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Separated Proton Local Fields in Polymers by Magic-Angle Carbon-13 Nuclear Magnetic Resonance

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ABSTRACT: Proton local dipolar fields have been determined by a transient cross-polarization transfer of proton dipolar order (generated by a Jeener–Broeckaert pulse pair) to carbon rotating-frame single-quantum coherence. A different proton local field (or proton line width) can be measured by each carbon line resolved by magic-angle spinning and dipolar decoupling. For example, proton local fields of 7 and 10 kHz, respectively, are observed for the aromatic and methylene protons of poly(α-methylstyrene). Knowledge of these local fields is important in estimating spin–spin contributions to carbon $T_{1\rho}$'s in polymers.

Introduction

Proton–proton dipolar interactions contain a wealth of information about the structure and dynamics of solids. Unfortunately, this information is seldom decipherable in a direct ^{1}H NMR relaxation experiment because the very interactions of interest generate broad, featureless NMR lines. Schemes to remove the broadening directly have not been uniformly successful.

We are trying a different approach in which proton relaxation parameters are obtained by ^{13}C NMR. As one example, we have recently examined[1] proton $T_{1\rho}$'s as measured in magic-angle ^{13}C cross-polarization experiments in order to specify the spatial homogeneity of solid polymeric blends of polystyrene and poly(phenylene oxide). In simple terms, all the line-narrowing tricks are played on the carbons so that the information about spatially sensitive proton–proton spin diffusion contained in $T_{1\rho}$(H) is undisturbed.

The magic-angle spinning experiment we wish to describe here involves measuring separate proton T_2's (line widths) for chemically different protons in the solid state using ^{13}C NMR. Dipolar order along local proton dipolar fields is created by a Jeener–Broeckaert[2,3] (JB) phase-shifted pair of proton radio-frequency pulses. The order established by the two-pulse sequence as a function of the spacing t between the pulses is then immediately read by a carbon radio-frequency pulse whose width is small compared to the rotor period (Figure 1).

This carbon readout of the proton dipolar order is a cross-polarization transfer under transient conditions.[4] Each high-resolution carbon-resonance intensity (as a function of t) becomes a measure of the derivative of the free induction decay (and therefore line shape) of a particular class, or chemical type, of proton. Each such line shape, in turn, is a measure of the individual (or separated) local dipolar field experienced by that type of proton. The full experiment is designated "JBSLF", denoting a separated *proton–proton* local field experiment using a Jeener–Broeckaert pulse preparation of dipolar order. Values for the separated proton local fields can be used in expressions[5,6] which quantitatively assess spin–spin contributions to carbon rotating-frame relaxation rates.

Local Dipolar Order

The zero-quantum, or dipolar, order created by the second pulse of the JB sequence operating on a proton i is characterized[2,3] by an individual dipolar order parameter β_i defined as

$$\beta_i = \beta_0 \sin\theta \cos\theta \frac{H_0}{\gamma H_{\mathrm{L}i}{}^2} \frac{\mathrm{d}}{\mathrm{d}\tau} G_i(\tau) \qquad (1)$$

where β_0 is the equilibrium lattice inverse spin temperature, θ is the angle of the second JB pulse, $H_{\mathrm{L}i}$ is the local field for proton i, γ is the gyromagnetic ratio, and $G_i(\tau)$ is the free induction decay of proton i resulting from the first JB pulse.

Different β_i's can occur because of variations in static proton–proton coupling due either to differences in local proton density or orientation. Immediately following a closely spaced JB pulse pair, there has been no time for equilibration by spin diffusion. Thus the β_i's established at that time are not inverse temperatures in any thermodynamic sense but rather measures of local dipolar fields.[7] The β_i's generated depend on the evolution following the 90° pulse as described by the derivative of $G_i(\tau)$. That is, dipolar order is optimized if the second JB pulse occurs at the maximum rate of change of the free induction decay following the first pulse. If all the protons in the sample are strongly coupled, spin diffusion in a time T_2 will result in a single value for β_i. This value is given by eq 1 with the subscript i suppressed. In this case, H_{L} and $G(\tau)$ represent the usual powder averages for the homogeneous proton line width of a polycrystalline or amorphous solid sample.

