Strongly entangled polymer chains in a melt. Description of n.m.r. properties associated with a submolecule model

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A model is proposed to illustrate properties of the transverse magnetic relaxation function, $G(t)$, of proton pairs linked to strongly entangled polymer chains in a melt. According to this model, any polymer molecule is described as a freely jointed chain and it is divided into submolecules of equal contour length L_e^v. Every link is supposed to carry a proton pair; dipolar spin couplings between different proton pairs are neglected. The disentanglement relaxation time is supposed to be much longer than any characteristic time of the spin system; consequently, any submolecule observed on an n.m.r. time scale is supposed to have fixed ends. It is considered that the residual spin-coupling energy resulting from such a constraint governs the magnetic relaxation process. The free induction decay is expressed as a contour length function; its time evolution is shown to exhibit two ranges, which might be characterized by two relaxation times. The model is easily extended to rotating methyl groups. Theoretical results are compared with magnetic relaxation properties observed on entangled real chains: polydimethylsiloxane (PDMS) and *cis*-1,4-polybutadiene (PB). An attempt to adjust the contour length value to experimental results leads to the determination of average submolecule molecular weights M_e^v equal to 8200 and 2000 for PDMS and PB, respectively; the values usually obtained from viscoelastic plateau modulus measurements are 8100 and 1900, respectively.

Keywords Nuclear magnetic resonance; polymers; entanglements; polybutadiene; poly(dimethyl siloxane); transverse relaxation

INTRODUCTION

It has been recognized for a long time that transverse magnetic relaxation functions observed on protons linked to strongly entangled polymer chains in a melt are generally found not to be pure exponential time functions[1-4]. Similar n.m.r. properties were observed on crosslinked samples[5-7]. In most cases, these functions exhibit a complicated shape described from approximate empirical formulae, which are not easily handled in current interpretations. Consequently, one or two mean time constants are usually defined as characteristic n.m.r. parameters; however, these parameters should reflect changes of polymer physical properties induced by chain length or polymer concentration variations, for example, rather than changes of internal properties of the spin system. Such a procedure of analysis greatly attenuates the accuracy necessary possibly to observe dynamical processes of entangled polymer molecules. One of the main problems encountered in n.m.r. studies of polymer systems is to define a standard description of the free induction decays.

The complex shape of the transverse magnetic relaxation function has probably several origins. In their previous work, McCall *et al.*[4] have shown that the non-exponential decay can be ascribed to chain molecular weight distribution; their statement was based on n.m.r. measurements performed on three branched polyethylenes characterized by very different breadths of the molecular weight distribution. However, it was emphasized by these authors that the situation needed to be clarified by considering experiments involving careful measurements of fractions and their mixtures. Polydispersity effects will not be considered throughout the present work.

It has long been supposed that chain entanglements should affect the motional averaging of spin–spin interactions in molten polymers[2,4,6,8-10]. In this work we propose a model which shows that the origin of non-exponential free induction decays may lie in the solid-like response of nuclear spins linked to strongly entangled chains. This model should be associated with chain molecular weights much larger than the characteristic value, M_c, of entanglement formation[11,12]. In that case, it has been well established that the spin system response exhibits a solid-like character: a spectrum-narrowing effect is induced by sample rotation around an axis perpendicular to the steady magnetic field direction. The transverse magnetic relaxation process can be ascribed to pure residual dipolar spin couplings whenever the resonance linewidth is divided by 2 upon sample rotation. This property was first observed and described from *cis*-1,4-polybutadiene melts[13,14]; it was then observed on polyisobutylene and polydimethylsiloxane (PDMS) chains and on some polymer network structures[5,15]. The residual spin–spin interaction must be related to the presence of a temporary network; it results from a partial motional averaging process induced by a non-isotropic rotation of monomeric units. This average orientational order of monomeric units is perceived because entanglement lifetimes are longer than characteristic times of the

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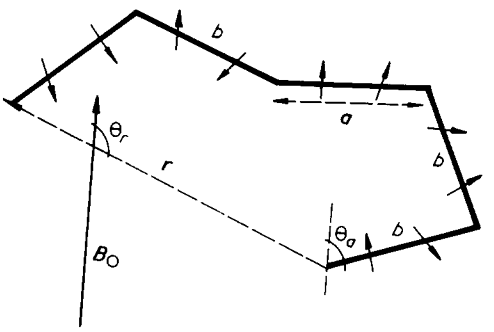

Figure 1 The freely jointed chain model. Every bond carries a proton pair. The bond length is *a*, and the distance between two nuclei is *b*

transverse spin system response. Similar n.m.r. properties have been unambiguously illustrated from recent studies of permanent PDMS gels[16] (infinite entanglement lifetimes). It has already been proposed to relate the partial averaging process of dipolar couplings to the presence of two sets of chain relaxation times by introducing the submolecule concept currently used to describe viscoelastic properties[17]. The wide relaxation time spectrum of strongly entangled polymer chains is generally considered to consist of two sets, well separated from each other[11,12]. In accordance with viscoelastic properties, the terminal spectrum corresponds to the longest relaxation times; it characterizes long-range configurational changes involving disentanglement processes which are strongly molecular weight dependent. The transition spectrum corresponding to short relaxation times is associated with short segment motions occurring within submolecules; it is not molecular weight dependent. An attempt to relate the spin system response to submolecule properties through residual dipolar spin couplings will be given here. It will be considered that the splitting of the chain relaxation spectrum into two sets is also perceived from n.m.r.; therefore, the partial motional averaging is ascribed to the transition spectrum while the terminal spectrum need not be taken into consideration. It will be shown that, even without polydispersity effects, transverse magnetization functions of proton pairs or of rotating three-spin systems are quite complex. According to such a model, free induction decays observed on very long chains in a melt should not be sensitive to molecular weight polydispersity since submolecules are not molecular weight dependent. However, it has been shown recently that the spin–spin relaxation process of protons bound to PDMS molecules in a melt may become sensitive to the slow motion of these chains when they are shortened enough to reduce disentanglement relaxation times[10,18]. Contrary to submolecules, terminal relaxation spectra associated with the chain diffusion processes are known to depend strongly on chain molecular weight; consequently, free induction decays should also become dependent upon the breadth of the chain molecular weight distribution. This approach is compatible with the results of n.m.r. measurements performed by McCall *et al.* on branched polyethylenes.

