A "Magic-Angle" Sample-Spinning Nuclear Magnetic Resonance Spectroscopic Study of Interference Effects in the Nuclear Spin Relaxation of Polymers*

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The proton-coupled, carbon-13 "magic-angle" sample-spinning nuclear magnetic resonance spin-lattice relaxation behavior of poly(*cis*-isoprene) and poly(*cis*-butadiene) as a function of temperature is reported. Analysis of the relaxation behavior of the methine carbons reveals strong temporal correlations between the ¹³C-H dipolar and ¹³C anisotropic chemical shielding interactions. Equations are presented which enable the interpretation of these interferences for non-axially symmetric shielding tensors, subject to cylindrically symmetric reorientation. In the context of these expressions, the results indicate that the methine moiety in each of the two polymers executes relatively rapid, isotropic motions, on the time scale of the carbon-13 Larmor frequency. It is also shown that in certain polymeric systems, the sign of the interference term may change with frequency. This intriguing property provides additional insight into the relative reorientational anisotropies of the low- and high-frequency motions, and the specific case of the spin-lattice relaxation and differential line broadening of the methine carbons in poly(*cis*-isoprene) and poly(*trans*isoprene) is considered in detail. (2) 1992 Academic Press, Inc.

Recently, nuclear magnetic resonance spectroscopy has experienced an explosive growth of activity in the area of relaxation-induced multispin order. Particularly important are those studies concerned with intramolecular dipolar-chemical shielding anisotropy (DxCSA) interferences, which transform variants of even-spin order into odd-spin order, and vice versa. There are numerous reasons for the growing interest in DxCSA interferences, the most obvious being: (i) the proliferation of high-field NMR spectrometers, which render anisotropic shielding and dipolar couplings com-

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petitive for common nuclei (e.g., ¹H, ¹³C), and (ii) the intimate relationship between relaxation-induced multispin order and various 2D NMR methodologies, which evolve via states with similar alignments.

Contrary to popular belief, the literature involving DxCSA interference is quite extensive. The basic source of interference was first considered by McConnell (1) some 35 years ago, in the context of electron spin resonance, and NMR applications of DxCSA interference can be traced back to the mid-1960s (2-4). Other exploratory investigations in this field include those discussed in Refs. (5-13). The introduction of operator descriptions of the relaxation processes represented a critical milestone, with new insights into the significance, symmetry, and unifying properties of DxCSA interference and cross correlation following from these developments. Although these points are implicit in Pyper's early work (14), subsequent studies made them more explicit (15-18). These NMR works are all concerned with spin systems, of varying complexity, composed of spin- $\frac{1}{2}$ nuclei, but analogous features for systems containing higher-spin nuclei are also possible (19-21).

Prior to 1980, experimental observations of DxCSA interference were rare, and frequently, relaxation experiments were performed in a manner which suppressed their manifestation. However, NMR methodologies have undergone radical change in the last 15 years, and observation of such effects has now become commonplace (22). Indeed, in our studies, we have found that DxCSA interference phenomena are ubiquitous at high fields (11.7 T) in proton-coupled ¹³C magic (or near magic)-angle sample-spinning (MAS) NMR spectra of biological lipids, membranes, liquid crystals, and highly mobile polymers (23).

As is well known, macromolecular systems, such as elastomers and lyotropic and thermotropic liquid crystals, display a complex variety of motional and orientational (ordering) effects. Needless to say, considerable efforts have been expended in the characterization of such materials, and NMR has been one of the more useful physical techniques employed (24, 25). With this in mind, a detailed NMR spin relaxation study of several elastomers under MAS has been undertaken, in the hope of ascertaining what detail can be extracted from an analysis of relaxation-induced two-spin order.