Since the second JB pulse is 45° (rather than 90°), *hetero*nuclear dipolar contributions to average local fields are deemphasized. The local fields arise predominantly from dipolar interactions between nearby protons. The JB sequence also generates higher quantum order[7,8] whose evolution will not concern us here.

Transient Cross-Polarization Transfer

The transfer of dipolar order among the protons to rotating-frame Zeeman order in the carbon spin system has been discussed before.[4] In particular

$$M_{\mathrm{S}}(\tau)/M_{\mathrm{S,eq}} = k \sin^2\theta\, M_2{}^{\mathrm{IS}} \int_0^{\tau} \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \cos(\omega_{\mathrm{eff,S}} t_2) C_{\mathrm{z}}(t_2) \qquad (2)$$

where $M_{\mathrm{S}}(\tau)$ is the carbon magnetization, $M_{\mathrm{S,eq}}$ is the carbon equilibrium magnetization in a cross polarization with no dissipative processes, $\theta = \tan^{-1}(\omega_{1\mathrm{S}}/\omega_{\mathrm{eff,S}})$, $M_2{}^{\mathrm{IS}}$ is the heteronuclear Van Vleck second moment, $\omega_{\mathrm{eff,S}} = \gamma H_{\mathrm{eff}}/2\pi = (\gamma/2\pi)[H_{1\mathrm{S}}{}^2 + (H_{\mathrm{L}}{}^{\mathrm{IS}})^2]^{1/2}$, $H_{1\mathrm{S}}$ is the applied carbon radio-frequency field $[H_1(\mathrm{C})]$, $H_{\mathrm{L}}{}^{\mathrm{IS}}$ is the local field experienced by the carbons due to dipolar coupling to protons, $C_{\mathrm{z}}(t)$ is the dipolar fluctuation autocorrelation function for protons under a condition of zero-quantum coherence, and k is a constant related to the relative heat capacities of proton (I) and carbon (S) spin systems.

The autocorrelation function, $C_{\mathrm{z}}(t)$, describes proton–proton spin–spin fluctuations and is analogous to a free induction decay. For short times, then, before $C_{\mathrm{z}}(t)$ has decayed, there is substantial overlap between cos $(\omega_{\mathrm{eff,S}} t)$

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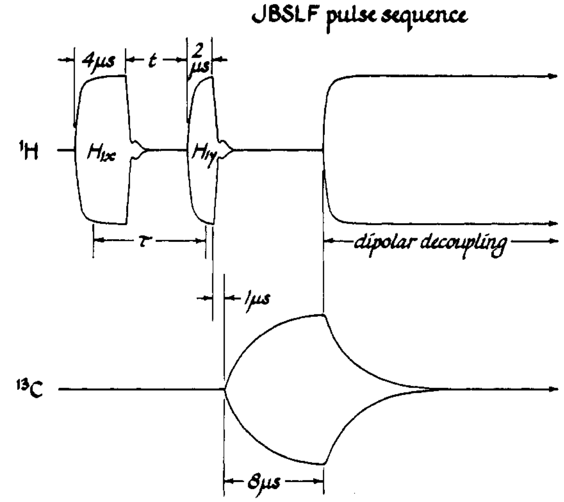

Figure 1. Pulse sequence for the ^{1}H–^{13}C Jeener–Broeckaert separated local field experiment. Approximate pulse shapes are represented schematically. No attempt was made to shape the carbon pulse. Transient proton–carbon cross-polarization transfer will occur even for rectangular carbon pulses.

and $C_z(t)$. This overlap produces a sharp rise, or transient step, in $M_S(\tau)$, which, for large H_{1S}, is proportional to M_2^{IS}/H_{1S}^2, or $(H_L^{IS})^2/H_{1S}^2$.

