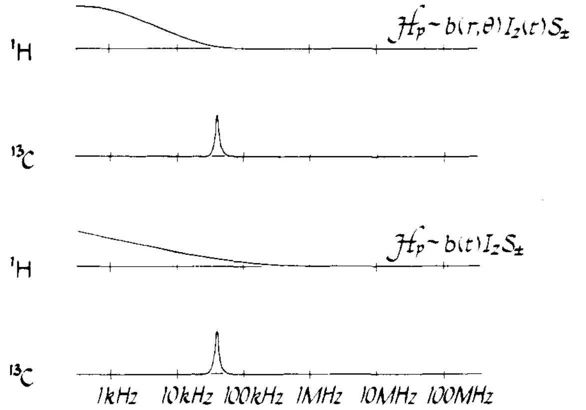

Figure 6. Spectral overlap between protons and carbons in a situation in which the spin–spin contribution (top) to the average $T_{1\rho}$(C) is minor and the spin–lattice contribution (bottom) is dominant. The coupling interaction H_p is identified in terms of standard spin operators I_z and $S_\pm$ multiplied by a spatial factor b which can be time dependent. Line widths on the logarithmic frequency scale are schematic.

all measurements described in this paper were of truncated samples.

Discussion

A. Spin–Spin and Spin–Lattice Character of $T_{1\rho}$(C). A qualitative description of $T_{1\rho}$(C) of protonated carbons involves an estimate of the competition between two relaxation pathways. For carbons in rigid polymers having tightly coupled protons, a likely relaxation mechanism is by a spin–spin interaction. Strong, static ^{1}H–^{1}H interactions give rise to proton spin flips and a broad dipolar fluctuation spectrum having substantial spectral density at the ^{13}C rotating-frame Larmor frequency. Consequently, mutual spin flips can occur from spin-locked carbons to protons resulting in a polarization transfer characterized by a spin–spin time constant T_{IS}(ADRF) which, in the absence of any spin–lattice process, is equal to $T_{1\rho}$(C). Polymers for which this is known to occur at room temperature include crystalline poly(oxymethylene)[9] and crystalline polyethylene.[12]

For carbons in glassy polymers in which strong ^{1}H–^{1}H static dipolar interactions are absent because of molecular motion, large interproton distances, or some combination of these, a completely different situation can exist. The proton dipolar fluctuation spectrum now has little density at the carbon Larmor frequency for typical H_1(C)'s of 30 kHz or so (Figure 6, top). Instead, spectral density generated by fluctuating dipolar fields associated with rotations of ^{13}C–^{1}H internuclear vectors can be effective in producing ^{13}C spin flips (Figure 6, bottom). In other words, the dominant mechanism for $T_{1\rho}$(C) relaxation is now spin–lattice, not spin–spin, in character. Polymers for which this situation holds[2] include polycarbonate and poly(phenylene oxide), both glassy polymers having an assortment of side- and main-chain motions and both proton-deficient polymers having weak ^{1}H–^{1}H static interactions.

Occasionally, on qualitative grounds, a decision as to the character of $T_{1\rho}$(C) can be made even for proton-rich polymers. For example, the observed ratios of magic-angle $\langle T_{1\rho}(C)\rangle$'s of the methine and methylene carbons of polystyrene and of a completely alternating copolymer of polystyrene and SO$_2$[13] are about 1.9 and 2.0, respectively, at 37 kHz. (The methine and methylene carbon resonances are completely resolved for the latter polymer but only partially resolved for the former.) If these $\langle T_{1\rho}(C)\rangle$'s were, in fact, spin–spin in origin, a ratio of methine to methylene carbon values could be as small as 2 only if the methine proton were as tightly coupled to the methylene protons as the methylene protons were to each other. Then, the proton–proton dipolar fluctuation spectra would be the same, and the factor of 2 in the relative rates would arise from a doubling of the carbon–proton static coupling by a doubling of directly bonded protons. This situation would lead to a prediction that the ratios of methine to methylene *matched* spin-lock cross-polarization times would also be given by about the same factor of 2.[14,15] In fact, for both polymers, the methine carbon value is *smaller* than the methylene carbon value so that the corresponding ratios are less than 1. This result is only consistent with a relatively weak coupling between methine and methylene protons. The observed $\langle T_{1\rho}(C)\rangle$'s are not, therefore, qualitatively consistent with a description based exclusively on spin–spin interactions.

