Entangled Poly(dimethylsiloxane) Chains. Characteristic Broadening Effect of ^{13}C NMR Spectra

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ABSTRACT: ^{13}C resonance spectra observed for methyl groups attached to long poly(dimethylsiloxane) chains ($\bar{M}_w \sim 4.5 \times 10^6$) in a melt were found to exhibit an anomalous broadening effect: of the expected quartet the two outermost resonance lines are about 2 times broader than the inner two lines. It is shown how this effect can be closely related to a residual energy of ^{13}C–^{1}H dipole–dipole interactions within methyl groups, this nonzero average energy being associated with the temporary network structure induced by chain entanglements. This specific effect is not perceptible for very short poly(dimethylsiloxane) chains ($\bar{M}_w \sim 2 \times 10^4$).

I. Introduction

^{13}C resonance spectra currently observed for methyl groups attached to molecules in ordinary liquids are known to consist of four lines,[1] and their resonance frequencies are determined by the relationships $\omega_s \pm 3J/2$ and $\omega_s \pm J/2$. The midpoint of the quartet of lines is the Larmor frequency ω_s of the ^{13}C nucleus, while $\hbar J$ represents the strength of the energy of the scalar coupling of this nucleus with its three neighboring protons within a methyl group; the structure of the ^{13}C resonance spectrum is induced by the presence of protons. The two following properties usually characterize ^{13}C resonance spectra observed in ordinary liquids: (i) all resonance lines have the same width and (ii) the integrated line intensity of the inner two lines (resonance frequencies $\omega_s \pm J/2$) is exactly 3 times larger than the integrated line intensity of the outermost lines ($\omega_s \pm 3J/2$); this last characteristic property also results from the presence of three protons within a methyl group (Figure 1).

It is shown in the present paper that ^{13}C resonance spectra observed for methyl groups attached to strongly entangled macromolecules in a melt are quite different from those usually observed in ordinary liquids; the integrated line intensity of the inner two resonance lines ($\omega_s \pm J/2$) is still 3 times larger than the integrated line intensity of the outermost resonance lines ($\omega_s \pm 3J/2$), but the former resonance lines are 2 or 3 times narrower than the latter.

The purpose of the present paper is to show that the anomalous broadening mechanism of the ^{13}C quartet is a characteristic NMR property of entangled polymer chains and that it reflects temporary topological constraints exerted on chains by entanglements.[2] It will be shown that, within a methyl group, this anomalous broadening is governed by the nonzero average of dipole–dipole interactions of one ^{13}C nucleus with its three neighboring protons; the nonzero average results from topological constraints.[3,4]

The anomalous broadening mechanism of the quartet disappears when the molecular weight $\bar{M}_w$ of the polymer chains is small: $\bar{M}_w \lesssim 10^5$; in that case, either entanglements do not form at all ($\bar{M}_w < M_c$; M_c is the characteristic molecular weight[2] or entanglements dissociate quickly enough to average dipole–dipole interactions of nuclear spins to zero within the time scale of NMR measurements.

This characteristic effect will be illustrated from ^{13}C spectra observed for poly(dimethylsiloxane) chains in a melt. It will be shown that the observation of the anomalous broadening may be used to give qualitative information about the nature of the diffusional rotations of methyl groups in molten poly(dimethylsiloxane) (PDMS). Also, it is worth noting that the exact description of the broadening mechanism of the two outermost lines may be closely related to low-frequency chain skeletal motions; the width of these two lines observed for high molecular weight PDMS melt ($\bar{M}_w \gtrsim 10^6$) may be used as a calibrated reference frequency to investigate the terminal chain relaxation spectrum at intermediate chain molecular weight values ($10^5 \lesssim \bar{M}_w \lesssim 10^6$). The corresponding procedure has already been described in several previously published papers.[5-7]

II. PDMS ^{13}C Spectra

A. Samples. ^{13}C resonance spectra were recorded for two commercially available samples (Rhône-Poulenc-Recherches). The polydispersity of polymer chains was not a crucial parameter for the following reasons. The low molecular weight sample had an average chain molecular weight equal to $\sim 2 \times 10^4$; it was mainly used to illustrate NMR properties induced by polymer chain entanglements which dissociate very quickly, whatever the detailed mechanism of chain diffusional motions. The high molecular weight sample had an average chain molecular weight equal to $\sim 4.5 \times 10^6$; it was used to illustrate NMR properties induced by the presence of a temporary network structure determined by coupling junctions.[2] It has already been shown that properties of the transverse magnetization of protons attached to macromolecules only depend upon the mesh size of the temporary network.[7,8] It is well established from properties of the plateau of the stress relaxation modulus that this mesh size does not depend upon the chain molecular weight.[2] Consequently, the polydispersity of polymer chains is expected to have negligible effects on NMR properties we are interested in, for either short chains or long ones.

B. Spectra. All ^{13}C resonance spectra were recorded with a WP100 Bruker spectrometer, operating at 25 MHz with heteronuclear gated decoupling; some spectra were accumulated $\sim 10^4$ times. All samples were kept at room temperature (310 K). All resonance quartets were found to be characterized by a constant of scalar coupling $J = 118$ Hz.

