Macromolecules 1985, *18*, 1101-1109

Nuclear Magnetic Resonance Investigations of Properties of the Terminal-Chain Diffusional Spectrum of Molten Poly(dimethylsiloxane)

J. P. Cohen Addad* and R. Dupeyre

Laboratoire de Spectrométrie Physique, Université Scientifique et Médicale de Grenoble, BP 87, 38402 St. Martin d'Heres Cedex, France.

Received July 18, 1984

ABSTRACT: Fractionated poly(dimethylsiloxane) samples were used to attempt to characterize the terminal-chain diffusional spectrum in a melt, by observing the relaxation process of transverse magnetic components of protons or ^{13}C nuclei, attached to polymer chains. The intrinsic viscosity and the radius of gyration of studied samples were shown to obey satisfactory chain molecular weight dependences. The residual energy of dipole–dipole interactions of protons, expressed in frequency units ($\simeq$60 Hz), was used as an internal reference to control the chain relaxation spectrum. Disentanglement NMR curves observed from ^{13}C nuclei and protons by varying the chain molecular weight of samples were found to be similar to each other. This basic result indicates that single-chain magnetic properties are observed although all chains are in dynamical interaction with one another. The macroscopic rotation of samples was shown to compete with chain diffusional processes. The chain diffusional model was characterized as a function of the weight-average chain molecular weight $\bar{M}_w$, in the range $10^5 \leq \bar{M}_w \leq 10^6$; the best agreement with experimental results was obtained from a terminal relaxation time T_{Re} depending upon $\bar{M}_w$ according to the relationship $T_{Re} \propto (\bar{M}_w)^{3\pm0.3}$, in reasonable agreement with the reptational model, while the chain relaxation is described from a multiple-mode terminal spectrum. The order of magnitude of T_{Re} is 3 s, at 303 K, for $\bar{M}_w = 10^6$.

I. Introduction

It has been long recognized that low-frequency viscoelastic properties of a polymer melt are closely related to diffusional effects of long macromolecules through entanglements that they can form. Both the mean square displacement of any point of a chain in a melt and the stress relaxation modulus of the melt, in the terminal region, are currently expressed from similar formulas; the same basic dynamics parameters characterize both properties. If one uses, for example, the model of chain reptation proposed by de Gennes,[1] the mean square displacement $\langle \Delta\vec{r}_n^{\,2}(t) \rangle$ of a labeled point $\vec{r}_n(t)$ of any chain, corresponding to a time interval t, is expressed as

$$\langle \Delta\vec{r}_n^{\,2}(t) \rangle = 6D_S t + \sum_{p=1}^{\infty} \frac{4\sigma_T^2}{\pi^2 p^2} \cos^2\left(\frac{\pi p n \sigma_e^2}{\sigma_T^2}\right)(1 - \exp[-p^2 t/T_{Re}]) \tag{1}$$

where D_S is the center of mass self-diffusion coefficient of a chain in the melt, σ_T^2 is the mean square end-to-end distance of the real chain (this is divided into submolecules), the mean square end-to-end distance of a submolecule is σ_e^2, and $T_{Re} = \sigma_T^2/(3D_S\pi^2)$ is the terminal relaxation time.[2]

Correspondingly, the stress relaxation modulus calculated by Doi and Edwards according to the same model of chain reptation is written as[3]

$$G(t) = (8G_N^0/\pi^2) \sum_{p=1}^{\infty} \frac{e^{-tp^2/T_{Re}}}{p^2} \tag{2}$$

where G_N^0 is the plateau modulus.