Similarly, the short protonated aromatic carbon $\langle T_{1\rho}(C)\rangle$ of *p,p*-polycarbonate (short compared to that of the *o,p*-isomer despite the latter's stronger ^{1}H–^{1}H interactions) and its near independence of H_1(C) simply cannot be explained in terms of spin–spin processes. A typical spin–spin $\langle T_{IS}(\text{ADRF})\rangle$ increases by about a factor of 10 for each increase in H_1(C) equal to half of the proton line width.[14] For polycarbonate the full proton line width is about 20 kHz, so if $\langle T_{1\rho}(C)\rangle$ were equivalent to $\langle T_{IS}(\text{ADRF})\rangle$, $\langle T_{1\rho}(C)\rangle$ would have increased by about 10^4 for an increase of H_1(C) from 20–60 kHz. The observed increase is less than a factor of 2 (Table I).

We have developed a wide variety of arguments, similar to those above, to convince ourselves that for all the glassy polymers we have examined, $\langle T_{1\rho}(C)\rangle$'s near or above 30 kHz and room temperature are, in fact, predominantly spin–lattice or motional in character.[2] However, qualitative arguments are seldom entirely convincing. Consequently, we now present arguments not only which are inherently more quantitative but also which can be used in the analysis of complicated situations where both spin–lattice and spin–spin interactions may be important in determining $\langle T_{1\rho}(C)\rangle$.

B. Comparison of $T_{1\rho}$(C) and T_{IS}(ADRF). The most direct and quantitative measure of the relative importance of spin–spin and spin–lattice contributions to $T_{1\rho}$(C) is a comparison of the *average* steady-state values of polarization transfers observed in the T_{IS}(ADRF) and $T_{1\rho}$(C) experiments, the pulse sequences for which are shown in Figure 1. These average values are determined experimentally from the rates of the initial polarization transfers, using plots such as those shown in Figures 3–5. Naturally, complications in the determination of the initial steady-state transfer due to spin–spin transients must be avoided. This is possible in the ADRF experiment by measuring the polarization transfer following the stepwise appearance of S_i (see Results). The transients associated with S_i are stabilized in times of the order of a few tens of microseconds, short compared to subsequent transfer times.[14] We generally wait at least 50 μs before measuring a steady-state transfer rate. Values for $\langle T_{IS}(\text{ADRF})\rangle$ obtained from initial steady-state transfer rates can be confirmed by comparison with calculated fits to $S(t)$ for longer contact times (Figure 5).

Transients in the $T_{1\rho}$(C) experiment following turnoff of the proton radio-frequency field are of the same origin as those associated with the appearance of S_i in the ADRF experiment.[12] In both situations, the amplitude of the transient depends upon $(H_L(C)/H_1)^2$, where H_L(C) is the local field experienced by the carbons.[14] The duration of the transient is specified by the dipolar correlation time

τ_D which is of the order of the proton T_2.[16] For most glassy polymers the amplitude of the transient involves only a few percent of the total carbon magnetization,[9] for H_1(C)'s of the order of 30–40 kHz. These glassy-polymer transients may persist for some 20–50 μs.

VanderHart and Garroway[12] report transients in these experiments lasting 70 μs for nonspinning *oriented* crystalline polyethylene. We have observed that especially for amorphous, but even for polycrystalline materials, including, for example, poly(oxymethylene), transients are damped in a time shorter than the longest τ_D (arising from orientations in the sample associated with small H_L's) because of destructive interferences between components with different H_L's and τ_D's. Thus, for an H_1(C) of 36 kHz, the total intensity of S_i for nonspinning poly(oxymethylene) is reached and maintained reasonably constant after 20 μs despite some line-shape changes which persist for another 20–30 μs.