EXPERIMENTAL

Carbon-13 MAS NMR spectra were obtained on a "homebuilt" Fourier-transform NMR spectrometer, which operates at 125 MHz for ¹³C. This instrument utilizes an Oxford Instruments (Osney Mead, UK) 11.7 T, 2 in. bore superconducting solenoid magnet, a Nicolet (Madison, Wisconsin) Model 1280 computer system, and a variety of digital and radiofrequency electronics. The MAS NMR sample probe was from Doty Scientific (Columbia, South Carolina). Poly(*cis*-butadiene), poly(*cis*-isoprene), and poly(*trans*-isoprene) were from Aldrich (Milwaukee, Wisconsin). The longitudinal relaxation measurements were performed under magic-angle spinning at 4.0 kHz. Inversion of the ¹³C magnetization was accomplished with composite pulses (26). In all cases, the inversion efficiency was greater than 95%. To obtain adequate signal-tonoise ratios, between 40 and 200 scans were obtained for each different τ value. The recycle delays were at least 15 times $T_1(1/\rho_C)$ of the methine carbons. Temperature was controlled to within $\pm 2^{\circ}$ C. Chemical shifts are all referenced with respect to an external sample of tetramethylsilane, with low-field, high-frequency, paramagnetic, or deshielded values designated as positive (IUPAC δ scale).

THEORETICAL ASPECTS

The relaxation characteristics of the longitudinal magnetizations for a two-spin- $\frac{1}{2}$ system subject to dipolar and anisotropic chemical shielding interactions can be written in the following product-operator (magnetization-mode) form (27-29):

$$(-d/dt) \begin{bmatrix} \langle S_z(t) \rangle \\ \langle I_z(t) \rangle \\ \langle 2I_z S_z(t) \rangle \end{bmatrix} = \begin{bmatrix} \rho_{\rm C} & \sigma & -4K_{\rm C}(\omega_{\rm C}) \\ \sigma & \rho_{\rm H} & -4K_{\rm H}(\omega_{\rm H}) \\ -4K_{\rm C}(\omega_{\rm C}) & -4K_{\rm H}(\omega_{\rm H}) & \rho_{\rm CH} \end{bmatrix} \begin{bmatrix} \langle S_z(t) \rangle - S_z^0 \\ \langle I_z(t) \rangle - I_z^0 \\ \langle 2I_z S_z(t) \rangle \end{bmatrix}.$$
 [1]

Spin S denotes ¹³C whereas spin I is associated with the proton, and $I_z^0(S_z^0)$ signifies a thermalized value. The various rate constants are identified as

$$\rho_n = \frac{1}{3} J_{\rm D}(\omega_{\rm H} - \omega_{\rm C}) + J_{\rm D}(\omega_n) + 2J_{\rm D}(\omega_{\rm H} + \omega_{\rm C}) + 4J_{\rm CSA}^n(\omega_n)$$
$$\sigma = 2J_{\rm D}(\omega_{\rm H} + \omega_{\rm C}) - \frac{1}{3}J_{\rm D}(\omega_{\rm H} - \omega_{\rm C})$$
$$\rho_{\rm CH} = J_{\rm D}(\omega_{\rm C}) + J_{\rm D}(\omega_{\rm H}) + 4J_{\rm CSA}^{\rm C}(\omega_{\rm C}) + 4J_{\rm CSA}^{\rm H}(\omega_{\rm H}).$$

The cross-correlation spectral density, $K_n(\omega_n)$, and the autocorrelation spectral densities, J_D and J_{CSA}^n , are defined as

$$\begin{split} K_n(\omega) &= (1/20)(\xi_{\text{CSA}}^n \xi_{\text{D}})(3\cos^2\theta - 1 - \eta\sin^2\theta\cos 2\gamma)\tau_c/[1 + (\omega_n\tau_c)^2] \\ J_{\text{D}}(\omega) &= (3/10)\xi_{\text{D}}^2\tau_c/[1 + (\omega\tau_c)^2] \\ J_{\text{CSA}}^n(\omega) &= (1/30)(\xi_{\text{CSA}}^n)^2(1 + \eta^2/3)\tau_c/[1 + (\omega\tau_c)^2], \end{split}$$

where $\xi_{CSA}^n = \omega_n \Delta \sigma$, and $\xi_D = \gamma_C \gamma_H \hbar / r_{CH}^3$. The chemical shielding anisotropy, $\Delta \sigma$, and its asymmetry parameter, η , are defined as $\sigma_{zz} - (1/2)(\sigma_{yy} + \sigma_{xx})$ and $3(\sigma_{yy} - \sigma_{xx})/2\Delta\sigma$, respectively.

These identifications are valid for isotropic motions. The angular factors in the cross-correlation term position the dipolar vector in the CSA principal-axis system. More general expressions for these terms are presented in the Appendix.