With increasing time, $M_S(\tau)$ shows oscillatory behavior with a period determined by $\omega_{\mathrm{eff,S}}$. However, these oscillations are not seen in ordinary polycrystalline materials because of phase incoherence introduced by different $C_z(t)$'s for different orientations. For most solid organic polymers, the transient is over in 20 μs or so.[6] The duration of the transient and its dependence on M_2^{IS} are the same as for the transient transfer from spin-locked carbon magnetization to disordered protons immediately following the turn off of the proton H_1 in a carbon $T_{1\rho}$ experiment.[6] For longer times, $M_S(\tau)$ increases monotonically with τ, but at a much slower rate than during transient. This slower rate is determined by the Fourier component of $C_z(t)$ at $\omega_{\mathrm{eff,S}}$ (eq 2) and decreases with increasing H_{1S}. The time constant for the slow process is sometimes called T_{IS}(ADRF).[4-6]

The idea of the JBSLF experiment is to monitor the order stored by a JB pulse sequence in individual local proton dipolar fields by a fast (on a time scale determined by proton T_2's) transient cross-polarization transfer before averaging by proton–proton spin diffusion. A transient cross-polarization transfer, or carbon readout of the dipolar order, does involve some averaging, however. This averaging occurs by chemical type. That is, we measure an average local dipolar field for the protons of the aromatic ring of polystyrene, for example, by monitoring the intensity of the transient aromatic-carbon resonance as a function of the separation of the JB pulses. This average local field will differ from that of the aliphatic protons as measured by the intensity of the aliphatic-carbon resonance. The carbon readout performs an effective spatial average over all aromatic protons and over all aliphatic protons, even though physically complete spin diffusion within the two types of protons has not taken place. We will discuss later the question of whether this averaging by a short carbon readout pulse leads to faithful representations of all the interactions involved.

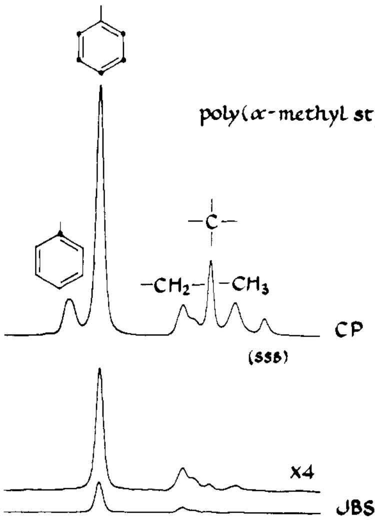

Figure 2. Matched spin-lock cross-polarization (top) and Jeener–Broeckaert separated local field (bottom) ^{13}C NMR spectra of a poly(α-methylstyrene) powder spinning at the magic angle at 2 kHz.

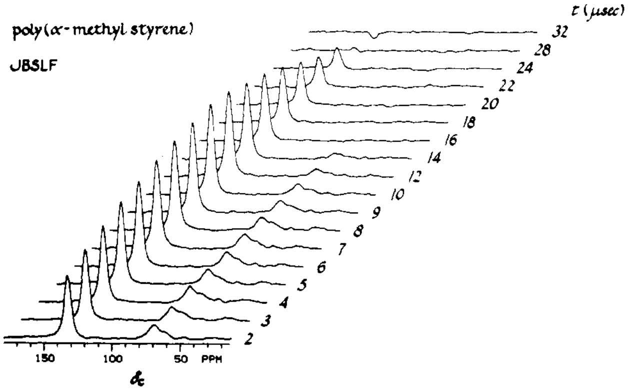

Figure 3. Jeener–Broeckaert separated local field ^{13}C NMR spectra of a poly(α-methylstyrene) powder spinning at the magic angle at 2 kHz as a function of the nominal time separation between the two phase-shifted proton radio-frequency pulses.

JBSLF Experiments on Poly(α-methylstyrene)

The results of 15.1-MHz ^{13}C cross-polarization (CP) and JBSLF experiments performed on poly(α-methylstyrene) are illustrated in Figure 2. The CP experiment employed matched spin-lock transfers of 1 ms with H_1's of 60 kHz and magic-angle spinning at 2 kHz. (Details of the cross-polarization and spinning procedures and of polymer sample preparations have been presented earlier.[6]) The JBSLF experiment employed a proton 4-μs 90° pulse separated from the 2-μs 45° pulse by 6 μs, together with a carbon readout pulse of 8 μs. Only protonated carbons give rise to any significant intensity in the JBSLF experiment, and even these lines are weak compared to CP intensities. The methyl-carbon intensity is weak relative to the other protonated carbon lines because internal rotation of the methyl group reduces static CH coupling and so the efficiency of the cross-polarization transfer. The methylene-carbon resonance shows the presence of a broad distribution of isotropic shifts.