The resonance quartet observed for short PDMS chains in a melt (the average molecular weight equals $\sim 2 \times 10^4$) is shown in Figure 2a. This spectrum was recorded during sample rotation; the half-width measured at half-height of any of the four lines is 1.4 Hz. This resonance quartet looks exactly like that observed from any methyl group attached to molecules in ordinary liquids.[1] The resonance spectrum observed for the same polymer melt in the absence of sample rotation is shown in Figure 2b; integrated line intensities are also reported in Figure 2a,b, and they illustrate the characteristic ratio 1:3:3:1, which is predicted from the theoretical description of such a spectrum.[9]

^{13}C resonance spectra obtained for methyl groups attached to high molecular weight PDMS chains ($\bar{M}_w \simeq 4.5 \times 10^6$) are reported in Figure 3. The resonance quartet recorded during sample rotation is shown in Figure 3a, using two different frequency scales. The reduced spectrum clearly shows that integrated line intensities still obey the characteristic ratio 1:3:3:1 (Figure 3aI), whereas very

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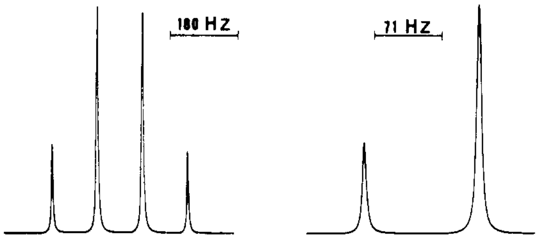

Figure 1. Ideal ^{13}C resonance spectrum drawn from Lorentzian lines characterized by a half-width at half-height equal to 2 Hz. Spectra are drawn for two different frequency scales.

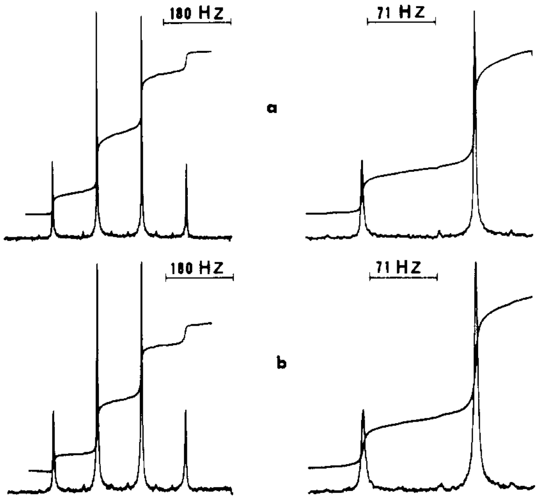

Figure 2. ^{13}C resonance spectra observed from short PDMS chains in a melt ($\bar{M}_w \sim 2 \times 10^4$). Spectra were recorded on two different frequency scales: (a) with sample rotation; (b) without sample rotation.

different line widths are measured from the extended spectrum (Figure 3aII). The spectrum recorded for the same polymer melt in the absence of sample rotation also exhibits an anomalous broadening effect of the two outermost lines compared with the inner two lines. Furthermore, the strong narrowing effect induced by sample rotation is similar to that widely observed from spectra of protons attached to entangled long polymer chains.[7] This effect clearly indicates the presence of a residual energy of dipole–dipole interactions between nuclear spins; this residual energy must be responsible in part for the broadening mechanism of the ^{13}C quartet. It has previously been shown from proton spectra that the spectrum narrowing effect is a characteristic property of entangled polymer chains and cannot be confused with diamagnetic effects, which would be explained by assuming that inhomogeneities exist through a polymer sample; line widths of proton spectra recorded for methyl groups attached to PDMS chains in a melt do not exhibit any dependence upon the steady magnetic field strength.

III. ^{13}C Magnetic Relaxation Function

A. Spin Hamiltonian. The description of the transverse magnetization dynamics of a ^{13}C nucleus attached to a methyl group and interacting with protons of this group starts from the following spin Hamiltonian:

$$\mathcal{H}_T = \mathcal{H}_s + \mathcal{H}_0 + \mathcal{H}_J' + \sum_{j=1}^{3} \mathcal{H}_{sj}' \tag{1}$$

with

$$\mathcal{H}_s = \omega_s S_Z \tag{2}$$

ω_s is the Larmor frequency of the ^{13}C nucleus, $\vec{S}$ is its spin operator, and $\hbar\mathcal{H}_s$ is the Zeeman energy of this nucleus. The Zeeman energy of protons is

$$\hbar\mathcal{H}_0 = \hbar\omega_0 I_Z$$

ω_0 is the Larmor frequency of one proton; $\vec{i}^1$, $\vec{i}^2$, and $\vec{i}^3$ are the spin operators of protons 1, 2, and 3, attached to one methyl group, respectively. Also

$$\vec{I} = \vec{i}^1 + \vec{i}^2 + \vec{i}^3$$

is the total spin operator of the three protons. The truncated scalar coupling of the ^{13}C nucleus with its three neighboring protons within a methyl group is

$$\hbar\mathcal{H}_J' = \hbar J S_Z I_Z \tag{3}$$

Also

$$\hbar\mathcal{H}_{sj}' = \frac{\gamma_s\gamma_0\hbar^2}{b^3} S_Z i_Z^j (1 - 3\cos^2\theta_j) \qquad j = 1, 2, 3 \tag{4}$$

is the truncated energy of dipole–dipole interactions of the ^{13}C nucleus with one of its three neighboring protons, "flip-flop" terms are neglected in both $\mathcal{H}_J'$ and $\mathcal{H}_{sj}'$, b is the distance between the ^{13}C nucleus and one proton within a methyl group, θ_j is one of the angular coordinates