Similarly, the relaxation of single-quantum (1Q) transverse magnetization is determined by the expression

$$(-d/dt) \begin{bmatrix} \langle I_{+}(t) \rangle \\ \langle 2I_{+}S_{z}(t) \rangle \\ \langle S_{+}(t) \rangle \\ \langle 2I_{z}S_{+}(t) \rangle \end{bmatrix} = \begin{bmatrix} \rho_{H}^{\prime} & X_{H} & 0 \\ X_{H} & \rho_{H}^{\prime} & 0 \\ 0 & X_{C} & \rho_{C}^{\prime} \end{bmatrix} \begin{bmatrix} \langle I_{+}(t) \rangle \\ \langle 2I_{+}S_{z}(t) \rangle \\ \langle S_{+}(t) \rangle \\ \langle 2I_{z}S_{+}(t) \rangle \end{bmatrix},$$
[2]

where $\rho'_n = \frac{2}{3}J_D(0) + \frac{1}{2}J_D(\omega_C) + \frac{1}{2}J_D(\omega_H) + \frac{1}{6}J_D(\omega_H - \omega_C) + J_D(\omega_C + \omega_H) + \frac{8}{3}J_{CSA}^n(0) + 2J_{CSA}^c(\omega_C) + 2J_{CSA}^H(\omega_H) = \frac{2}{3}[J_D(0) + 4J_{CSA}^n(0)] + \frac{1}{4}(\rho_C + \rho_H + \rho_{CH}),$ and $X_n = -\frac{8}{3}K_n(0) - 2K_n(\omega_n)$. Equation [2] is applicable if motional narrowing obtains and the doublets are well resolved. If the scalar coupling constant is positive, then the high-field component is expected to relax more rapidly than the low-field component, if X_n is positive. The relaxation properties of the zero- and double-quantum coherences are also of interest (30), but were not pursued in the current study.

RESULTS AND DISCUSSION

We show in Fig. 1 a typical series of carbon-13 inversion-recovery spectra for a poly(*cis*-isoprene). Using raw data of this type, the perturbation response of each member of the methine doublet is readily deduced. As clearly demonstrated in Fig. 2, a linear response occurs during the first 50–80 ms, which renders the initial rate approximation appropriate. This greatly simplifies application of Eq. [1]. For example, assuming complete nonselective inversion of the ¹³C doublet, it follows that

$$(d/dt)\langle S_z(t \to 0)\rangle/\langle S_z(eq)\rangle = 2\rho_{\rm C}$$
[3]

and

$$(d/dt)\langle 2I_z S_z(t \to 0)\rangle/\langle S_z(\text{eq})\rangle = -8K_{\text{C}}(\omega_{\text{C}}).$$
[4]

For a positive C-H scalar coupling constant, the high-field member of the doublet is associated with the composite operator $S_z^+ = (S_z + 2I_zS_z)/2$, whereas the low-field component is associated with the operator $S_z^- = (S_z - 2I_zS_z)/2$. Hence, the initial



FIG. 1. Proton-coupled carbon-13 MAS NMR inversion-recovery spectra for the methine C–H spin grouping in poly(*cis*-isoprene). Spectra were obtained at 40° C and at an operating frequency of 125.7 MHz (11.7 T).



FIG. 2. Plot of the amplitude of the high (A_+) - and low (A_-) -field components of the methine doublet shown in Fig. 1, as a function of recovery time (τ) subsequent to the inversion pulse. Each component can be fitted to an expression of the form $A_{\pm}(\tau) = A_{\pm}(0)[1 - \tau/(T_1)_{\pm}]$. Since the high-field component is slightly broader than the low-field component, $|A_-(0)| > |A_+(0)|$.

rate approximation identifies $(1/T_1)_+$, the apparent $1/T_1$ of the high-field component, with $\rho_C - 4K_C(\omega_C)$ and $(1/T_1)_-$ with $\rho_C + 4K_C(\omega_C)$. Obviously, in the absence of interference, both components respond to perturbations in an identical manner. We show these apparent T_1 values as determined from the initial relaxation rates in Table 1. The values of ρ_C and $-4K_C(\omega_C)$ are also included, as are values of the carbon-13 $T_1(1/\rho_C)$ and the ratio, $-\rho_C/4K_C(\omega_C)$. Although the values for $(T_1)_+$ and $(T_1)_-$ (and ρ_C) are highly reproducible, and presumably accurate (±3-4% error), the uncertainty in $K_C(\omega_C)$ [and $-\rho_C/4K_C(\omega_C)$] is not less than 10-15%.