For most carbons, we feel it is safe to begin a determination of the initial steady-state rate of polarization transfer after 50 μs, although waiting for an additional 100–200 μs is not unreasonable. (Long delay times can result in an error in determining the average $T_{1\rho}$(C) since, as is the case for *p,p*-polycarbonate,[17] the fast-relaxing, motionally broadened components of the total magnetization will have disappeared.) Since the semilog $T_{1\rho}$(C) relaxation plots for polymers are not linear (Figure 3), there is a certain subjectivity as to what constitutes an "initial" slope. This problem has been alluded to earlier in the Results section, where the variations encountered by different estimates of initial slopes were illustrated. In our early work,[2] we constructed tangents to the $T_{1\rho}$(C) decay curves in an attempt to obtain true initial slopes. This procedure overemphasized relaxation during the period 20–100 μs following turnoff of the proton radio-frequency and so resulted in generally smaller values of $\langle T_{1\rho}(\mathrm{C})\rangle$'s. In addition, construction of the tangents proved to be highly subjective and difficult to use. Now in comparing $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$'s with $\langle T_{1\rho}(\mathrm{C})\rangle$'s, for both experiments, we use linear fits to the polarization transfer for the first several hundred microseconds following stabilization of the spin–spin transients (Table II, footnotes *a* and *b*). In using $\langle T_{1\rho}(\mathrm{C})\rangle$'s for other purposes, such as, for example, examining the effects of annealing on $T_{1\rho}$(C) relaxation of a polymer for which spin–spin interactions are known to be small, we sometimes use more conservative determinations of the initial rate of decay, averaging over the first millisecond or averaging over the first 10% of decay. In these situations, we are more concerned with detecting small differences between similar decay curves than we are with determining accurate *absolute* average values. A statement of the method of measuring $\langle T_{1\rho}(\mathrm{C})\rangle$ should always be made.

A simple ratio of $\langle T_{1\rho}(\mathrm{C})\rangle$ to $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$ determines the relative importance of spin–spin and spin–lattice contributions to $\langle T_{1\rho}(\mathrm{C})\rangle$. As mentioned above, if the ratio is close to 0, $\langle T_{1\rho}(\mathrm{C})\rangle$ is determined by motional processes; if the ratio is close to 1, $\langle T_{1\rho}(\mathrm{C})\rangle$ is spin–spin in origin. For example, the spin–spin contribution to $\langle T_{1\rho}(\mathrm{C})\rangle$ for quenched poly(ethylene terephthalate) is no more than a few percent, while for the oriented film it is some 30–40% (Table I). These results are consistent with the reduction in static ^{1}H–^{1}H interactions (and so reduction in a spin–spin contribution to $\langle T_{1\rho}(\mathrm{C})\rangle$) in the disordered glass by large-amplitude rotational motions within sterically unhindered gauche conformations. These same motions result in a proton T_2 some 2.5 times longer for the glass than for the film. For polystyrene, a ratio of $\langle T_{1\rho}(\mathrm{C})\rangle$ to $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$ of about 0.2 is consistent with the complete $S(t)$ in an ADRF experiment (Figure 5), so that the spin–spin contribution to $\langle T_{1\rho}(\mathrm{C})\rangle$ in this polymer is about 20% when $H_1(\mathrm{C}) = 36$ kHz.

Uncertainties in ϵ and H_L of about 10% result in a possible error in $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$ of about 20%. An error (or misestimate) of $\langle T_{1\rho}(\mathrm{C})\rangle$ of 10% is also a possibility. Thus, an *absolute* determination of the ratio of $\langle T_{1\rho}(\mathrm{C})\rangle$ to $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$ may be good to no better than ±30% with the present level of experimental precision. This means, for example, the ratio of $\langle T_{1\rho}(\mathrm{C})\rangle$ to $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$ for polystyrene could be as large as 0.4. Naturally, *relative* comparisons for similar polymers can be made with much greater confidence.