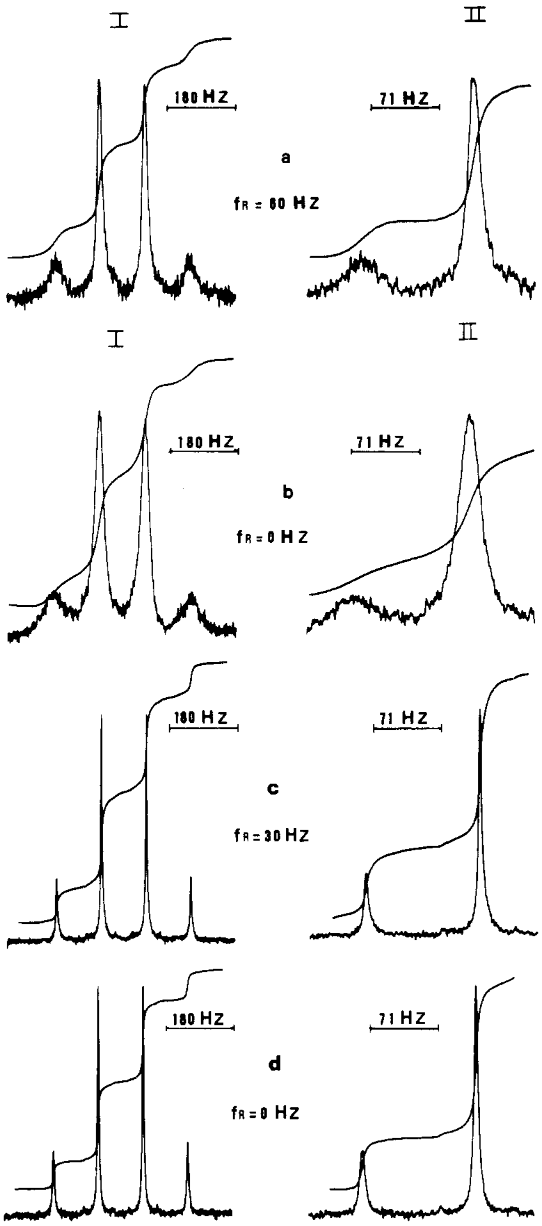

Figure 3. ^{13}C resonance spectra recorded for entangled PDMS chains in a melt: (a) $\bar{M}_w \simeq 4.5 \times 10^6$, with sample rotation; (b) $\bar{M}_w \simeq 4.5 \times 10^6$, without sample rotation; (c) $\bar{M}_w \simeq 0.07 \times 10^6$, with sample rotation; (d) $\bar{M}_w = 0.07 \times 10^6$, without sample rotation. Spectra c and d are reported to show that the specific broadening effect is perceptible as soon as about ten coupling junctions affect polymer chains.

of the vector joining these two nuclei, and the reference axis, $\tilde{Z}$, of the laboratory frame is defined along the steady magnetic field direction, B_0.

B. Relaxation Function. The relaxation function of the transverse magnetization of one ^{13}C nucleus is defined as usual by[9]

$$G_s(t) = \mathcal{T}_r\langle S_X(t)S_X\rangle \tag{5}$$

with

$$S_X(t) = e^{i\mathcal{H}_T t}S_X e^{-i\mathcal{H}_T t} \tag{6}$$

and

$$G_s(t) = \cos(\omega_s t)g_s(t) + \sin(\omega_s t)g_s(t) \tag{7}$$

with

$$g_s(t) = \mathcal{T}_r(s_X(t)S_X) \tag{8}$$

and

$$h_s(t) = \mathcal{T}_r(s_Y(t)S_X) \tag{9}$$

The operator $s_X(t)$ is defined by

$$s_X(t) = \exp[i(\mathcal{H}_J' + \sum_{j=1}^{3}\mathcal{H}_{sj}')t]S_X \exp[-i(\mathcal{H}_J' + \sum_{j=1}^{3}\mathcal{H}_{sj}')t] \tag{10}$$

In the same way

$$s_Y(t) = \exp[i(\mathcal{H}_J' + \sum_{j=1}^{3}\mathcal{H}_{sj}')t]S_Y \exp[-i(\mathcal{H}_J' + \sum_{j=1}^{3}\mathcal{H}_{sj}')t] \tag{11}$$

Spin system responses $g_s(t)$ and $h_s(t)$ may be easily expressed from the parameters J and A_{sj} ($j = 1, 2, 3$) with

$$A_{sj} = D_{CH}(3\cos^2\theta_j - 1)/2 \tag{12}$$

$D_{CH} = \gamma_s\gamma_0\hbar/b^3$ characterizes the strength of the dipole–dipole interaction of one ^{13}C nucleus and one proton:

$$\mathcal{H}_{sj}' = -2A_{sj}S_Z i_Z^j \qquad j = 1, 2, 3 \tag{13}$$

Calculations are developed in Appendix A; they lead to

$$g_s(t) + ih_s(t) = (1/8)(\exp[\pm i(3J/2 - a)t] + \sum_{j=1}^{3}\exp[\pm i(J/2 - b_j)t]) \tag{14}$$

where

$$a = \sum_{j=1}^{3}A_{sj} \tag{15}$$

and

$$b_1 = -A_{s1} + A_{s2} + A_{s3} \tag{16a}$$

$$b_2 = A_{s1} - A_{s2} + A_{s3} \tag{16b}$$

and

$$b_3 = A_{s1} + A_{s2} - A_{s3} \tag{16c}$$

The resonance spectrum $\chi''(\omega)$ is defined from the Fourier transform of $G_s(t)$:

$$G_s(t) = (1/8) \times (\cos(\omega_s \pm (3J/2 - a))t + \sum_{j=1}^{3}\cos(\omega_s \pm (J/2 - b_j))t) \tag{17}$$

and

$$\chi''(\omega) \propto \int_{-\infty}^{\infty}\cos(\omega t)G_s(t)\,\mathrm{d}t \tag{18}$$

The resonance spectrum consists of eight lines of equal intensity; the resonance frequencies are $\omega_s \pm 3J/2$ and $\omega_s \pm {}^1/_2$, respectively. The broadening mechanism is governed by angular parameters a and b_j ($j = 1, 2, 3$). The characteristic ratio of integrated line intensities is predicted to be 1.3.3.1.