Formulas 1 and 2 clearly show that the viscoelastic behavior of polymer systems is a macroscopic property induced by macromolecular motions, as expected. They illustrate the nature of the relationship which may exist between chain diffusional effects and viscoelastic properties. Also, it is worth emphasizing from formula 1 that diffusional properties of a macromolecule in a melt may exhibit a complex time dependence involving a spectrum of relaxation modes ($t < T_{Re}$). These are not observed with experimental procedures intended to measure only diffusion coefficients in molten polymers. Most experimental methods are actually based on the observation of labeled chains using radiotracers[4] or partly deuterated macromolecules.[5] A so-called forced Rayleigh light scattering technique has been recently developed;[6] this elegant method corresponds to a measurement of the time interval necessary for chains labeled with a photochromic probe to explore a calibrated diffusion path; this is defined from a pattern of interference fringes; diffusion coefficients of long chains in semidilute solutions accurately measured according to this experimental procedure are in agreement with the dependence upon the chain molecular weight M, predicted from the model of chain reptation[7]

$$D_S \propto M^{-2} \tag{3}$$

A pulsed field gradient NMR method has been recently shown to conveniently apply to measurements of chain diffusion coefficients larger than about 10^{-9} cm^2·s^{-1}; it does not necessitate any labeling of macromolecules;[8] however, the analysis of the spin-system response may give rise to some ambiguity when long chains are observed; this method id appropriate to studies of dilute or semidilute solutions.

The purpose of the present paper is to illustrate an NMR approach to the characterization of the diffusion process of a chain in molten polymers. This method was developed by observing the transverse magnetization of protons attached to poly(dimethylsiloxane) (PDMS) macromolecules. It is based on a comparison of the spectrum of chain relaxation modes with a low internal NMR reference frequency ($\simeq 10^2$ Hz).[9] This can be done by observing the loss of quantum coherence of nuclear spins instead of observing the exchange of energy between the spin system and its thermal bath;[10] this resonant exchange would allow the characterization of molecular motions occurring only about the Larmor frequency. Furthermore, the present approach permits not only the evaluation of the terminal relaxation time T_{Re} of a chain in a melt but also the qualitative characterization of its terminal relaxation spectrum. Similar studies concerning concentrated solutions of polystyrene or of polyisobutylene chains have been already reported.[11,12] The best agreement of experimental results with the proposed interpretation

0024-9297/85/2218-1101$01.50/0

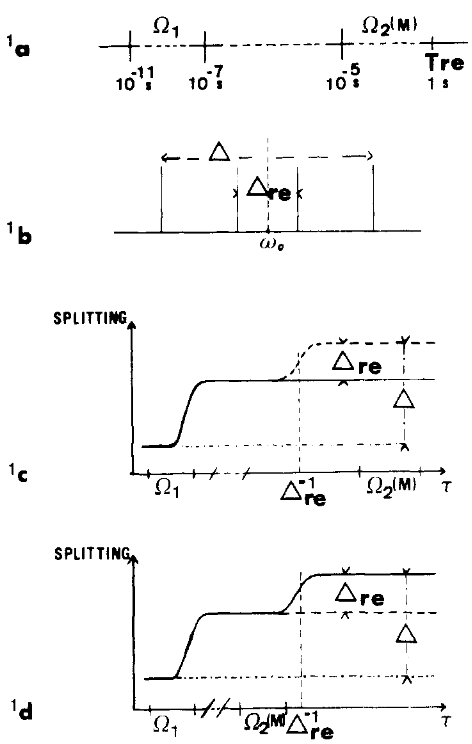

Figure 1. (a) Two-dispersion chain relaxation spectrum. (b) Δ: fine structure of a fixed proton pair; Δ_{re}: partial fine structure. (c) Schematic motional averaging for long chains. (d) Schematic motional averaging for short chains.

was obtained by mixing properties of both the reptation model and the Rouse model.[13]

Before we report experimental results, the principle of NMR observation of chain migration in a melt will be recalled in the next section.

II. Principle of NMR Observation

The principle of NMR characterization of chain migration in a melt is based on the description of a two-step motional averaging of nuclear spin interactions responsible for the spin-system response. The theoretical support has been developed in several papers previously published;[9-12] it rests upon a few basic features which may be illustrated in the following qualitative way.[14]