Relaxation and Cross-Correlation Spectral-Density Results for Poly(cis-butadiene) and Poly(cis-isoprene)						
$T(^{\circ}C)^{a}$	$T_{1+}(s)^{b}$	$T_{1-}(\mathbf{s})^b$	$\rho_{\rm C}({\rm s}^{-1})$	$1/\rho_{\rm C}({\rm s})$	$-4K_{\rm C}(\omega_{\rm C})({\rm s}^{-1})$	$-\rho_{\rm C}/4K_{\rm C}(\omega_{\rm C})$
			Poly(cis-bu	itadiene)		
-15	0.27	0.50	2.85 ± 0.15	0.35	0.82	3.4 ± 0.3
20	0.56 ^c	0.88 ^c	1.46 ± 0.07	0.69	0.32	4.6 ± 0.6
40	0.79 ^{<i>d</i>}	1.25 ^d	1.03 ± 0.05	0.97	0.23	4.5 ± 0.7
			Poly(cis-iso	oprene) ^e		
20	0.21	0.46	3.45 ± 0.2	0.29	1.31	2.6 ± 0.2
40	0.25	0.48	3.05 ± 0.15	0.32	0.98	3.1 ± 0.3
60	0.37	0.65	2.12 ± 0.1	0.47	0.58	3.6 ± 0.5

TABLE I

^a ±2°C.

^b T_{1+} and T_{1-} are the T_1 values determined from the initial rate behavior of the upfield and downfield components, respectively. Errors associated with these measurements are $\pm 3\%$.

^{c-e} Average of six, five, and two data sets, respectively (at each temperature).

Rationalization of these macroscopic rate constants can be made only in the context of a plausible microdynamical framework. Without loss of generality, motions will be modeled as diffusive rotations, rather than as the jump-like motions commonly found in side-chain groups in more rigid polymers. It is assumed that modulation of the dipolar and anisotropic shielding interactions is characterized by two unique motional constants: one (D_{\parallel}) indicative of motions about the C=C axis and a second (D_{\perp}) for motions of this axis.

In this symmetric-top approximation, only the angle between the C—H vector and the C==C linkage is needed in order to position the dipolar interaction in the diffusion frame. Similarly, the relative orientation of the anisotropic shielding tensor requires two angles for placement in the diffusion frame. Two additional angles are necessary in order to specify the relative orientation of the dipolar and shielding anisotropy, which then enables us to determine the cross-correlation spectral density, $K_{\rm C}(\omega_{\rm C})$. Unstrained olefinic linkages have been investigated thoroughly (31, 32), and it is well documented that the most-shielded component (σ_{xx}) of the shielding tensor is perpendicular to the sp^2 plane, whereas the least-shielded component (σ_{zz}) lies in this plane and is perpendicular to the double bond. The third element, σ_{yy} , is parallel to the double-bond axis. It is assumed that the antisymmetric components of the shielding tensor are negligible.

For the interaction frames defined above and displayed in Fig. 3, the appropriate angular terms appearing in Eqs. [A1] and [A2] are $\cos \beta_D = \frac{1}{2}$, $\cos \beta_{CSA} = 0$, $\cos 2\alpha_{CSA} = -1$, and $\cos(2\gamma_D - 2\gamma_{CSA}) = 1$. Since the dipolar interaction is axially symmetric, the third Euler angle specifying the dipolar interaction, α_D , is arbitrary. With these identifications, Eqs. [A1] and [A2] yield

$$J_{CSA}^{C} = (1/360)(\xi_{CSA}^{C})^{2} \\ \times \{3(1-\eta)^{2}\tau_{0}/[1+(\omega\tau_{0})^{2}] + (3+\eta)^{2}\tau_{2}/[1+(\omega\tau_{2})^{2}]\}$$
[5]

 $K_{\rm C}(\omega) = (1/160)\xi_{\rm CSA}^{\rm C}\xi_{\rm D}$

$$\times \{ (1-\eta)\tau_0 / [1+(\omega\tau_0)^2] + 3(3+\eta)\tau_2 / [1+(\omega\tau_2)^2] \}.$$
 [6]