C. Spectrum Angular Dependence. The angular parameter $A_{sj}(\theta_j)$ may also be written as

$$A_{sj} = (4\pi/5)^{1/2}D_{CH}Y_2^0(\theta_j) \tag{19}$$

where Y_2^m ($m = \pm2, \pm1, 0$) functions are spherical harmonics. A reference frame is associated with the methyl group: protons have fixed positions in this frame, the z axis is parallel to the $\vec{c}$ axis of the methyl group, and the x axis is defined in the plane determined by the carbon nucleus, the $\vec{c}$ axis, and proton 1. The positive direction of the x axis is chosen to render the projection of the CH$_1$ vector on it positive. Angular coordinates of the three protons in this reference frame are (θ_c, $\phi_1 = 0$), (θ_c, $\phi_2 = 2\pi/3$), and (θ_c, $\phi_3 = 4\pi/3$), respectively; $\theta_c = 71°$. The rotation that brings this reference frame into coincidence with the laboratory frame is defined by Euler angles α, β, and γ as usual. Then A_{sj} is expressed as

$$A_{sj} = (4\pi/5)D_{CH}\sum_{m=-2}^{2}Y_2^{m*}(\beta,\alpha)Y_2^m(\theta_c,\phi_j) \tag{20}$$

β is the angle between the $\tilde{Z}$ axis and the $\vec{c}$ axis and α actually describes the rotation of the frame associated with the methyl group around the $\vec{c}$ axis; α is an azimuthal angle in the plane of the triangle determined by the three protons of one methyl group. It is shown in Appendix B that

$$a = (3D_{CH}/4)(3\cos^2\theta_c - 1)(3\cos^2\beta - 1) \tag{21}$$

The broadening mechanism of the outermost resonance lines ($\omega_s \pm 3J/2$) is not governed by the azimuthal angle of the methyl group; it only depends upon the angle β that the $\vec{c}$ axis makes with the steady magnetic field direction. In the same way

$$b_1 = a/3 - 2d_c^* \tag{22}$$

$$b_2 = a/3 + d_c^* + d_s^* \tag{22'}$$

and

$$b_3 = a/3 + d_c^* - d_s^* \tag{22''}$$

where

$$d_c^* = (3D_{CH}/4)[(\sin 2\theta_c)d_c + (\sin^2\theta_c)d_c'] \tag{23}$$

and

$$d_s^* = (3(3^{1/2})D_{CH}/4)[(-\sin 2\beta_c)d_s + (\sin^2\theta_c)d_s'] \tag{23'}$$

and with

$$d_c + id_s = (\sin 2\beta)e^{i\alpha} \propto Y_2^1(\beta,\alpha) \tag{24}$$

and

$$d_c' + id_s' = (\sin^2\beta)e^{2i\alpha} \propto Y_2^2(\beta,\alpha) \tag{24'}$$

The broadening mechanism of the inner two resonance lines (resonance frequencies $\omega_s \pm J/2$) depends upon both the azimuthal angle α and the orientation β of the $\vec{c}$ axis with respect to the steady magnetic field direction. The magnetic relaxation function of one ^{13}C nucleus is now analyzed by assuming that the methyl group it belongs to undergoes fast diffusional rotations.

D. Effects of Molecular Motions. The only part of the spin Hamiltonian (1) sensitive to molecular motions is the energy of dipole–dipole interactions of the ^{13}C nucleus with its three neighboring protons:

$$\hbar A_{sj}' = -2A_{sj}S_Z I_Z^j$$

Angular variables θ_j are now considered as time-dependent random functions, and A_{sj} terms ($j = 1, 2, 3$) fluctuate with time. There is no difficulty in replacing formula 17 with the following expression:

$$G_s^{M}(t) = (1/8)\left(\cos\left[\omega_s t \pm \left(3Jt/2 - \int_0^t a(t')\,\mathrm{d}t'\right)\right] + \sum_{j=1}^{3}\cos\left[\omega_s t \pm \left(Jt/2 - \int_0^t b(t')\,\mathrm{d}t'\right)\right]\right) \quad (25)$$

The broadening term $a(t)$ only depends upon the time-dependent random function $\beta(t)$, while $b_j(t)$ broadening contributions ($j = 1, 2, 3$) are defined from the two time-dependent random functions $\beta(t)$ and $\alpha(t)$. Effects of molecular motions on the magnetic relaxation function $G_s^{M}(t)$ must now be carefully considered. The analysis will be illustrated from general properties of monomeric motions supposedly encountered in a system of strongly entangled chains in a melt.

In this respect, it is worth emphasizing that the order of magnitude of the width of the outermost ^{13}C resonance lines is 50 Hz while the strength of the ^{13}C–H dipole–dipole interaction is $D_{CH}/2\pi = 2.3 \times 10^4$ Hz; furthermore, a spectrum narrowing effect is simply induced by slow sample rotation ($\lesssim 10^2$ Hz). From these two properties, it is considered that resonance lines necessarily reflect small residual dipole–dipole interactions resulting from a partial motional averaging process. Accordingly, we assume that methyl groups attached to entangled PDMS chains obviously undergo diffusional rotations that are nonisotropic because of temporary topological constraints exerted on chain segments by coupling junctions.[4] More precisely, we assume that diffusional rotations of methyl groups observed during the lifetime of entanglements are nonisotropic; they consequently originate temporary nonzero averages of dipole–dipole interactions. Nevertheless, they are fast enough to induce a partial motional averaging of dipole–dipole interactions; whatever the exact nature of monomeric motions, temporary averages are defined within the lifetime of entanglements:

$$\langle a(t)\rangle = a_v \neq 0$$

and

$$\langle b_j(t)\rangle = b_v^{\,j} \neq 0 \qquad j = 1, 2, 3$$

The motional averaging process observed as a partial one from NMR is the basic property underlying the interpretation of the anomalous broadening mechanism of the ^{13}C resonance quartet; it can be given the following more explicit description. The observation of a temporary nonzero average necessarily implies the existence of a chain relaxation spectrum divided into two well-separated dispersions Ω_1 and $\Omega_2(\bar{M}_w)$. The Ω_1 dispersion of chain correlation times is associated with short-range monomeric motions, independent of the chain molecular weight $\bar{M}_w$, while the dispersion $\Omega_2(\bar{M}_w)$ corresponds to the terminal chain relaxation spectrum; it is associated with the description of long-range collective motions of all parts of a chain. The longest correlation time T_{Re} is known to be strongly dependent upon the chain molecular weight $\bar{M}_w$: $T_{Re} \propto \bar{M}_w^{\,\epsilon}$ ($\epsilon \gtrsim 3.$). The hypothesis of such a two-dispersion chain relaxation spectrum is strictly in accordance with viscoelastic properties currently observed in a polymer melt.[10] The Ω_1 and Ω_2 ranges of correlation times are supposed to roughly obey the inequalities

$$\Omega_1 \ll D_{CH}^{-1} < |a_v^{-1}|, \qquad |(b_v^{\,j})^{-1}| < \Omega_2(\bar{M}_w) \quad (26)$$