A. Chain Relaxation Spectrum. The only basic hypothesis used to analyze properties of the transverse nuclear magnetization dynamics observed in strongly entangled macromolecules is to assume that the broad spectrum of relaxation times characterizing any long chain consists of two well-separated dispersions called Ω_1 and $\Omega_2(M)$.[15] Suppose the observation of motions of a given chain starts at an initial time t_0; then this chain cannot be pictured as moving all its points at any time; in a first step, it is supposed to be divided into temporary submolecules defined by some points considered as temporarily frozen; these fixed points may be supposed to experimence the zero resultant of many topological constraints exerted on chain segments. The size of temporary submolecules is usually characterized on average from the apparent molecular weight between coupling junctions:

$$M_e \simeq \rho RT/G_N^0 \qquad (4)$$

ρ is the undiluted polymer density and G_N^0 is the plateau modulus.[16] The dispersion Ω_1 is associated with local motions occurring within submolecules; Ω_1 does not depend upon the chain molecular weight; submolecule; relaxation times of the Ω_1 dispersion usually range from about 10^{-11} to about 10^{-7} s.

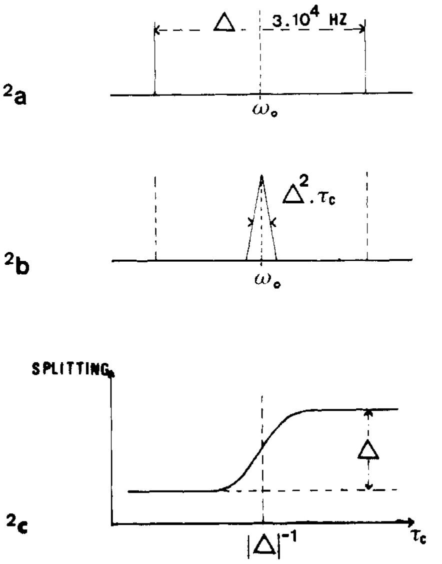

Figure 2. (a) Fine structure of a fixed proton pair. (b) Motional averaged line width. (c) Spectrum-narrowing effect.

In the second step of the observation of chain motions, temporarily fixed points start slowly moving and submolecules progressively lose their orientational memory and vanish when the relaxation process of the whole chain is completed. These collective motions of all parts of a chain are governed by the dispersion $\Omega_2(M)$, also called the terminal relaxation spectrum (Figure 1a); they strongly depend upon the chain molecular weight M and the terminal relaxation time $T_{Re} \propto \sigma_T^2/D_S$ is expected to vary as M^3 according to the reptation model.

B. Spectrum-Narrowing Effect. The spectrum of any fixed proton pair (H_2O in ice; a CH_2 group in the glassy state) exhibits a fine structure consisting of two resonance lines (Figure 2a); this well-known property is induced by the dipole–dipole interaction of the two nuclei.[17,18] The splitting Δ depends upon the orientation $\theta_{\vec b}$ of the vector $\vec b$ joining the two nuclei with respect to the steady magnetic field direction B_0:

$$\Delta(\vec b) = 2D_p(1 - 3\cos^2\theta_{\vec b}) \qquad (5)$$

$D_p = 3\gamma_p^2\hbar/4b^3$ is the dipole–dipole interaction; γ_p is the gyromagnetic ratio of a proton; b is the proton–proton distance. The order of magnitude of D_p is $2\pi(2 \times 10^4)$ rad·s^{-1} for $b = 1.6$ Å.

The progressive onset of the rotational diffusion of the proton pair induces an averaging effect of the dipole–dipole interaction; the fine structure is expected to collapse as soon as the statistical period of rotation τ_c of the proton pair is smaller than $|\Delta|^{-1}$:

$$\tau_c|\Delta| \lesssim 1 \qquad (6)$$

Then, a single central line is observed; its width is proportional to $|\Delta| \times |\Delta|\tau_c$, which is much less than $|\Delta|$, assuming isotropic molecular motions.

This well-known property, also called a spectrum-narrowing effect,[19] is used to conveniently estimate τ_c from the measurement of $|\Delta|$ (Figure 2b,c).