The present model is appropriate to the illustration of n.m.r. properties associated with proton groups like (CH_2) or (CH_3) linked to the main skeleton of a chain, considering that relaxation properties are mainly governed by internal spin interactions within each group; interactions between neighbouring spin groups are supposed to give rise to small additional relaxation mechanisms, only. In other words, single-chain magnetic properties should be observed although all chains are in dynamical interactions with one another. It will be shown below that methine, methylene or methyl groups are convenient examples of such spin systems.

Theoretical properties of the transverse component of the spin system response of a proton pair will be described in the next section; they will then be compared with experimental results obtained from *cis*-1,4-polybutadiene in the third section. Properties of methyl groups will be analysed in the following section, being compared with n.m.r. data obtained from PDMS chains.

PROTON PAIRS: THEORETICAL RESPONSE

Details about the basic chain model, which will be used below to calculate the n.m.r. response of a proton pair, have already been described in previous studies[16,18,19]. We consider that the polymer molecule is a freely jointed chain, built from N links of equal length a. Every link is supposed to carry a proton pair; the internal distance between two nuclei of a pair is b (*Figure 1*). All magnetic interactions between different pairs are neglected, considering internal dipolar interactions within each pair, only. The relaxation function of the transverse magnetization of protons bound to a freely jointed chain will be calculated within the adiabatic approximation, neglecting non-adiabatic contributions induced by fast isomerization processes of monomeric units.

The glassy state

In the glassy state, chain segments have no large-amplitude motions; they only undergo high-frequency vibrations of small amplitude, which cannot govern the spin–spin relaxation process. Any link may be considered as having a fixed orientation in space. Considering a proton pair linked to a given link, its relaxation function expressed in the frame rotating at the Larmor frequency, ω_0, is well known[20]:

$$g^{G}(t)=\cos(\omega_0(\boldsymbol{a})t) \qquad (1)$$

with $\omega_0(\boldsymbol{a})=3\gamma^2\hbar(3\cos^2\theta_a-1)/4b^3$; γ is the gyromagnetic ratio of a proton; θ_a is the angle which the bond $\boldsymbol{a}$ makes with the steady magnetic field direction, $\boldsymbol{B}_0$. The relaxation function corresponding to the whole sample is:

$$G^{G}(t)=\langle\cos(\varepsilon_0(\boldsymbol{a})t)\rangle_{\text{orient}} \qquad (2)$$

where $\langle\ \rangle_{\text{orient}}$ means an average value calcualted over all orientations of links in the glassy state. The resonance line spectrum is the Fourier transform of $G^G(t)$; it has already been described in several references[20,21]. Its second moment is:

$$M_2^{G}=-\left(\frac{d^2G^{G}}{dt^2}\right)_{t=0}=\langle\varepsilon_0^2\rangle_{\text{orient}}=0.45\frac{\gamma^4\hbar^2}{b^6} \qquad (3)$$

The fourth moment is:

$$M_4^{G}=\langle\varepsilon_0^4\rangle_{\text{orient}}=15(M_2^{G})^2/7 \qquad (4)$$

M_2^G will be compared with the second moment observed in the molten state.

The molten state

We now consider strongly entangled chains in a pure molten polymer system. It has long been supposed that the wide relaxation time spectrum of long polymer molecules consists of two sets Ω_1 and Ω_2 well separated from each other, in accordance with viscoelastic properties of such materials. Such a description is based on the partition of a chain into submolecules defined between coupling junctions and characterized by the apparent average molecular weight M_e; M_e is usually related to the plateau modulus G_N^0 through the formula:

$$M_e = \rho RT/G_N^0 \tag{5}$$

ρ is the polymer density and T the temperature[12]. Values of M_e for a number of polymers have already been tabulated, and some of them are given in refs. 11, 12 and 23). It is usually postulated that the two relaxation time ranges reflect the existence of a temporary network structure due to rope-like interlooping of chains. The set Ω_1 of short relaxation times corresponds to short-range configurational changes within a submolecule; chain segment motions occur on a short space scale. The set Ω_2 of long relaxation times characterizes long-range configurational changes; chain motions occur beyond entanglement points, involving several submolecules. It is not the purpose of the present paper to analyse recent quantitative theories about viscoelastic properties of polymer systems[24,27]. We only consider that as a consequence of the presence of two sets of chain relaxation times, the averaging process of tensorial spin interactions is expected to occur in two steps[28]. N.m.r. properties are analysed in the following way. We first consider that any entangled chain is divided into n.m.r. submolecules of equal contour length L_e^v; n.m.r. submolecules may be slightly different from viscoelastic submolecules of contour length L_e. Any submolecule is supposed to be fully characterized from its end-to-end vector $\boldsymbol{r}_e^v$. Then, the time variation of $\boldsymbol{r}_e^v$ is supposed to be negligible when it is observed on a timescale smaller than all relaxation times of the Ω_2 dispersion but longer than all relaxation times of the Ω_1 dispersion. Accordingly, within a given submolecule, any link of the freely jointed chain is a random time function $\boldsymbol{a}(t)$; however, it is not free to rotate completely in space because of the fixed end-to-end vector $\boldsymbol{r}_e^v$. An isotropic motion of $\boldsymbol{a}(t)$ would be observed on a timescale longer than all relaxation times of Ω_2. The partial average of the dipolar spin coupling of a proton pair linked to a freely jointed chain has already been calculated[16,18,19] as a function of the fixed end-to-end vector $\boldsymbol{r}_e^v$:

$$\langle \varepsilon_0(\boldsymbol{a}(t))\rangle_{\boldsymbol{r}_e^v} = 3\gamma^2\hbar L^*(x)(3\cos^2\theta_{\boldsymbol{r}_e^v} - 1)/4b^3 \tag{6}$$

with

$$L^*(x) = [(3x^{-2}+1)\sin h(x) - 3x^{-1}\cos h(x)]/\sin h(x) \tag{7}$$

and $x = 3\boldsymbol{r}_e^v/N_e^v a$; N_e^v is the number of links of a n.m.r. submolecule. The limit value of $L^*(x)$ is unity when x goes to infinite values; while at small x values $L^*(x) \simeq x^2/15$. The angle $\theta\boldsymbol{r}_e^v$ is that which the end-to-end vector of the submolecule makes with the steady magnetic field $\boldsymbol{B}_0$. The width of $L^*(x)$ is about $N_e^v a$, while the width of the distribution function of $\boldsymbol{r}_e^v$ associated with a freely jointed chain is $(N_e^v)^{1/2}a$. Therefore, only small values of $\boldsymbol{r}_e^v$ are involved in calculations, and:

$$\langle \varepsilon_0(\boldsymbol{a}(t))\rangle_{\boldsymbol{r}_e^v} \simeq 9\gamma^2\hbar(3\cos^2\theta_{\boldsymbol{r}_e^v} - 1(\boldsymbol{r}_e)^2/20b^3(N_e^v)^2a^2 \tag{8}$$