The JBSLF intensities for poly(α-methylstyrene) as a function of t for a fixed 8-μs carbon readout pulse are shown in Figure 3. Both aromatic- and methylene-carbon intensities first increase with increasing t and then decrease, each with its own rate. Relative intensities (peak heights) as a function of τ, the effective pulse spacing (taking into account the nonrectangular shapes of the JB pulses), are shown as semilog plots in Figure 4a,b. The exact value of τ is uncertain. For pulse shapes as shown in Figure 1, we have chosen $\tau = t + 4$ μs. The curves in Figure 4 were calculated from the derivatives of Gaussians

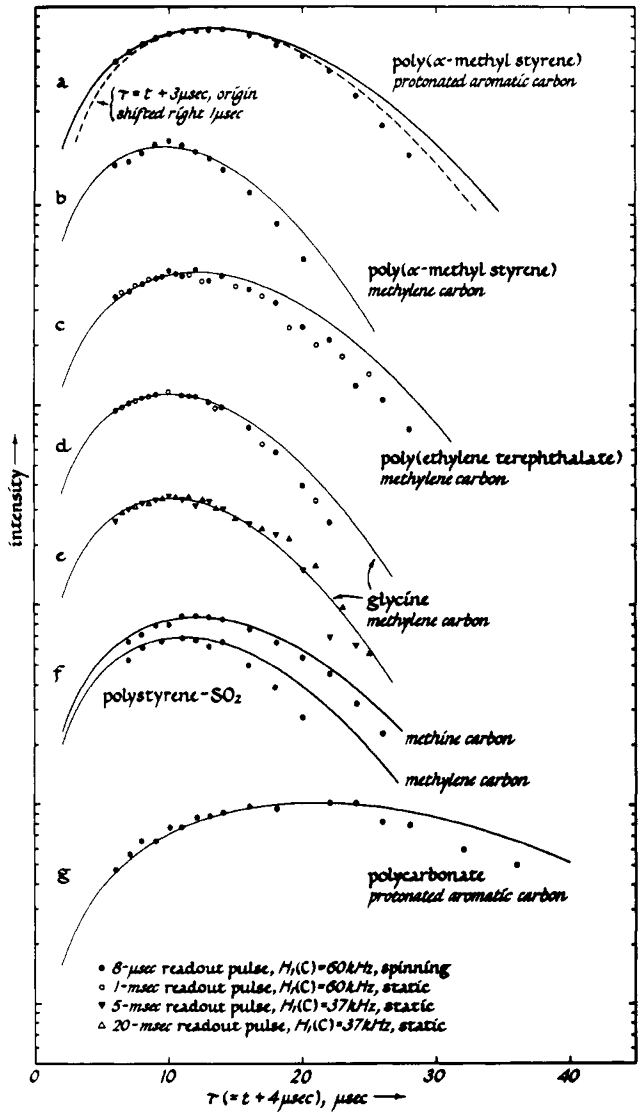

Figure 4. Jeener–Broeckaert separated local field ^{13}C NMR intensities as a function of the effective time separation between the phase-shifted proton radio-frequency pulses. Pulses with shapes as illustrated in Figure 1 were used with H_1's = 60 kHz, except for the experiment of plot 4e, where H_1(C) was 37 kHz. The solid lines are calculated derivatives of Gaussians whose maxima have been matched to the data. Except for one of the plots [dashed, for the aromatic carbon of poly(α-methylstyrene)], the effective time separation between pulses equals the nominal time pulse 4 μs. For the dotted line of plot 4a, the effective time is the nominal time plus 3 μs, and zero time has been shifted 1 μs.

whose widths were determined by the relative maxima in the JBSLF intensities. A choice of $\tau = t + 3$ μs for the aromatic-carbon line of poly(α-methylstyrene) fits the observed intensities a little better for long t, but worse for short t (Figure 4a, dashed line; zero time shifted 1 μs). We feel it may be more important to match the data for short t since information about individual local dipolar fields is only available for short t and since proton free induction decays often appear to decay at long times somewhat faster than Gaussians. A choice of $\tau = t + 3.5$ μs would give an acceptable fit to the data.