C. Interpretation of the Average $T_{1\rho}$(C). (1) In measurements on polymers, we always deal with distributions and averages, certainly for multiphase partially crystalline materials, but even for nominally homogeneous glasses.[18] On a microscopic scale different regions of the sample behave differently, with their own motions and their own characteristic relaxation times. Thus, it is reasonable to suppose that, for example, a densely packed part of a nearly crystalline component of the glassy poly(ethylene terephthalate) may have a T_{IS}(ADRF) which is less than $\langle T_1\rho(\mathrm{C})\rangle$. A part of the initial slope of a $T_{1\rho}$(C) plot will, therefore, be spin–spin in origin. However, it is unreasonable to suppose that this will be a large component of the initial slope. If it were, this component would also be a major contributor to the overall average T_{IS}(ADRF), resulting in a ratio of $\langle T_{1\rho}(\mathrm{C})\rangle$ to $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$ close to 1. Since this is not observed, we can conclude that the average $T_{1\rho}$(C) relaxation process in the glassy poly(ethylene terephthalate) sample is predominantly spin–lattice in character. We can now use this result and compare observed $\langle T_{1\rho}(\mathrm{C})\rangle$'s with other physical phenomena such as the effects of annealing, diluents, applied stresses, or orientation, correlating qualitative microscopic chain behavior with macroscopic properties.[2] Naturally, we qualify our correlations by the extent to which the weighted average $T_{1\rho}$(C) is not spin–lattice in origin. In general, for any polymer system, the fact that 1, 10, or 30% of $\langle T_{1\rho}(\mathrm{C})\rangle$ may be spin–spin in origin and unrelated to molecular motion does not prohibit its use in making correlations. We can make these chemically and physically meaningful correlations (using what is necessarily always a composite parameter describing a heterogeneous material) in a *simple* way, as long as we can establish unambiguously the relative importance of spin–spin and spin–lattice processes to $\langle T_{1\rho}(\mathrm{C})\rangle$'s and as long as we deal with *average* $T_{1\rho}$(C)'s and not the details of distributions of relaxation times.

(2) We reach a quantitative conclusion regarding the relative importance of spin–lattice and spin–spin mechanisms in determining $\langle T_{1\rho}(\mathrm{C})\rangle$ in poly(ethylene terephthalate), without assumptions regarding models of molecular motion in the solid state. In particular, we need not assume the applicability of a liquid-state theory[19] for simple rotational motion and its predicted H_1(C) dependence of $T_{1\rho}$(C) in order to determine the contributions of motional processes.

(3) In analyzing the $\langle T_{1\rho}(\mathrm{C})\rangle$'s of poly(ethylene terephthalate) and polystyrene, we have used $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$'s as determined experimentally at room temperature or, more accurately, at the same temperature as the experimental values of $\langle T_{1\rho}(\mathrm{C})\rangle$. VanderHart and Garroway have suggested using $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$ calculated under rigid-lattice conditions.[12] They note that if $\langle T_{1\rho}(\mathrm{C})\rangle$ were much less than this calculated $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$, there would

be no question that $\langle T_{1\rho}(\mathrm{C})\rangle$ were motional in origin.

Actually, most of the main-chain protonated $\langle T_{1\rho}(\mathrm{C})\rangle$'s we have measured[2] for glassy polymers at room temperature using $H_1(\mathrm{C})$'s greater than 25 kHz satisfy the condition that $\langle T_{1\rho}(\mathrm{C})\rangle$ is much less than the calculated rigid lattice $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$.[20] This is an easy condition to satisfy because polycarbonates, polysulfones, and poly(phenylene oxides) are not proton rich and so have no strong static main-chain ^{1}H–^{1}H interactions.