In this same motional/geometrical limit, the more familiar dipolar autocorrelation spectral density is defined as (33)

$$J_{\rm D}(\omega) = (3/640)\xi_{\rm D}^2 \times \{\tau_0/[1+(\omega\tau_0)^2] + 36\tau_1/[1+(\omega\tau_1)^2] + 27\tau_2/[1+(\omega\tau_2)^2]\}.$$
 [7]

In these expressions, $1/\tau_n = 6D_{\perp} + n^2(D_{\parallel} - D_{\perp})$. The values of the interaction constants are $\xi_D = (1.45 \pm 0.12) \times 10^5 \text{ s}^{-1}$, $\xi_{CSA} = (-1.27 \pm 0.02) \times 10^5 \text{ s}^{-1}$, and $\eta = 0.8 \pm 0.1$. It is assumed that $r_{CH} = 1.095 \pm 0.015$ Å, and $\Delta \sigma = -162 \pm 2$ ppm. [For poly(*cis*-butadiene) (34), $\Delta \sigma = -161$ ppm and $\eta = 0.75$; for *cis*-2-butene (31), $\Delta \sigma = -162$ ppm and $\eta = 0.90$; and for *trans*-2-butene (31), $\Delta \sigma = -161$ ppm and $\eta = 0.71$.]

Utilizing the microscopic model summarized by Eqs. [5]–[7], it is straightforward to determine ρ_C and $K_C(\omega_C)$ as a function of the pertinent motional parameters. Results are given in Figs. 4 and 5, which plot $\rho_C \equiv (1/T_1) = (1/2)[(1/T_1)_+ + (1/T_1)_-]$ and $-\rho_C/4K_C(\omega_C)$ as a function of the axial correlation time ($\tau_0 = 1/6D_\perp$) for



FIG. 3. Orientation of the 13 C methine shielding tensor, and the diffusion tensor, relative to the molecular plane.

selected values of motional anisotropy $(D_{\parallel}/D_{\perp} = (1/2)[3(\tau_0/\tau_2) - 1])$. Unfortunately, the three-dimensional contour surfaces of $\rho_C(\tau_i)$ and $K_C(\omega, \tau_i)$ do not overlap (intersect) at sharp angles, and attempts to solve for the correlation times and motional anisotropy by a Newton–Raphson method were unsuccessful. [This may be understood in the context of Eqs. [5]–[7], where it may be seen that $J_D(\omega)$, $J_{CSA}^C(\omega)$, and $K_C(\omega)$ primarily sample the in-plane motion (τ_2). Although uncommon, similar dependencies between auto- and cross-correlation terms have been noted elsewhere (35).] Therefore,



FIG. 4. Plot of $\rho_C(1/T_1)$ as a function of $\omega_C \tau_0$ ($\tau_0^{-1} = 6D_{\perp}$) for axially symmetric reorientation. Curves a, b, c, d, and e correspond to D_{\parallel}/D_{\perp} values of 1, 3, 10, 100, and 1000, respectively. The dashed curve illustrates the limit when $D_{\parallel}/D_{\perp} \leq 1$. It is assumed that only dipolar and chemical shielding anisotropy interactions induce nuclear spin relaxation. Additional parameters used to construct these curves are defined in the text.



FIG. 5. Plot of $-\rho_C/4K_C(\omega_C)$ as a function of $\omega_C \tau_0$ ($\tau_0^{-1} = 6D_{\perp}$) for axially symmetric reorientation. Curves a, b, c, d, and e correspond to D_{\parallel}/D_{\perp} values of 1, 3, 10, 100, and 1000, respectively. The dashed curve illustrates the limit when $D_{\parallel}/D_{\perp} \ll 1$. It is assumed that only dipolar and chemical shielding anisotropy interactions induce nuclear spin relaxation. Additional parameters used to construct these curves are defined in the text.

the values of these motional parameters were determined by a visual fit of the experimental results given in Table 1 to the curves shown in Figs. 4 and 5. Given the uncertainties associated with these parameters, this approach is justified.