The relaxation function associated with a proton pair linked to a given submolecule characterized by a fixed end-to-end vector $\boldsymbol{r}_e^v$ is obtained as follows. In the molten state, $g^G(t)$ is replaced with:

$$g_{\boldsymbol{r}_e^v}^M(t) = \overline{\cos\left(\int_0^t dt'\varepsilon_0(\boldsymbol{a}(t'))\right)} \tag{9}$$

The average is calculated over all random values of the time function $\boldsymbol{a}(t)$), compatible with the fixed end-to-end vector $\boldsymbol{r}_e^v$. In other words, the average must be calculated considering the Ω_1 set of relaxation times and leaving the Ω_2 aside, because chains are supposed to be strongly entangled. A cumulant expansion is used to calculate $g_{\boldsymbol{r}_e^v}^M(t)$:

$$g_{\boldsymbol{r}_e^v}^M(t) = \frac{1}{2}\left[\exp[i\langle\varepsilon_0(\boldsymbol{a}(t))\rangle_{\boldsymbol{r}_e^v}t]\exp\left(-\int_0^t dt_1\int_0^{t_1} dt_2\langle\varepsilon_0(\boldsymbol{a}(t_1))\varepsilon_0(\boldsymbol{a}(t_2))\rangle_{\boldsymbol{r}_e^v}\right) + \text{c.c}\right] \tag{10}$$

or

$$g_{\boldsymbol{r}_e^v}^M(t) = \Gamma_{\boldsymbol{r}_e^v}^M(t)\gamma_{\boldsymbol{r}_e^v}^M(t) \tag{11}$$

The function

$$\Gamma_{\boldsymbol{r}_e^v}^M(t) = \cos[\langle\varepsilon_0(\boldsymbol{a}(t))\rangle_{\boldsymbol{r}_e^v}t] \tag{12}$$

reflects residual spin coupling interactions induced by entanglements, while the function

$$\gamma_{\boldsymbol{r}_e^v}^M(t) = \exp\left(-\int_0^t dt_1\int_0^{t_1} dt_2\langle\varepsilon_0(\boldsymbol{a}(t_1))\varepsilon_0(\boldsymbol{a}(t_2))\rangle_{\boldsymbol{r}_e^v}\right) \tag{13}$$

reflects internal motions of links within a given submolecule. The latter has the mathematical structure of formulae describing conventional relaxation processes in ordinary liquids. It will be roughly written as:

$$\gamma_{\boldsymbol{r}_e^v}^M(t) \simeq \exp(-t/T_{i,\boldsymbol{r}_e^v}) \tag{14}$$

where the relaxation rate $T_{i,\boldsymbol{r}_e^v}^{-1}$ depends upon the Ω_1 set. Here we are mainly interested in the $\Gamma_{\boldsymbol{r}_e^v}^M(t)$ function. The relaxation function of proton pairs observed over the whole sample is expressed as an average over all fixed end-to-end vectors of submolecules:

$$G^M(t) = \exp(-t/T_i)\int d\boldsymbol{r}_e^v\mathscr{P}(\boldsymbol{r}_e^v)\cos[\langle\varepsilon_0(\boldsymbol{a}(t))\rangle_{\boldsymbol{r}_e^v}t] \tag{15}$$

In the above formula, the dependence of T_2 upon $\boldsymbol{r}_e^v$ is considered as negligible; also $\mathscr{P}(\boldsymbol{r}_e^v)$ is defined as a Janssian distribution function:

$$\mathscr{P}(\boldsymbol{r}_e^v) = (2\pi N_e^v a^2/3)^{-3/2}\exp[-3(\boldsymbol{r}_e^v)^2/2N_e^v a^2] \tag{16}$$

It is convenient to define the second moment associated with the $\Gamma_{\boldsymbol{r}_e^v}^M(t)$ function:

$$M_2^M = -\int\left(\frac{d^2\Gamma_{\boldsymbol{r}_e^v}^M(t)}{dt^2}\right)_{t=0}\mathscr{P}(\boldsymbol{r}_e^v)d\boldsymbol{r}_e^v \tag{17}$$

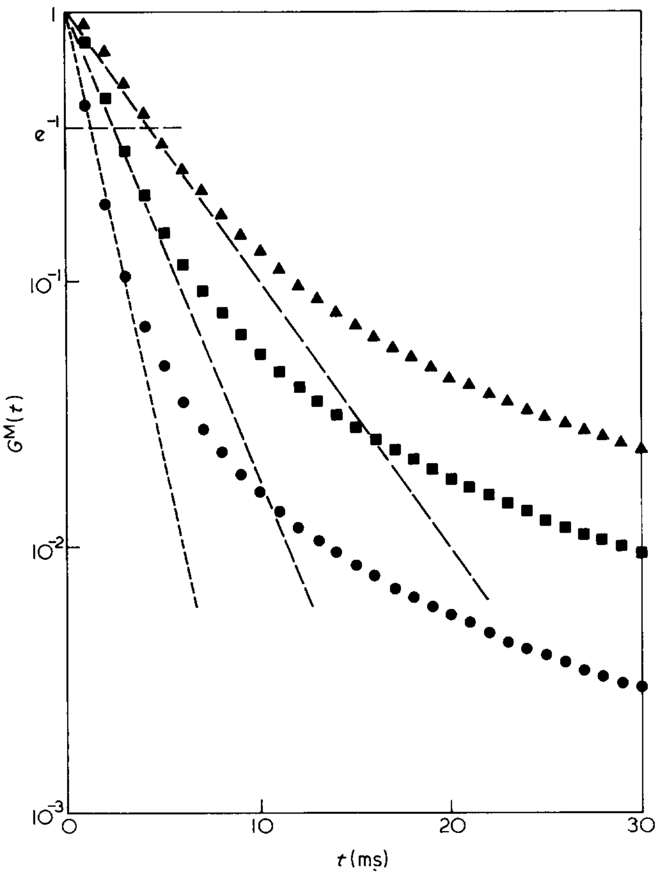

Figure 2 Numerical illustration of the relaxation function $G^{M}(t)$. Numbers of skeletal bonds are: ▲, $N_e^{\nu} = 148$; ■, $N_e^{\nu} = 83$; ●, $N_e^{\nu} = 38$

or

$$M_2^{M} = \int \langle \varepsilon_0(\boldsymbol{a}(t)) \rangle_{r_e^{\nu}}^2 \mathscr{P}(\boldsymbol{r}_e^{\nu}) \mathrm{d}\boldsymbol{r}_e^{\nu} \tag{18}$$

$$M_2^{M} = 0.6 M_2^{G}/(N_e^{\nu})^2 = 0.27 \gamma^4 \hbar^2/(N_e^{\nu})^2 b^6 \tag{19}$$