In many situations, however, use of a rigid-lattice criterion may be impractical. A difficulty with using this criterion is that no reliable a priori calculation of the effects of ^{1}H–^{1}H interactions of interchain packing and intrachain conformational distribution is possible. This problem can be serious because nonbonded proton–proton interactions in many rigid or nearly rigid proton-rich polymers are not well represented by those of relatively simple models, such as the interactions of the all-trans configuration of polyethylene. Thus, using proton dipolar fluctuation spectra suitable for polyethylene-like systems, methylene carbon 37-kHz $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$'s of less than 1 ms are calculated[12] for proton-rich crystalline components of poly(oxymethylene) and poly(ethylene terephthalate) while values of 10 and 25 ms, respectively, are observed.[21]

These results are a reflection of the fact that the origin of a proton dipolar fluctuation spectrum is a genuine many-body problem. It is unreasonable to assume that methine and methylene proton dipolar fluctuation spectra are related by a simple factor or that fluctuation spectra are transferrable parameters, so that one polymer system can model another. The discrepancies resulting from such assumptions are not the 20% or so uncertainty in a calculated second moment but the much larger uncertainty in the size of the distant tail of the dipolar fluctuation spectrum. In short, the calculation of a rigid-lattice $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$ is itself inherently a complicated problem.

Naturally, the use of a rigid-lattice criterion in the analysis of $T_{1\rho}(\mathrm{C})$ of glassy polymers having substantial motion can be unnecessarily stringent. This point has been illustrated by VanderHart and Garroway.[12] These authors have made comparisons of the spin–spin and spin–lattice contributions to $T_{1\rho}(\mathrm{C})$, calculated under various assumptions about the nature of the lattice motions, and have found situations in which motion dominates even though $\langle T_{1\rho}(\mathrm{C})\rangle$ is greater than the rigid-lattice $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$. Cheung and Yaris[20] have found a somewhat broader class of such conditions by their calculations, which start with different assumptions. It comes as no surprise, then, that for glassy polymers such as polystyrene and poly(styrene sulfone), the dipolar fluctuation spectra for methine and methylene protons are not the same (cf. above) and, along with the corresponding $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$'s, are not given by values calculated for rigid-lattice systems. Of course, for an analysis which is independent of the details of the theoretical modeling of motion, the experimental determination of $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$ and comparison to $\langle T_{1\rho}(\mathrm{C})\rangle$, as discussed above, will always permit a determination of the relative importance of any spin–spin contribution to $T_{1\rho}(\mathrm{C})$.

(4) We have made determinations of main-chain $\langle T_{1\rho}(\mathrm{C})\rangle$'s and $\langle T_{\mathrm{IS}}(\mathrm{ADRF})\rangle$'s for a wide variety of glassy polymers,[2,9] including poly(methyl methacrylate), poly(phenylene oxide), polycarbonate, poly(ethylene terephthalate), and polystyrene. In all cases we find that spin–lattice processes are important contributors to $\langle T_{1\rho}(\mathrm{C})\rangle$ at room temperature for $H_1(\mathrm{C})$'s on the order of 30 kHz and higher. Garroway et al. have reached a similar conclusion regarding $T_{1\rho}(\mathrm{C})$ measurements on some epoxy glasses at room temperature.[22] We recognize that there is no physical law which demands that $\langle T_{1\rho}(\mathrm{C})\rangle$'s be predominantly motional in character. We have emphasized[2] the possibility of the dual spin–spin and spin–lattice character of $T_{1\rho}(\mathrm{C})$, especially for rigid, brittle, or cross-linked glasses or glasses at low temperatures. Rather than dismiss $T_{1\rho}(\mathrm{C})$ as too difficult or ambiguous a parameter with which to deal, we recommend its clarification by the combination of $T_{1\rho}$ and $T_{\mathrm{IS}}(\mathrm{ADRF})$ experiments. We feel this clarification is of practical importance since the option of arbitrarily large $H_1(\mathrm{C})$'s (to ensure the complete spin–lattice character of $T_{1\rho}(\mathrm{C})$) may not be experimentally available or even desirable, the latter situation arising when the effects of low-frequency motions are of particular interest. With a determination of the average contribution of spin–spin and spin–lattice processes to $\langle T_{1\rho}(\mathrm{C})\rangle$, for a particular sample, coil geometry, and $H_1(\mathrm{C})$, we can interpret the spin–lattice part, with confidence, in terms of qualitative features of restricted rotational motions in the important low-to-mid-kilohertz frequency range.