There is a two-step motional averaging of dipole–dipole interactions. However, for methyl groups attached to strongly entangled chains, the second step of the averaging process is not achieved during the time scale of NMR measurements because of the inequality

$$|a_v^{-1}|,\ |(b_v^{\,j})^{-1}| < \Omega_2(\bar{M}_w) \quad (27)$$

Therefore, monomeric unit motions are observed from NMR as nonisotropic diffusional rotations. For methyl groups attached to short chains, the above inequality does not hold anymore; it is replaced by

$$|a_v^{-1}|,\ |(b_v^{\,j})^{-1}| > \Omega_2(\bar{M}_w) \quad (28)$$

the second step of the averaging process is achieved within the NMR time scale; monomeric unit motions are observed as isotropic ones.

We now assume that the relaxation functions may be written from the usual second-order cumulant expansion; for example, the outermost resonance lines are represented by the relaxation function

$$\gamma_a(t) \propto \mathrm{Re}\,(\exp|i\omega_s t \pm i(3J/2 - a_v)t - C_a(t)|) \quad (29)$$

where Re means the real part of the exponential function and

$$C_a(t) = \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2\ \langle (a(t_1) - a_v)(a(t_2) - a_v)\rangle \quad (30)$$

The two inner lines are described in the same way:

$$\gamma_b^{\,j}(t) \propto \mathrm{Re}\,(\exp|i\omega_s t \pm i(J/2 - b_v^{\,j})t - C_b^{\,j}(t)|) \qquad j = 1, 2, 3 \quad (31)$$

$C_b^{\,j}(t)$ contributions have expressions similar to that of $C_a(t)$. Second-order cumulant terms $C_a(t)$ and $C_b^{\,j}(t)$ are associated with the partial motional averaging process of dipole–dipole interactions while partial averages a_v and $b_v^{\,j}$ are first-order cumulant terms. For the sake of simplicity, it is supposed that the partial motional averaging process leads to broadening contributions written in the usual way as

$$C_a(t) = \epsilon_a t \quad (32)$$

and

$$C_b^{\,j}(t) = \epsilon_b^{\,j} t \qquad j = 1, 2, 3 \quad (32')$$

where ϵ_a depends upon the mean square value $\langle (a(t) - a_v)^2\rangle$ multiplied by a correlation time or an equivalent one characterizing fast nonisotropic monomeric motions; $\epsilon_b^{\,j}$ ($j = 1, 2, 3$) has a similar mathematical structure. Contributions a_v and $b_v^{\,j}$ depend upon orientational parameters determining nonisotropic motions of one monomeric unit with respect to the magnetic field, and the resulting spectrum is an average over all values of these parameters, whereas contributions ϵ_a and $\epsilon_b^{\,j}$ may be supposed to be independent of orientational parameters; this will be discussed in section IV.

E. Sample Rotation Effect. The spectrum narrowing effect induced by sample rotation can be given the following general description. The angular parameter $A_{sj}(\theta_j)$ is expressed in the laboratory frame associated with the steady magnetic field B_0 as a function of spherical harmonics defined in the reference frame associated with the sample tube:

$$A_{sj}(\mathrm{lab}) = (4\pi/5)^{1/2} D_{CH} \sum_{m'} \mathcal{R}_{m'0}^{\,2}\, Y_2^{\,m'}(\mathrm{tube}) \quad (33)$$

Matrix elements $\mathcal{R}_{m'0}^{\,2}$ ($m' = 0, \pm 1, \pm 2$) describe the rotation that brings the sample tube reference frame into coincidence with the laboratory reference frame; which is defined from conventional Euler angles $\alpha' = \Omega_R t$, $\beta' = \pi/2$, and $\alpha' = \pi/2$; Ω_R is the angular frequency of sample rotation:

$$A_{sj}(\mathrm{lab}) = (4\pi/5)D_{\mathrm{CH}}\sum_{m'} Y_2^{m'*}(\pi/2,\Omega_{\mathrm{R}}t)Y_2^{m'}(\mathrm{tube}) \tag{34}$$

Spherical harmonics $Y_2^{m'}(\mathrm{tube})$ associated with the orientation of the ^{13}C–H$_j$ bond in the sample tube reference frame are now expressed in a local reference frame associated with coupling junctions created by entanglements; fast nonisotropic motions of monomeric units are described within this local reference frame:

$$Y_2^{m'}(\mathrm{tube}) = \sum_n \mathcal{R}_{nm'}^{\;2} Y_2^n(\mathrm{local}) \tag{35}$$

and

$$A_{sj}(\mathrm{lab}) = (4\pi/5)D_{\mathrm{CH}}\sum_{m'n} Y_2^{m'*}(\pi/2,\Omega_{\mathrm{R}}t)\mathcal{R}_{nm'}^{\;2} Y_2^n(\mathrm{local}) \tag{36}$$

Matrix elements $\mathcal{R}_{nm'}^{\;2}$ ($n = 0, \pm1, \pm2$) describe the rotation that brings the local reference frame into coincidence with the sample tube reference frame. The partial temporary average is written as

$$\langle A_{sj}(\mathrm{lab})\rangle = (4\pi/5)D_{\mathrm{CH}}\sum_{m'n} Y_2^{m'*}(\pi/2,\Omega_{\mathrm{R}}t)\mathcal{R}_{nm'}^{\;2}\langle Y_2^n(\mathrm{local})\rangle \tag{37}$$