Because the Fourier transform of a Gaussian line shape is Gaussian, from JBSLF carbon intensities we obtain separated Gaussian line shapes for the aromatic and methylene protons of poly(α-methylstyrene), and find separated local fields of 7.1 and 9.7 kHZ, respectively. These values can be determined directly from the maxima of the JBSLF plots since, at the maximum,[3] $H_L = 1/(2\pi 3^{1/2}\tau_{max})$.

Line Shape Distortions

The effective duration of the JBSLF experiment on poly(α-methylstyrene) is just the length of the carbon readout pulse (together with any delay time between the 45° pulse and the start of the carbon readout pulse), or about 9 μs in our experiments. Since the rotation period of the rotor under 2-kHz magic-angle spinning is 500 μs, the JBSLF experiment can be considered executed on a static sample. Spinning only provides the convenience of resolving separate signals from chemically different carbons during the data collection period.

The problem arises that the short carbon readout pulse may produce distorted information since both M_2^{IS} and the proton dipolar fluctuation autocorrelation function are orientation dependent.[4] Hence some parts of an amorphous or polycrystalline sample may be underrepresented in a short contact time spectrum, if a strong I–S interaction tends to ignore a weak I–I local field.

To test how serious this distortion is, we performed JBSLF experiments on two samples, amorphous poly(ethylene terephthalate)[6] and polycrystalline glycine powder, using carbon readout pulses which varied from 6 μs to 1 ms, H_{1S}'s, or H_1(C)'s, of 60 kHz, and static (nonspinning) conditions. The nonspinning condition is a necessity with long carbon readout pulses since dipolar order quickly disappears in a sample spinning at the magic angle.[9] Both poly(ethylene terephthalate) and glycine have reasonably well-resolved methylene-carbon resonances even without magic-angle spinning. The 1-ms readout pulse gives time for a complete transient carbon polarization to form, while a 6–8-μs readout pulse does not. (For both samples, the steady-state cross-polarization time constant is at least 100 ms at these radio-frequency fields[10] so only a transient carbon signal develops.)

As shown in Figure 4c,d, the same proton line shape is observed in the JBSLF experiment with either long (open circles) or short (closed circles) 60-kHz carbon readout pulses. Thus, distortion resulting from using only a part of the transient carbon polarization does not occur. Even though a full 1-ms transfer time is used, the bulk of the transient transfer is complete in 10–20 μs. Thus, a 1-ms JBSLF determination of this methylene-proton local field for poly(ethylene terephthalate) is not affected by relatively slow spin diffusion between methylene and aromatic protons. Figure 4e shows the glycine methylene-proton line shape from a nonspinning JBSLF experiment with 5- and 20-ms readout pulses and an H_1(C) of 37 kHz. Under these conditions, a substantial steady-state carbon magnetization is generated, even for orientations of the CH internuclear vector associated with relatively weaker static dipolar coupling.[5] (The average steady-state cross-polarization time constant is about 10 ms). Again the same proton line shape is observed, although the match between calculated and observed values for longer JB pulse spacing is somewhat better.