It is clearly seen from formula (19) that the strength of the dipolar coupling is divided by N_e^{ν}, when it is associated with a given submolecule. Formula (15) is easily calculated by noticing that X_e^{ν}, Y_e^{ν} and Z_e^{ν} components of the end-to-end vector $\boldsymbol{r}_e^{\nu}$ are independent of one another; the relaxation function $G^{M}(t)$ reads:

$$G^{M}(t) = \exp(-t/T_2)\left(\frac{1 + 3\theta^2 + [(1+3\theta^2)^2 + 4\theta^6]^{1/2}}{2[(1+3\theta^2)^2 + 4\theta^6]}\right)^{1/2} \tag{20}$$

with $\theta = t(M_2^{M})^{1/2}/3$. For large time values ($\theta \gg 1$), the relaxation function behaves like $\theta^{-3/2}$. As is expected, $G^{M}(t)$ differs from a pure exponential time function. The reference frequency involved in this time function is $(M_2^{M}/3)^{1/2} = (0.6 M_2^{G})^{1/2}/N_e^{\nu}$.

The relaxation function $G^{M}(t)$ was computed according to formula (20), with $T_2^{-1} = 0$. Three numbers of bonds were considered: $N_e^{\nu} = 38$, 83 and 148; corresponding relaxation functions are represented on *Figure 2*. It is clearly perceived that the $t^{-3/2}$ dependence of $G^{M}(t)$ induces a very slow decay of the magnetization amplitude, at large time values. Each free induction decay may be compared with a pure exponential time function, with a time constant, τ, defined from the amplitude $G^{M}(\tau) = 1/2$. Fast Fourier transforms $F^{M}(\Delta\nu)$ of the decays shown on *Figure 2* are drawn on *Figure 3*; they may be compared

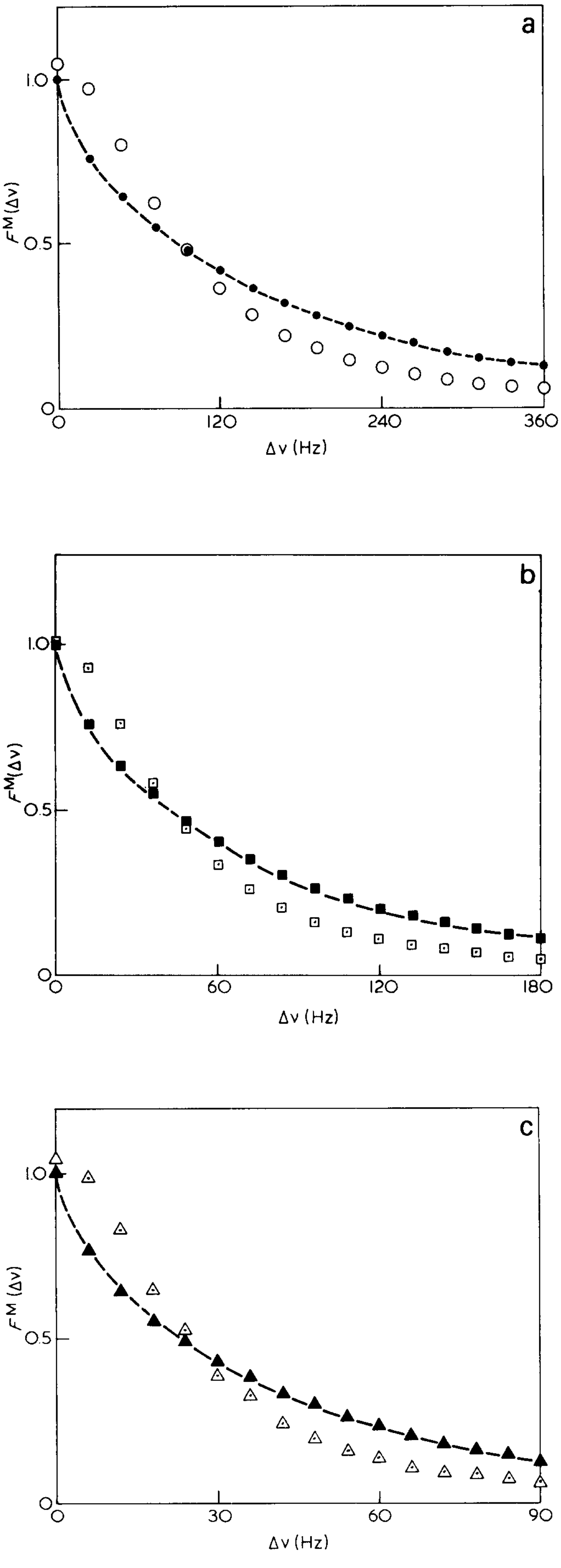

Figure 3 Fast Fourier transforms $F^{M}(\Delta\nu)$ of the decays shown on *Figure 2*. Numbers of skeletal bonds are: ▲, $N_e^{\nu} = 148$; ■, $N_e^{\nu} = 83$; ●, $N_e^{\nu} = 38$. Lorentzian curves associated with these $F^{M}(\Delta\nu)$ functions are also drawn (see text): ○ (A); □ (B); △ (C)