During fast sample rotation, the only nonzero terms of formula 37 are given by $m' = 0$:

$$\langle A_{sj}(\mathrm{lab})\rangle^{\mathrm{R}} = (4\pi/5)D_{\mathrm{CH}}\sum_n Y_2^0(\pi/2)\mathcal{R}_{n0}^{\;2}\langle Y_2^n(\mathrm{local})\rangle \tag{38}$$

$$= -\frac{1}{2}(4\pi/5)^{1/2}D_{\mathrm{CH}}\sum_n \mathcal{R}_{n0}^{\;2}\langle Y_2^n(\mathrm{local})\rangle \tag{39}$$

while without sample rotation

$$\langle A_{sj}(\mathrm{lab})\rangle = \langle A_{sj}(\mathrm{tube})\rangle = (4\pi/5)^{1/2}D_{\mathrm{CH}}\sum_n \mathcal{R}_{n0}^{\;2}\langle Y_2^n(\mathrm{local})\rangle \tag{40}$$

Therefore, temporary averages of angular parameters A_{sj} ($j = 1, 2, 3$) are exactly divided by two upon sample rotation, whatever the exact nature of nonisotropic motions; the only condition to be fulfilled is

$$\Omega_{\mathrm{R}} \gg |\langle A_{sj}(\mathrm{tube})\rangle|$$

Consequently, parameters a_{v} and b_{v}^j are also expected to be divided by two, whatever their expressions derived from the detailed description of diffusional motions of monomeric units. ^{13}C resonance quartets observed with or without sample rotation result from an average over all orientational parameters used to define matrix elements $\mathcal{R}_{n0}^{\;2}$; in a homogeneous, isotropic sample all possible orientations of local frames determined from coupling junctions have a uniform statistical weight.

IV. Anomalous Broadening Effect: Characterization

This characterization concerns orders of magnitude of broadening contributions a_{v} and b_{v}^j ($j = 1, 2, 3$), on the one hand, compared with those of ϵ_a and ϵ_b^j ($j = 1, 2, 3$), on the other hand. An estimate of possible field inhomogeneity effects can be first obtained according to the following analysis.

A. Field Inhomogeneity Effects. Let us consider the conventional ^{13}C resonance quartet observed from methyl groups attached to short PDMS chains in a melt. In that case, no contribution from residual dipole–dipole interactions is brought to the broadening mechanism of resonance lines. Consequently, differences between the resonance spectrum observed without sample rotation and the spectrum recorded during sample rotation only come from a possible field inhomogeneity effects; the amplitude $\Delta\delta^*$ of this effect can be given an estimate from Figure 2: $\Delta\delta^* \simeq 1.$ Hz. Let us now consider ^{13}C resonance spectra observed from methyl groups attached to long PDMS chains in a melt. They were carefully recorded considering that the field inhomogeneity effect also has the amplitude $\Delta\delta^*$; furthermore, this effect obviously applies to each line of the quartet in the same way. Consequently, it is considered that the large difference between the width of the outermost lines ($\delta_a = 32$ Hz) and the width of the inner lines ($\delta_b = 14$ Hz) observed in the absence of sample rotation is not induced by field inhomogeneity effects; it is closely associated with specific values of ϵ_a, a_{v}, ϵ_b^j, and b_{v}^j ($j = 1, 2, 3$). Similarly, corresponding resonance line widths $\delta_a^{\mathrm{R}} = 19$ Hz and $\delta_b^{\mathrm{R}} = 7$ Hz, observed during sample rotation only reflect characteristic properties of the ^{13}C spectrum, since field inhomogeneity effects are completely negligible in that case.

B. Angular Average. The outermost line shapes observed from methyl groups attached to long PDMS chains in a melt were found to be close to Lorentzian curves (Figure 3) although they result from an angular average of the parameter a_{v}. These resonance lines are now supposed to be Fourier transforms of pure exponential time functions characterized from two parameters, ϵ_a and $\overline{a_{\mathrm{v}}}^0$. It is not necessary to give any details about the probably tedious average procedure applied to ^{13}C spectra over all orientational parameters defining nonisotropic monomeric units motions; we only consider that $\overline{a_{\mathrm{v}}}^0$ results from such an average. Similarly, the inner two resonance lines will be characterized from two parameters only: ϵ_b and $\overline{b_{\mathrm{v}}}^0$.

C. Anomalous Broadening Effect. Parameters ϵ_a and $\overline{a_{\mathrm{v}}}^0$ are now evaluated from the half-width at half-height of resonance lines using the two following relationships:

$$\delta_a = \epsilon_a + \bar{a}_{\mathrm{v}}^0$$

defined in the absence of sample rotation, and

$$\delta_a^{\mathrm{R}} = \epsilon_a + \bar{a}_{\mathrm{v}}^0/2$$

defined for ^{13}C spectra recorded during sample rotation; therefore

$$\bar{a}_{\mathrm{v}}^0 = 2b \pm 1 \text{ Hz}$$

and

$$\epsilon_a = 6 \pm 1 \text{ Hz}$$

The inner two lines are characterized by

$$\bar{b}_{\mathrm{v}}^0 = 13 \pm 1 \text{ Hz}$$

and

$$\epsilon_b \simeq 1 \pm 1 \text{ Hz}$$

It is clearly seen that the contribution of a_{v} to ϵ_a in formula 30 is negligible:

$$\bar{a}_{\mathrm{v}}^0 \simeq 26 \text{ Hz} \ll |a(t)| \simeq 10^4 \text{ Hz}$$

ϵ_a must not exhibit any angular dependence.