The calculated proton local field for an isolated CH_2 fragment is 8.2 kHz.[11] The glycine proton local field obtained from Figure 4c is 9.2 kHz. Using an effective pulse spacing $\tau = t + 3$ μs (rather than the +4 μs of Figure 4c) produces a value of 10.1 kHz. From direct proton measurements using a dipolar echo technique we obtain a value for the local field of 10.0 kHz, while a value of 10.4 kHz has been observed[12] with a single 90° proton pulse and a fast-recovery spectrometer. Thus, the JBSLF measurements on glycine yield local fields in reasonable agreement with both theoretical estimates and direct proton mea-

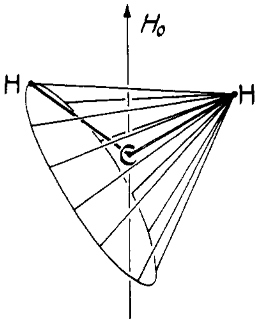

Figure 5. Variation of the orientation of the HH internuclear vector relative to the static field H_0 for a fixed orientation of one of the CH internuclear vectors of a methylene group.

surements. The methylene-proton local field for glassy poly(ethylene terephthalate) is about 7.6 kHz, substantially less than that of glycine.

Apparently, on the basis of the results for poly(ethylene terephthalate) and glycine, the fact that the methylene-carbon CH internuclear vector has a different orientation from that of the HH internuclear vector is sufficient to ensure that any particular CH direction samples most HH local fields in powder average, at least to first order (Figure 5). Some distortion does appear to occur in the tail of a short carbon pulse JBSLF plot, corresponding to a misrepresentation of weaker local dipolar fields, or the narrower contributions to the overall proton line shape. Naturally, one can imagine situations in which, because of orientation or because of dynamic heterogeneity, a short carbon readout pulse in a JBSLF experiment could produce a line shape in which weaker H-H contributions tend to be missing. The JBSLF line shapes should always be interpreted with the knowledge that significant distortion may exist if correlations between M_2^{IS} and M_2^{II} stronger than those typical of the systems of Figure 4 are present.

JBSLF Experiments on Poly(styrene sulfone) and Polycarbonate

The JBSLF plots of Figure 4 illustrate the fact that different proton local fields (of 7.6 and 8.3 kHz, respectively, determined from the local maxima) are observed for the methine and methylene protons of the completely alternating copolymer, poly(styrene sulfone), $-(\mathrm{CH_2CHPhSO_2})_x-$. This is true because the time required for the transient transfer between protons and carbons is short enough that complete averaging by spin diffusion among the protons does not obscure all differences in the local fields of the relatively tightly coupled protons. In other words, the readout time is less than the proton T_2's of interest. However, this condition is only marginally satisfied for the methine and methylene protons of poly(styrene sulfone), so the observed difference in local fields of 0.7 kHz should be considered a minimum value.

The last plot in Figure 4 (bottom) illustrates the extremely small local fields of the aromatic proton of polycarbonate (about 4 kHz), which are the direct result of large-amplitude, high-frequency segmental reorientations of the main chain of the polymer, a phenomenon which also manifests itself in a variety of $T_{1\rho}(\mathrm{C})$ experiments.[6,13]

Use of Proton H_{L}'s

A prime motivation for obtaining separated local proton dipolar fields is for the interpretation of carbon $T_{1\rho}$ experiments on polymers. A quantitative description of $T_{1\rho}(\mathrm{C})$ involves an estimate of the competition between two relaxation pathways.[5,6,13] Spin–lattice relaxation, which predominates for most glassy polymers at room temperature with H_1's of 30 kHz or more, arises from fluctuating dipolar fields associated with molecular rotations of carbon–proton internuclear vectors. Spin–spin relaxation, which is important for crystalline polymers, arises from the Fourier component of the proton–proton dipolar fluctuation spectrum at the carbon rotating-frame frequency. This spectrum depends upon the strength of the local proton dipolar field. Thus, using the JBSLF experiment, one can distinguish the fluctuation spectrum of the methine protons of poly(styrene sulfone), for example, from that of the methylene protons, and the fluctuation spectrum of the methyl protons of polycarbonate can be distinguished from that of the aromatic protons. Values for these individual proton local fields can then be used in expressions[5,6] for $T_{1\rho}(\mathrm{C})$ and $T_{\mathrm{IS}}(\mathrm{ADRF})$, which ultimately lead to unambiguous separations of spin–spin from spin–lattice contributions to individual $T_{1\rho}(\mathrm{C})$'s, even in complicated situations in which contributions from both relaxation pathways are important.

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