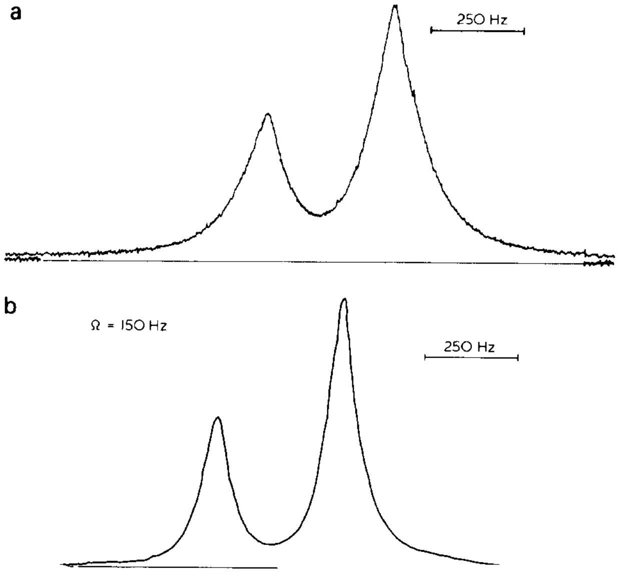

Figure 4 *cis*-1,4-Polybutadiene spectrum recorded at 100 MHz (297K): (a) without sample rotation; (b) with sample rotation at $\Omega = 150$ Hz

with Lorentzian lineshapes defined from the halfwidth, δ, corresponding to the half-amplitude of $F^{M}(\Delta\nu) = 1/2$. In the range $\Delta\nu \simeq \delta$, Lorentzian and $F^{M}(\Delta\nu)$ curves do not differ very much from each other; however, wing amplitudes of $F^{M}(\Delta\nu)$ curves are larger than wing amplitudes of Lorentzian curves. Resonance lines $F^{M}(\Delta\nu)$ are quite different from the well known spectrum resulting from a powder average of properties of a proton pair, characterized by a dipolar coupling strength depending only upon the orientation of the vector joining the two nuclei[21]. The average over all end-to-end vector lengths of submolecules in addition to the average over all orientations induces new properties. The distance, b, between two protons of a given pair was set equal to 1.78 Å, in the above numerical examples. Spectrum-narrowing effects induced by sample rotation and currently observed on real entangled chains should be described according to the above model by only dividing the second moment M_2^{M} by 4.

PROTON PAIRS: REAL CHAINS

The purpose of the present section is not to prove that the above model gives an exact description of the n.m.r. response obtained from real chains, it only aims to compare its predictions with properties actually observed; *cis*-1,4-polybutadiene chains were chosen because they are known to give a high density of entanglements[12]. The structural unit of these chains $\text{-(}CH_2\text{-}CH{=}CH\text{-}CH_2\text{)-}$, consists of two methylene groups and one methine group. The average chain molecular weight, $M_w \simeq 2 \times 10^5$, was determined from the intrinsic viscosity $[\eta] = 170\,\text{cm}^3\,\text{g}^{-1}$, measured in benzene at room temperature. It is now inferred that formula (8) expressing the residual tensorial spin coupling of a proton still applies to a real chain by introducing a factor $\beta(T)$, which takes rotational isomerizations into consideration (T is the temperature). Also, numerical factors coming from angular parameters are included in $\beta(T)$ because proton pairs are not directly bound to a skeletal bond as in the model; therefore:

$$\langle \varepsilon_0(\boldsymbol{a}(t)) \rangle_{\boldsymbol{r}_e^{\nu}} = 9\gamma^2 \hbar \beta(T)(3\cos^2\theta_{\boldsymbol{r}_e^{\nu}} - 1)(\boldsymbol{r}_e^{\nu})^2 20 b^3 (N_e^{\nu})^2 a^2 \tag{21}$$

This yields a relaxation function $(G^{M}(t))^*$ of the transverse component of the magnetization analogous with $G^{M}(t)$; the time variable has only been replaced with $t\beta(T)$. The *cis*-1,4-polybutadiene study consists of two steps. In the first one, experimental conditions are determined to observe residual dipolar interactions clearly; numerical comparisons with experimental results will be given in the second step.

Spectrum-narrowing effect

It is now well established that n.m.r. spectra observed on strongly entangled polymer chains exhibit a spectrum-narrowing effect induced by sample rotation, which is due to the presence of residual dipolar spin interaction. The linewidth must be exactly divided by 2 when the sample rotation axis is perpendicular to the steady magnetic field direction and when the contribution to the broadening mechanism comes from residual dipolar interactions only[7,29–31]. Spectra observed on a pure molten *cis*-1,4-polybutadiene sample at 297K without and with sample rotation are shown on *Figures 4a* and *4b*, respectively; they were recorded at 100 MHz using a WP 100 Bruker spectrometer. We first analyse methylene proton properties.

Methylene protons. It is seen from *Figures 4a* and *4b* that the halfwidth, δ, at half-amplitude, of the upper field resonance line is divided by 1.63 upon sample rotation, going from 75 to 46 Hz. Spectra were also run on a 60 MHz Jeol spectrometer at the same temperature (*Figures 5a* and *5b*); the same halfwidths of the upper field parts of the spectra were observed: 71.6 and 44.8 Hz, without and with sample rotation, respectively. It is clearly observed that the broadening mechanism of the resonance line is not significantly magnetic field dependent.

The linewidth is not divided by 2 during sample rotation because some of the chain relaxation times of the Ω_2 set are probably shorter than $[\langle \varepsilon_0(\boldsymbol{a}(t)) \rangle^* \boldsymbol{r}_e^{\nu}]^{-1}$, the inverse of the residual dipolar interaction strength. To

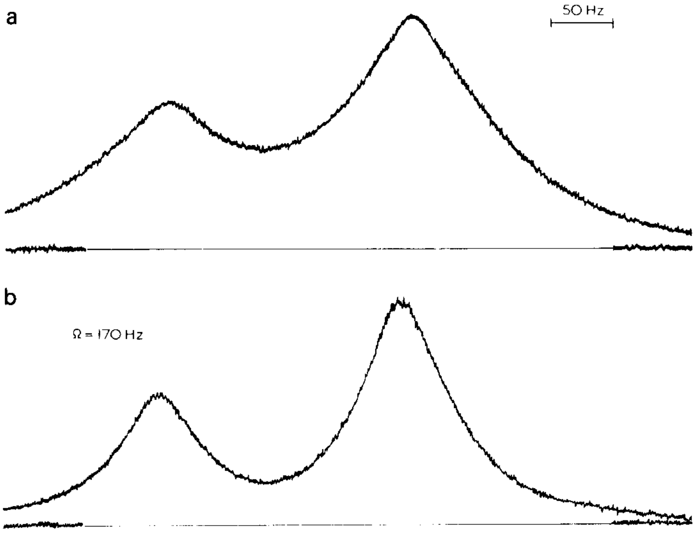

Figure 5 *cis*-1,4-Polybutadiene spectrum recorded at 60 MHz (197K): (a) without sample rotation; (b) with sample rotation at $\Omega = 170$ Hz