The anomalous broadening mainly comes from residual dipole–dipole interactions existing between a given ^{13}C nucleus and its three neighboring protons in a methyl group. It is seen from the mathematical structures of parameters a and b_j (formula 22) that magnetic quantum numbers of three protons $m_{\mathrm{H}} = \pm^3/_2$ enhance the residual broadening effect observed on the outermost lines of the quartet compared with that observed on the inner two lines associated with magnetic quantum numbers of protons equal to $m_{\mathrm{H}}' = \pm^1/_2$.

The anomalous broadening property obviously ceases when chain entanglements dissociate quickly enough to eliminate the effect of the temporary averages $\overline{a_v}^0$ and $\overline{b_v}^0$, within the time scale of NMR measurements.

D. Methyl Group Nuclear Magnetizations. The rotational diffusion of any methyl group around its own axis is usually supposed to be stochastically independent of the diffusional process of the 3-fold axis. In this case, mean values of d_c, d_s, d_c') and d_s' terms are obtained by breaking the average procedure into two parts:

$$\langle d_c + id_s \rangle = \langle \sin 2\beta \rangle \langle e^{i\alpha} \rangle_\infty \langle Y_1^2(\beta,\alpha) \rangle$$

and

$$\langle d_c' + id_s' \rangle = \langle \sin^2 \beta \rangle \langle e^{2i\alpha} \rangle_\infty \langle Y_2^2(\beta,\alpha) \rangle$$

Considering that the rotational diffusion of any methyl group around its own axis exhibits a character of uniformity, the above mean values are equal to zero:

$$\langle e^{i\alpha} \rangle = 0 = \langle e^{2i\alpha} \rangle$$

Therefore, the average values of d_c^* and d_s^* terms are also equal to zero:

$$\langle d_c^* \rangle = 0 = \langle d_s^* \rangle$$

Consequently, mathematical structures of a and b_j random function (formulas 22, 22′, and 22″) show that the mean values a_v and b_v^j should obey the specific relationship

$$b_v^j = \langle b_j \rangle = \langle a/3 \rangle = a_v/3$$

The value of the ratio $\overline{a_v}^0/\overline{b_v}^0$ should then be equal to 3, while the observed value is 2 ± 0.2. A possible explanation of this discrepency may be founded on a slight coupling of the two mechanisms contributing to the relaxation process associated with the outermost resonance lines. The two contributions were supposed to be represented by ϵ_a and $\overline{a_v}^0$, respectively; roughly, as a consequence of the slight coupling, the resulting line width should not be expressed as a simple addition of ϵ_a and $\overline{a_v}^0$. The same remark applies to the inner two lines, too. Therefore, $\overline{a_v}^0$ and $\overline{b_v}^0$ cannot represent total contributions due to the residual energy of dipole–dipole interactions; accordingly, the ratio $\overline{a_v}^0/\overline{b_v}^0$ cannot be equal to 3 exactly.

Also, such a slight coupling probably originates properties of the proton magnetic relaxation function observed from methyl groups attached to long PDMS chains in a melt; the spin system response does not exhibit the two well-defined parts predicted by assuming that the diffusional rotation motion of the $\vec{c}$ axis is distinguishable from the diffusional rotation around the $\vec{c}$ axis.[11]

On the other hand, on a close inspection of formula 14, it is clearly seen that J couplings and the residual energy of dipole–dipole interactions play the same basic role in the determination of the relaxation function. To reinforce the interpretation given in the present paper, a ^{13}C resonance spectrum was recorded with heteronuclear broadband decoupling to simultaneously eliminate J-coupling effects and the broadening induced by residual dipole-dipole interactions. Figure 4 shows that a single narrow line is actually observed; this result shows that both contributions cancel out from the determination of the ^{13}C quartet.

Finally, it is worth noting that the parameter $3D_{\mathrm{CH}}/4$ is equal to $0.62D_{\mathrm{HH}}$, where D_{HH} represents the dipole-dipole interaction strength of protons within any methyl group; this explains why the widths of ^{13}C and proton resonance lines observed from methyl groups attached to long PDMS chains in a melt have about the same order of magnitude, induced by residual dipole–dipole interactions.

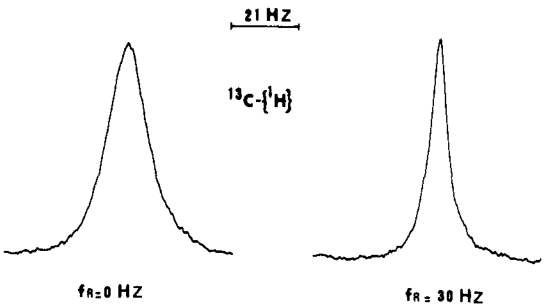

Figure 4. ^{13}C resonance spectra recorded with heteronuclear broad-band decoupling ($\bar{M}_w \simeq 4.5 \times 10^6$). Frequencies of sample rotation are reported on the spectra.

On the other hand, methyl groups have been widely used as molecular probes to investigate local fast motions of monomeric units,[12] observing spin–lattice relaxation rates.

V. Conclusion

The residual energy of dipole–dipole interactions of one ^{13}C nucleus with its three neighboring protons, existing within any methyl group attached to long poly(dimethylsiloxane) chains in a melt, originates a specific broadening mechanism of the ^{13}C resonance line quartet; the widths of the two outermost resonance lines exhibit an enhancement effect with respect to the widths of the inner two lines. This effect gives new clear evidence for the presence of nonzero averages of nuclear spin tensorial interactions, resulting from a field of constraints exerted on monomeric units by chain entanglements. This specific broadening property adds to several experimental NMR procedures proposed until now to reveal coupling junctions in a polymer melt: spectrum narrowing effect induced by sample rotation,[3,13–17] magic angle spectroscopy,[18] and coherent averaging.[19]