From this analysis, the following general features are worth noting: (i) Since differential relaxation is observed, proton-proton cross relaxation is relatively ineffective. Any additional mechanism that would efficiently relax the proton would add to the ρ_{CH} terms in Eqs. [1] and [2] and, hence, quench relaxation-induced two-spin order. (It is important to note here that the *initial* growth of two-spin order is *in*dependent of proton-proton cross relaxation.) (ii) For both polymers, the relatively large value of ρ_{C} indicates a dense spectrum of motions near the Larmor frequency. Since $(\partial/\partial T)\rho_{C} < 0$, these motions apparently lie on the fast motional side of a T_{1} minimum. (iii) For poly(*cis*-isoprene), the small value of $|\rho_{C}/4K_{C}(\omega_{C})|$ indicates that the motions are relatively isotropic $(D_{\parallel}/D_{\perp} \approx 1)$. (iv) For poly(*cis*-butadiene), the larger value of $|\rho_{C}/4K_{C}(\omega_{C})|$ implies a slightly greater degree of motional anisotropy: the value of D_{\parallel}/D_{\perp} increases from near unity at -15° C to near 2 at $+20^{\circ}$ C.

For both polymers, $(\partial/\partial T)[-\rho_C/4K_C(\omega_C)] > 0$. Thus, within the temperature range studied, it is apparent that ρ_C has not yet achieved an extreme-narrowed frequency (in)dependence. [Using the interaction constants defined previously, if extreme narrowing and isotropic motions are obtained, the limiting value of $-\rho_C/4K_C(\omega_C)$ is 4.5, whereas if $J(0) \ge J(\omega_C)$, the limiting value for $-\rho_C/4K_C(\omega_C)$ is 1.7.] Of course, the motions "observed" in any longitudinal relaxation study are seen through a relatively narrow window, and one must recall that ρ_C and $K_C(\omega_C)$ are most sensitive to those motions characterized by frequencies near ω_C . Furthermore, in this motional regime, it is doubtful that a single well-defined correlation time exists. This could be partially responsible for the lack of success of the Newton-Raphson method noted above. It may seem surprising that the relatively fast motions observed in this study can be explained with a motional model which does not explicitly include any order parameters to account for restrictions in the angular excursions of the olefinic moiety. However, this is quite consistent with the known behavior of these special rubbers, which behave much more like liquids than solids on the fast motional time scale. Other groups who have studied polyisoprene (36-38) and polybutadiene (36, 39, 40)have reached basically similar conclusions.

For some perspectives, it is useful to compare the results of this work with those of a previous study by Fuson and Grant (40) of relaxation-induced three-spin order within the ¹³CH₂ spin grouping in a poly(*cis*-butadiene). One of their most interesting observations was the suggestion that motions about the axis perpendicular to the CH₂ plane are slightly more rapid than motions about the orthogonal axis bisecting the HCH angle. Since the methylene and methine carbons are not rigidly fixed relative to each other, it might be argued that the local dynamics at these two neighboring sites are uncorrelated. However, multiple bond rotations are necessary in order to avoid kink formation, and it seems plausible that the anisotropy in the motional constants along mutual axes in the two different segments will be similar. Thus, it is not too surprising that the D_{\parallel}/D_{\perp} values derived from the measured ρ_C and K_C for the two elastomers at various temperatures are close to one. In fact, for poly(*cis*isoprene) [and poly(*cis*-butadiene) at lower temperatures], this ratio is somewhat less than one.

Finally, it would clearly be desirable to investigate the motional behavior of these polymers through different motional windows, and attempts were made to measure linewidth differentials and related multispin signatures. Rotor-synchronized Hahn echoes were used to measure transverse relaxation, and it was found that the linewidths and linewidth differentials were weakly dependent on the sample spinning speed. Unfortunately, measurements were not sufficiently accurate to yield reliable quantitative information.

We have, however, found one particularly interesting observation when comparing T_1 and T_2 (linewidth) results for cis and trans segments in polybutadienes and polyisoprenes. Specifically, we find in poly(*cis.trans*-butadiene), poly(*cis*-isoprene), and poly(*trans*-isoprene) that the high-field components of the methine doublets are broader than the low-field components in cis segments, but narrower than the low-field components in trans segments, implying that the T_2 of the high-field component is shorter for cis but longer for trans double bonds. However, in both cis and trans segments, the high-field component has the shorter T_1 value! In poly(*cis,trans*-butadiene), due to severe spectral overlaps, the T_1 differentials for the trans segments are more difficult to detect. Figure 6 shows typical MAS NMR spectra of poly(*cis*-isoprene) and poly(*trans*isoprene), at 11.7 T, with the unusual differential line-broadening effect noted above quite apparent. For the cis form, we obtain $(T_1)_+ = 0.21$ and $(T_1)_- = 0.46$ at 20°C (Table 1); for the trans material, $(T_1)_+ = 0.35$ s, and $(T_1)_- = 0.43$ s.