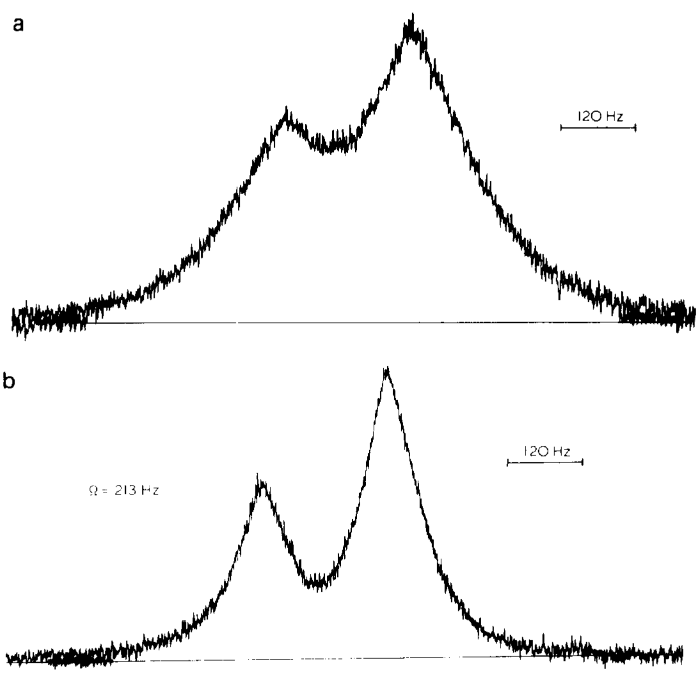

Figure 6 *cis*-1,4-Polybutadiene spectrum recorded at 60 MHz (274K): (a) without sample rotation; (b) with sample rotation at Ω = 213 Hz

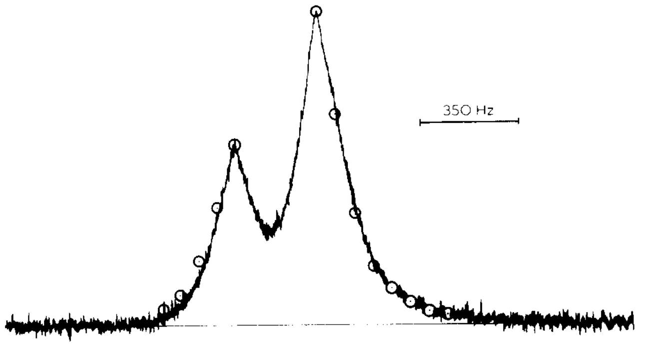

Figure 7 *cis*-1,4-Polybutadiene spectra recorded at 60 MHz (o) and 100 MHz are in coincidence with each other (274K)

lengthen these relaxation times, the sample was cooled to 274K, just above the melting point (273K). Resonance spectra run at 60 MHz at this temperature are shown on *Figures 6a* and *6b*. The halfwidth is now divided by nearly 2 (1.92) when the sample rotates at a frequency high enough (213 Hz) compared with the halfwidth equal to 105 Hz without sample rotation (this is equal to 55 Hz, during sample rotation). It is shown on *Figure* 7 that the upperfield parts of the $\left(CH_2 \right)$ resonance line observed at 60 and 100 MHz are exactly in coincidence with each other at 274K.

Methine protons. Similar observations were made on $\left(CH=CH \right)$ proton pairs at 297K (*Figures 4a* and *4b*); halfwidths at half-amplitude of the lower field part of the spectrum measured at 100 MHz were found to be equal to 80 and 48 Hz, without and with sample rotation, respectively. The same measurements performed at 60 MHz gave 75 and 43 Hz, respectively, at 297K (*Figures 5a* and *5b*). Halfwidth measurements of this lower field part of the spectrum performed at 274K and 60 MHz (*Figures 6a* and *6b*) and at 100 MHz (*Figure* 7) gave identical results: 108 and 56 Hz, without and with sample rotation, respectively.

Numerical analysis

We now consider that at 274K the average lifetime of entanglements is long enough to permit the observation of pure residual dipolar interactions associated with real submolecules.

Methylene protons. The unknown numerical factor $\beta(T)$ was set equal to unity. Formula (20) was found to fit experimental results observed on $\left(CH_2 \right)$ protons at 60 and 100 MHz, at 274K, by giving the value $(N_e^v)_{CH_2} = 80$ to the number of main bonds of an n.m.r. submolecule. The structural unit of *cis*-1,4-polybutadiene chains consists of three rotating skeletal bonds; accordingly, the number of structural units associated with $(N_e^v)_{CH_2}$ is about 30 and the average molecular weight of a submolecule (M_e^v) should be equal to 1600. The experimental value derived from viscoelastic measurements performed on *cis*-1,4-polybutadiene is equal to 1900 according to ref. 12. A broadening of theoretical resonance lines due to neighbouring protons and to the function $\gamma_{r_e^v}^{M}(t)$ was introduced through the exponential time function $\exp(-t/T_2^*)$ with $T_2^* = 4.2 \times 10^{-3}$ s; this is about 3 times the effective relaxation time $T_{2,exp} = 1.5 \times 10^{-3}$ s, obtained from the halfwidth at half-height of the experimental resonance line. A numerical fit was also made considering a resonance spectrum observed during sample rotation at 60 MHz. The numerical value of the dipolar coupling strength was supposed to be exactly divided by 2; the molecular weight of an n.m.r. submolecule was then found to be $(M_e^v)_{CH_2}^R = 2000$ with $(T_2^*)^R = 5.4 \times 10^{-3}$ s and $T_{2,exp}^R = 2.9 \times 10^{-3}$ s. Molecular weights of n.m.r. submolecules may be considered as determined within an uncertainty lower than 10%. The numerical fit is illustrated by *Figures 8a* and *8b*.

Methine protons. Numerical analysis was also performed considering $\left(CH=CH \right)$ proton pairs; the internal distance between two protons was set equal to $b = 2.43$; the average molecular weight of an n.m.r. submolecule was found to be $(M_e^v)_{CH} = 2000$; the broadening exponential function was characterized by $T_2^* = 1.8 \times 10^{-3}$ s, while $T_{2,exp} = 1.5 \times 10^{-3}$ s. Experimental curves and theoretical points are shown on *Figures 9a* and *9b*.

The numerical fit made from a resonance spectrum observed during sample rotation at 60 MHz also gave $(M_e^v)_{CH_2}^R = 2000$, with $T_2^* = 3.4 \times 10^{-3}$ s and $T_{2,exp} = 2.8 \times 10^{-3}$ s.