Appendix A

The relaxation function of the transverse magnetization of one ^{13}C nucleus is calculated by using the product spin space $\epsilon_s \times \epsilon_0$. ϵ_s is spanned by the two eigenfunctions of S_Z; they are called $|\gamma_+\rangle$ and $|\gamma_-\rangle$, respectively. ϵ_0 is the product spin space associated with the three protons; it is spanned by the eight eigenfunctions of $I_Z = i_Z^1 + i_Z^2 + i_Z^3$, and they are written as $|\alpha\alpha\alpha\rangle$, $|\alpha\alpha\beta\rangle$, $|\alpha\beta\alpha\rangle$, $|\beta\alpha\alpha\rangle$, $|\beta\alpha\beta\rangle$, $|\beta\beta\alpha\rangle$, $|\alpha\beta\beta\rangle$, and $|\beta\beta\beta\rangle$. We implicity introduced the spin eigenfunctions $|\alpha\rangle = |^1/_2\rangle$ and $|\beta\rangle = |{-}^1/_2\rangle$ of the Z component i_Z^j of any of the three protons. The product space $\epsilon_s \times \epsilon_0$ consists of the products of all wave functions of ϵ_s by all wave functions of ϵ_0. If, for example, we consider the function $g_s(t)$

$$g_s(t) = \mathcal{T}_r(s_X(t)S_X) \qquad \text{(A.1)}$$

one of the 16 terms corresponding to the trace procedure of formula A.1 is written as

$$\langle \gamma_+, \alpha\alpha\alpha | e^{iS_Zt[i_Z^1(J-2A_{s1})+i_Z^2(J-2A_{s2})+i_Z^3(J-2A_{s3})]} S_+ \\ e^{-iS_Zt[i_Z^1(J-2A_{s1})+i_Z^2(J-2A_{s2})+i_Z^3(J-2A_{s3})]} | \gamma_-, \alpha\alpha\alpha \rangle \qquad \text{(A.2)}$$

with

$$S_+ = S_X + iS_Y \qquad \text{(A.3)}$$

The illustrating term is equal to

$$e^{it(3J/2-A_{s1}-A_{s2}-A_{s3})}$$

There are no difficulties in calculating the 15 remaining terms of the trace of operators corresponding to formula A.1.

Appendix B

To calculate more explicite expressions of

$$a = A_{s1} + A_{s2} + A_{s3} \tag{B.1}$$

and of

$$b_1 = -A_{s1} + A_{s2} + A_{s3} \tag{B.2}$$

$$b_2 = A_{s1} - A_{s2} + A_{s3} \tag{B.3}$$

and

$$b_3 = A_{s1} + A_{s2} - A_{s3} \tag{B.4}$$

a reference frame associated with a given methyl group is chosen; its z axis is parallel to the $\vec{c}$ axis of the methyl group, while the x axis is in the plane determined by the carbon nucleus, the $\vec{c}$ axis, and proton 1. The positive direction of the x axis is chosen to render the projection of the $CH_{\bar{1}}$ on it positive.

Then the angular parameter A_{sj} is conveniently expressed as

$$A_{sj} = (4\pi/5)^{1/2} D_{CH} Y_2^0(\theta_j) \qquad j = 1, 2, 3 \tag{B.5}$$

$Y_2^m(\theta_j)$ ($m = \pm 2, \pm 1, 0$) are spherical harmonics.

Then

$$A_{sj} = (4\pi/5)^{1/2} D_{CH} \sum_{n=-2}^{2} \mathcal{R}_{n0}^2(\alpha,\beta,\gamma) Y_2^n(\theta_c,\phi_j) \tag{B.6}$$

θ_c and ϕ_j ($j = 1, 2, 3$) are the angular coordinates of the vectors joining one ^{13}C nucleus to its three neighboring protons ($\phi_1 = 0$, $\phi_2 = 2\pi/3$, $\phi_3 = 4\pi/3$; $\phi_c = 71°$); $\mathcal{R}_{n0}^2(\alpha,\beta,\gamma)$ ($n = \pm 2, \pm 1, 0$) are matrix elements associated with the rotation that brings the reference frame of the methyl group into coincidence with the laboratory frame; this rotation is defined from conventional Euler angles α, β, and γ. More precisely

$$\mathcal{R}_{n0}^2(\alpha,\beta,\gamma) = (4\pi/5)^{1/2} Y_2^{n*}(\beta,\alpha) \tag{B.7}$$

β is the angle that the $\vec{c}$ axis makes with the steady magnetic field direction; α is the azimuthal angle defined in the plane perpendicular to the $\vec{c}$ axis.

Therefore

$$a = 3D_{CH}(4\pi/5) Y_2^0(\beta) Y_2^0(\theta_c) \tag{B.8}$$

In the same way

$$b_1 = (4\pi/5) D_{CH} \sum_n Y_2^{m*}(\beta,\alpha) \times [-Y_2^m(\theta_c,\phi_1) + Y_2^m(\theta_c,\phi_2) + Y_2^m(\theta_c,\phi_3)] \tag{B.9}$$

or

$$b_1 = \frac{a}{3} - \frac{3D_{CH}}{2}[\sin 2\theta_c \sin 2\beta \cos \alpha + \sin^2 \theta_c \sin^2 \beta \cos 2\alpha] \tag{B.10}$$

Furthermore

$$b_1 = \frac{a}{3} + \frac{3D_{CH}}{4}[\sin 2\theta_c \sin 2\beta \cos \alpha - 3^{1/2} \sin 2\theta_c \sin 2\beta \cos \alpha + \sin^2 \theta_c \sin^2 \beta \cos 2\alpha + 3^{1/2} \sin^2 \theta_c \sin^2 \beta \sin 2\alpha] \tag{B.11}$$

and

$$b_3 = \frac{a}{3} + \frac{3D_{CH}}{4}[\sin 2\theta_c \sin 2\beta \cos \alpha + 3^{1/2} \sin 2\theta_c \sin 2\beta \sin \alpha + \sin^2 \theta_c \sin^2 \beta \cos 2\alpha - 3^{1/2} \sin^2 \theta_c \sin^2 \beta \sin 2\alpha] \tag{B.12}$$

Then expressions of d_c, d_s, d_c', and d_s' are easily found.

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