References and Notes

(1) D. W. McCall, *Acc. Chem. Res.*, **4**, 223 (1971).

(2) J. Schaefer, E. O. Stejskal, and R. Buchdahl, *Macromolecules*, **10**, 384 (1977).

(3) E. O. Stejskal and J. Schaefer, *J. Magn. Reson.*, **14**, 160 (1974).

(4) E. O. Stejskal and J. Schaefer, *J. Magn. Reson.*, **18**, 560 (1975).

(5) V. R. Cross, R. K. Hester, and J. S. Waugh, *Rev. Sci. Instrum.*, **47**, 1486 (1976).

(6) E. R. Andrew, A. Bradbury, and R. G. Eades, *Nature (London)*, 182, 1569 (1958).

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

(8) D. A. McArthur, E. L. Hahn, and R. E. Walstadt, *Phys. Rev.*, **188**, 609 (1969).

(9) E. O. Stejskal, J. Schaefer, and T. R. Steger, *Faraday Soc., Symp.*, **13**, 56 (1979).

(10) J. F. M. M. Pourquié and R. A. Wind, *Phys. Lett. A*, **55A**, 347 (1976).

(11) J. G. Powles and J. G. Strange, *Proc. Phys. Soc.*, **82**, 6 (1963).

(12) D. L. VanderHart and A. N. Garroway, *J. Chem. Phys.*, **71**, 2773 (1979).

(13) R. E. Cais, M. D. Sefcik, E. O. Stejskal, R. A. McKay, and J. Schaefer, unpublished results.

(14) D. E. Demco, J. Tagenfeldt, and J. S. Waugh, *Phys. Rev. B*, **11**, 4133 (1975).

(15) Orientation-dependent variations in local static proton–proton dipolar interactions are likely to be about the same for methine and methylene protons in glassy vinyl polymers. Thus, spin–spin fluctuations will not be preferentially inhibited by differential inhomogeneous broadening effects. (See M. Mehring, "High Resolution NMR Spectroscopy in Solids", Springer-Verlag, New York, 1976, p 149.) This means $T_{\mathrm{IS}}(\mathrm{SL})$ and $T_{\mathrm{IS}}(\mathrm{ADRF})$ can be compared directly. If the methylene ^{1}H–^{1}H dipolar interactions result in a broader dipolar fluctuation spectrum than that of the methine proton (and hence a reduced density at zero frequency), the matched spin-lock transfer rate for the methylene carbon can be less than that of the methine carbon.

(16) R. L. Strombotne and E. L. Hahn, *Phys. Rev.*, **133**, A1616 (1964).

(17) T. R. Steger, J. Schaefer, E. O. Stejskal, and R. A. McKay, *Macromolecules*, following paper in this issue.

(18) J. Schaefer, E. O. Stejskal, and R. Buchdahl, *J. Macromol. Sci., Phys.*, **B13**, 665 (1977).

(19) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **74**, 679 (1948).

(20) T. T. P. Cheung and R. Yaris, *J. Chem. Phys.*, **72**, 3604 (1980).

(21) The value for poly(oxymethylene) is reported in ref 9; the value for poly(ethylene terephthalate) is obtained from Table II together with the fact that the oriented film is 50% crystalline. Both values were obtained at room temperature.

(22) A. N. Garroway, W. B. Moniz, and H. A. Resing, *Faraday Soc., Symp.*, **13**, 63 (1979).