Conclusion

It is concluded from the above numerical analysis that the value of chain molecular weights, M_e^v, obtained from both $\left(CH_2 \right)$ and $\left(CH=CH \right)$ n.m.r. properties must be considered as a specific number, characterizing *cis*-1,4-polybutadiene chains, in the molten state. M_e^v is probably equivalent to the apparent average chain molecular weight defined from viscoelastic properties. This result shows that the two-set chain relaxation spectrum is an intrinsic property of molten polymer systems and that it is conveniently reflected by n.m.r. properties. The above study also shows that the low reference frequency associated with pure residual spin interactions which must be used to observe slow chain diffusion processes must be

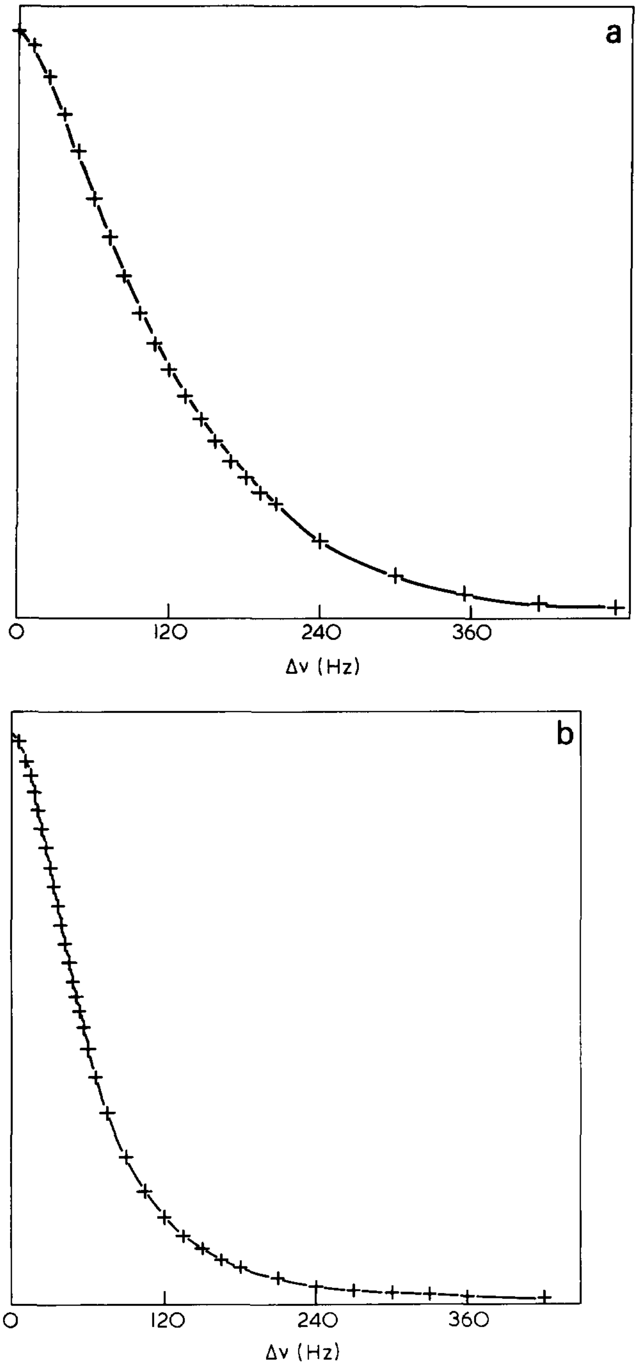

Figure 8 Numerical points (+) derived from formula (20) are compared with the $\text{-}(CH_2)$ resonance line observed at 60 MHz (274K): (a) without sample rotation; (b) with sample rotation

extracted from the linewidth actually measured. For example, at 274K, the halfwidth measured on $\text{-}(CH_2)\text{-}$ proton is 105 Hz, while the pure residual dipolar interaction is 67 Hz. The reasonable adjustment of parameter values of the model to experimental spectra does not demonstrate that this model is an exact description; however, it may serve as a convenient tool to illustrate effects of chain entanglements on free induction decays.

METHYL GROUPS

We now consider methyl groups rotating around their threefold axis while this axis is supposed to be rigidly bound to a chain skeleton.

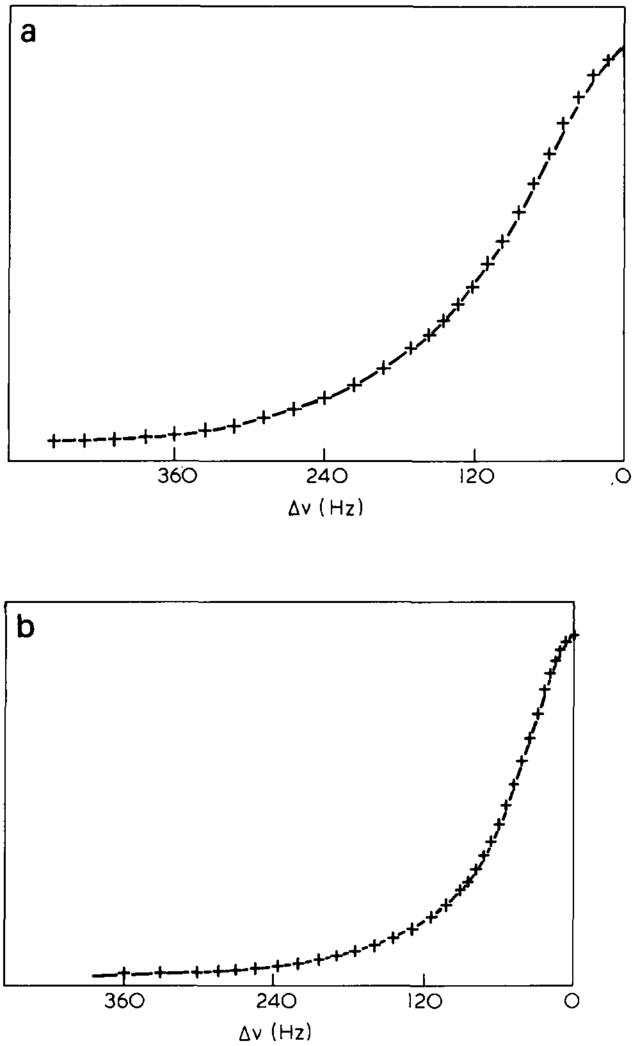

Figure 9 Numerical points (+) derived from formula (20) are compared with the $\text{-}CH\text{-}CH\text{-}$ resonance line observed at 60 MHz (274K): (a) without rotation; (b) with rotation