These observations can all be rationalized in the context of Eq. [2] with the aid of Fig. 7. Assuming that the linewidths in these systems are primarily determined by adiabatic terms, the natural linewidths of the high-field and low-field doublet components are $\frac{2}{3}[J_D(0) + 4J_{CSA}^c(0) - 4K_C(0)]$ and $\frac{2}{3}[J_D(0) + 4J_{CSA}^c(0) + 4K_C(0)]$, respectively. If motions about one axis, oriented in the sp^2 plane, and defining an



FIG. 6. Lineshape comparison between cis and trans methine carbons in (A) poly(*cis*-isoprene) and (B) poly(*trans*-isoprene). Both spectra recorded with \sim 4 kHz MAS at 125.7 MHz, at \sim 23°C.

angle, θ , with respect to the C-H bond axis, are relatively rapid compared to the reorientation of that axis, then the magnitudes of $J_D(0)$, $J_{CSA}^C(0)$, and $K_C(0)$ are strongly dependent on the angle θ and vary as shown in Fig. 7.



FIG. 7. Reduced auto- and cross-correlation spectral densities as a function of the angle, θ , between the C-H bond axis and the principal axis of a cylindrically symmetric diffusion tensor. The C-H bond axis is rotated 30° from the least-shielded component of the shift tensor (σ_{zz}). Hence, all relevant principal axes are coplanar. A value of $\eta = 0.75$ is assumed.

Note that when $90^{\circ} \leq \theta \leq 120^{\circ}$, $K_{\rm C}(0)/\xi_{\rm D}\xi_{\rm CSA}^{\rm C}$ is negative, and hence $K_{\rm C}(0)$ is positive. Here it is important to recognize that the signs of $K_{\rm C}(0)$ and $K_{\rm C}(\omega_{\rm C})$ are not necessarily the same. If extreme narrowing fails, it is apparent from Eqs. [1], [2], and [A2] that the multiplet component associated with the shortest T_2 may not correspond to the component identified with the shortest T_1 . Indeed, for intermediate frequencies, $K_{\rm C}(\omega)$ may vanish completely. Although related theoretical curiosities have been noted in the literature (41), our experimental results show, for the first time, that the sign of an interference may change, depending upon whether high-frequency or low-frequency motions are sampled. For the trans-olefinic segments, this observation suggests that the C-H vector is approximately perpendicular to an axis about which motion is relatively rapid. Furthermore, it is apparent that these slower motions are highly anisotropic.

CONCLUSIONS

Our results show that the spin-lattice relaxation rates of olefinic, methine carbons in polymeric species are characterized by substantial temporal cross correlations between the ¹³C-H dipolar and ¹³C chemical shielding anisotropy interactions. In the present application, the mutual orientation of the interfering interactions renders the auto- and cross-correlation terms strongly interdependent, which represses full exploitation. Nevertheless, it is evident that the magnitude and sign of the interferences can be explained only in the context of relatively isotropic motions of the methine carbons, on the time scale of ω_c^{-1} , in both poly(*cis*-isoprene) and poly(*cis*-butadiene). In addition, our results show for the first time that the sign of an interference may change, depending on the frequency (and type) of motional averaging being sampled, as exemplified by our results on the cis and trans polyisoprenes.

In more general applications, given the appropriate interaction constants, detection of the associated relaxation-induced two-spin order may be used to abstract precise and detailed motional information. The present MAS NMR work, which complements the study of relaxation-induced three-spin order (40, 42), provides a promising methodology for the investigation of motional heterogeneity in complex macromolecular and aggregated systems, such as polymers, liquid crystals, and lipid membrane systems.

APPENDIX: THE DIPOLAR-ANISOTROPIC CHEMICAL SHIELDING CROSS-CORRELATION SPECTRAL DENSITY

The autocorrelation spectral density for a non-axially symmetric shielding tensor has been derived by Stark *et al.* (43) for the planar rotor. Spiess (44) has described the more general case of an asymmetric rotor. These equations can be modified to yield the following expressions for a non-axially symmetric shielding tensor modulated by symmetric top-like diffusional reorientation,

$$J_{\rm CSA}(\omega) = \frac{1}{30} \xi_{\rm CSA}^2 \sum_{n=0}^2 c_n \{ \tau_n / [1 + (\omega \tau_n)^2] \}, \qquad [A1]$$

where $1/\tau_n = 6D_{\perp} + n^2(D_{||} - D_{\perp})$, and

$$c_{0} = (3\cos^{2}\beta - 1)^{2}/4 - (\eta/2)(3\cos^{2}\beta - 1)\sin^{2}\beta\cos 2\alpha + (\eta^{2}/4)\sin^{4}\beta\cos^{2}2\alpha$$

$$c_{1} = (3/4)\sin^{2}2\beta + (\eta/2)\sin^{2}2\beta\cos 2\alpha + (\eta^{2}/3)\sin^{2}\beta(1 - \cos^{2}2\alpha\sin^{2}\beta)$$

$$c_{2} = (3/4)\sin^{4}\beta - (\eta/2)\sin^{2}\beta\cos 2\alpha(\cos^{2}\beta + 1)$$

$$+ (\eta^{2}/3)(1 - \sin^{2}\beta + (1/4)\sin^{4}\beta\cos^{2}2\alpha).$$

The interaction constant, ξ_{CSA} , is defined as $(\gamma B_0 \Delta \sigma)$, where $\Delta \sigma = \sigma_{zz} - 1/2(\sigma_{yy} + \sigma_{xx})$, and γB_0 is the appropriate Larmor frequency. The asymmetry factor, η , is defined as $3(\sigma_{yy} - \sigma_{xx})/2\Delta\sigma$. The angular factors, α and β , are the familiar Euler angles (44) which define the rotation of the CSA frame into the frame diagonalizing the axially symmetric diffusion tensor.

To determine the dipolar-anisotropic chemical shielding cross-correlation spectral density, one can use standard methods (27, 44). For the asymmetric rotor, the resultant expressions are extremely complex and are not reproduced here. For the symmetric top rotor, the following expression results,

$$K_{\rm C}(\omega) = \frac{1}{10} \, \xi_{\rm D} \xi_{\rm CSA} \, \sum_{n=0}^{2} \, c'_{n} \{ \, \tau_{n} / [1 + (\omega \tau_{n})^{2}] \, \}, \qquad [A2]$$

where

$$\begin{aligned} c_0' &= (1/4)(3\cos^2\beta_{\rm D} - 1)(3\cos^2\beta_{\rm CSA} - 1 - \eta\sin^2\beta_{\rm CSA}\cos 2\alpha_{\rm CSA}) \\ c_1' &= (3/2)\sin 2\beta_{\rm D}\sin \beta_{\rm CSA} \{\cos \beta_{\rm CSA}\cos(\gamma_{\rm D} - \gamma_{\rm CSA}) \\ &+ (\eta/3)[\cos 2\alpha_{\rm CSA}\cos \beta_{\rm CSA}\cos(\gamma_{\rm D} - \gamma_{\rm CSA}) + \sin 2\alpha_{\rm CSA}\sin(\gamma_{\rm D} - \gamma_{\rm CSA})]\} \\ c_2' &= (3/4)\sin^2\beta_{\rm D} \{\sin^2\beta_{\rm CSA}\cos(2\gamma_{\rm D} - 2\gamma_{\rm CSA}) - (\eta/3)[\cos 2\alpha_{\rm CSA}(\cos^2\beta_{\rm CSA} + 1) \\ &\times \cos(2\gamma_{\rm D} - 2\gamma_{\rm CSA}) + 2\sin 2\alpha_{\rm CSA}\cos \beta_{\rm CSA}\sin(2\gamma_{\rm D} - 2\gamma_{\rm CSA})]\}. \end{aligned}$$

Once again, the (Euler) angles define the rotation of the dipolar frame (D) or the CSA frame into the frame diagonalizing the axially symmetric diffusion tensor.

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