The glassy state

It is considered that in the glassy state the *c*-axes of all methyl groups have fixed orientations, at random in space; but every methyl group is supposed to be free to rotate around its own axis. N.m.r. properties of such a rotating three-spin system have already been studied taking internal dipolar interactions into consideration[18,32,33]. We only recall that in the eight-dimensional space of the spin system, only four Zeeman energy levels are shifted to the first order of perturbation, by dipolar interactions of the three nuclei; these four levels correspond to quantum numbers ($m = \pm 1/2$, $\pm 3/2$) associated with the quantum number $J = 3/2$ of the resultant angular momentum of the spin system. The Zeeman energy level shifts are $-\bar{J}$ for $m = \pm 3/2$ and $\bar{J}$ for $m = \pm 1/2$, respectively; $\bar{J}$ is defined from the mean dipolar interaction of any two spins i and j, in a rotating $\text{-}(CH_3)\text{-}$ proton group:

$$\bar{J} = 3\bar{A}_{ij}/2 \qquad (22)$$

with

$$A_{ij} = \gamma^2\hbar(3\cos^2\theta_{ij} - 1)/2r_{ij}^3 \qquad (22')$$

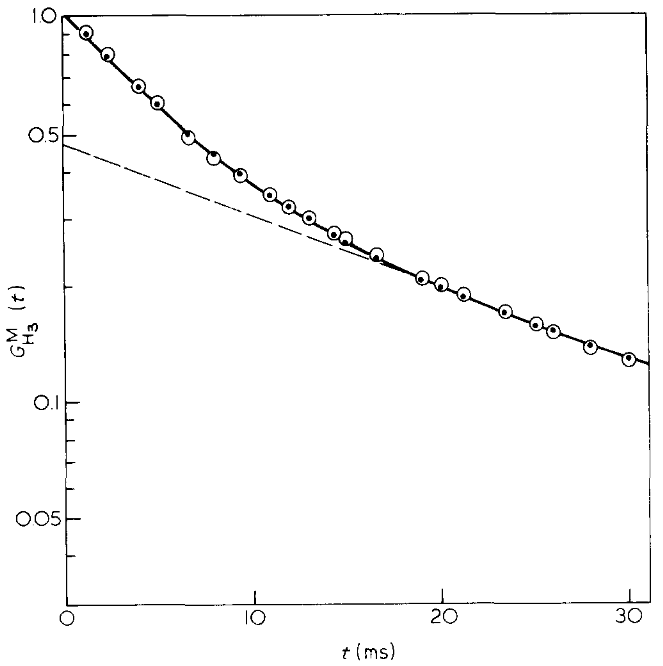

Figure 10 Spin-echo decay observed on PDMS chains in a highly concentrated solution (C = 0.95 g cm^{-3}), at 297K and 32 MHz: experimental points (●) and theoretical points (o)

θ_{ij} is the angle between the external field $\boldsymbol{B}_0$ and r_{ij}, the vector connecting nuclei i and j. Because of the rotation of a methyl group around its c-axis, the average of the dipolar interactions A_{ij} has a value which depends only on the orientation of the c-axis with respect to the steady magnetic field direction:

$$\bar{J}(c) = 3\gamma^2\hbar(3\cos^2\eta - 1)/8b^3 \qquad (23)$$

b is the smallest distance between any two nuclei; η is the angle between the external field and the rotation axis. The whole relaxation function of the transverse magnetic component of a rotating three-spin system reads:

$$G^{G}_{H_3}(t) = [\langle\cos(2\bar{J}(c)t)\rangle_{\text{orient}} + 1]/2 \qquad (24)$$

A part of the relaxation function is not governed by internal dipolar interactions. The constant term would of course disappear by considering external dipolar interactions between several methyl groups.

The molten state: real chains

The whole description of proton pair properties proposed in the second section hold for methyl groups since $\varepsilon_0(\boldsymbol{a}) = 2\bar{J}(c)$. We now consider long polymer chains in the molten state assuming the presence of n.m.r. submolecules due to entanglements. From formulae (20) and (24), the transverse magnetic relaxation function is supposed to be expressed as:

$$G^{M}_{H_3}(t) = [G^{M}(t) + 1]/2 \qquad (25)$$

It is not necessary to give a numerical illustration of $G^{M}_{H_3}(t)$; this can easily be derived from *Figures 2* and *3*. To illustrate n.m.r. properties actually observed on methyl groups, we chose to perform n.m.r. measurements on long PDMS chains ($M_w \simeq 4\times10^5$), at a high concentration ($C \simeq 0.95$ g cm^{-3}) in deuterated chloroform. A typical decay obtained from a spin-echo experimental procedure is shown on *Figure 10*. Two parts of the transverse magnetic relaxation function are clearly seen. In accordance with formula (25), it is considered that the long decay reflects a relaxation mechanism due only to external dipolar interactions between neighbouring methyl groups; it is conveniently described by the function $\exp(-t/T_2^*)$ with $T_2^* = 2\times10^{-2}$ s. This mechanism is also involved in the first decay, of course. The theoretical curve was found to fit experimental points by assuming that the number of links per n.m.r. submolecule is equal to $N_e^v = 222$, which corresponds to an apparent average chain molecular weight between coupling junctions equal to $M_e^v = 8224$. The apparent molecular weight determined from viscoelastic measurements given in ref. 2 is equal to 8100. N.m.r. measurements described above were performed at room temperature, and at a Larmor frequency equal to 32 MHz; the least-square fits based on the two parameters T_2^* and N_e^v gave an uncertainty lower than 5%. It is noticed that once again viscoelastic and n.m.r. measurements give similar results.

CONCLUSION

The purpose of the present paper was first to establish a simple model illustrating magnetic relaxation properties of proton pairs linked to strongly entangled chains. This model was then compared with n.m.r. spectra observed from real chains such as *cis*-1,4-polybutadiene and polydimethylsiloxane. A reasonable agreement between experimental results and the theoretical description was obtained, leading to the conclusion that the splitting of the chain relaxation spectrum into two well defined dispersions may be perceived from n.m.r.

The submolecule thus defined must be pictured as a small space volume ($\simeq 10^4$ Å^3) where a given chain segment is temporarily confined; as a consequence of this confinement, monomer units may be considered as experiencing a field of angular constraints giving rise to a partial orientational order unambiguously perceived from n.m.r. It has been recognized for some time that the temporary network evoked above to picture effects of entanglements on n.m.r. properties easily is not adequate. De Gennes proposed that the effect of topological constraints on the motion of polymer molecules could be treated in terms of a tube constraint[25,34]. The n.m.r. subchain may be identified with the submolecule of a Rousekiin enclosed within such a fixed tube.

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