C. A Specific Polymer Chain Effect. Consider now noninteracting proton pairs attached to long chains in a pure polymer sample. The spectrum of any given proton pair observed in the glassy state is characterized by a fine structure. Then, a spectrum-narrowing effect is induced when the sample temperature is raised above the glass transition temperature T_g. This effect has been used as a way to roughly determine the glass transition temperature range. However, a two-step rotational average of the fine structure is expected to occur because of the two dispersions Ω_1 and Ω_2 of the spectrum of relaxation times of a chain. Starting observations again from an initial time t_0, the first step of the rotational average associated with the Ω_1 dispersion is expected to lead to only a partial reduction of the splitting of the fine structure of a given proton-pair spectrum. The diffusional motion of any monomeric unit cannot be considered as fully isotropic during the first step; accordingly, there exists a temporary residual splitting Δ_{re} of the fine structure. The order of magnitude of $|\Delta_{re}|$ is usually $2\pi \times 10^2$ rad·s^{-1} (Figure 1b).

Two situations must now be examined to take the second step of the motional averaging process into consideration. Considering first the limiting case of the polymer melt made of very long entangled chains, the dispersion $\Omega_2(M)$ may be considered as much longer than $|\Delta_{re}|^{-1} \simeq$ 1 ms; consequently, the motional averaging condition (6) applied to the residual fine structure $|\Delta_{re}|$ cannot be fulfilled (Figure 1c). The spin-system response is then governed by Δ_{re} and exhibits solidlike properties; it is called a pseudosolid response. This is easily controlled from a spectrum-narrowing effect induced by rotating the polymer sample at a frequency slightly higher than $|\Delta_{re}|$.[20] The pseudosolid response of *cis*-1,4-polybutadiene has been recently observed from NMR coherent averaging methods, too.[21] The other limiting case corresponds to a polymer melt made of chains small enough to give a dispersion $\Omega_2(M)$ entirely shorter than $|\Delta_{re}|^{-1}$. Then, temporary submolecules keep their own specific properties but they move faster; accordingly, the residual fine structure is averaged to near zero within a time interval $\Omega_2(M)$ compatible, with the time scale of NMR measurements; a single line must be observed. There is a liquidlike spin-system response (Figure 1d).

Clearly, the residual quantity $|\Delta_{re}|$ plays a role of an internal reference frequency characterizing a given polymer system. The pseudosolid spin-system response is a specific NMR property of entangled polymer chains.

D. Temporary Average Orientational Order. The temporary residual splitting Δ_{re} has already been calculated by using a model built from noninteracting proton pairs attached to freely jointed skeletal bonds of equal length a of a chain segment; the state of a given submolecule is represented as being fully characterized by its temporary end-to-end vector $\vec{r}_e$ during the first step of the motional averaging:

$$\Delta_{re}(\vec{r}_e,N) = 0.67\Delta_G \vec{r}_e \begin{bmatrix} 1 & & \\ & 1 & \\ & & -2 \end{bmatrix} \vec{r}_e / N_e^{\,2}a^2 \qquad (7)$$

a may be considered as the average bond length^2; $\Delta_G{}^2$ is the second moment of the resonance line which would be observed on noninteracting proton pairs in the glassy state ($\Delta_G = 0.9D_p$). N_e is the number of bonds in a submolecule. Formula 7 actually reflects the reduction of chain entropy induced by the nonzero end-to-end vector $\vec{r}_e$; the smaller the number of bonds or the longer the end-to-end vector $|\vec{r}_e|$, the stronger the deviation of monomeric motions from isotropic rotation; $|\Delta_{re}|$ also measures a small temporary average orientational order of skeletal bonds, associated with the temporary end-to-end vector $\vec{r}_e$; it corresponds to a transfer of NMR properties from a space scale about equal to 2 Å (rotational isomerization) to a space scale about equal to 30 Å and determined from the root mean square dimension of a temporary submolecule. The validity of the dependence of Δ_{re} predicted from fromula 7 upon both $|\vec{r}_e|$ anmd N_e variables has been shown from NMR measurements performed on real elementary chains of calibrated poly(dimethylsiloxane) (PDMS) gels, using a methyl group as a probe instead of a proton pair;[22] three-spin systems and two-spin systems have similar NMR properties; the right-hand side of eq 7 is the first term of a series expansion of a general function of $\vec{r}_e$, the width of which is much broader than that of the Gaussian probability distribution function of the end-to-end vector $\vec{r}_e$.[20]

During the second step of the motional averaging process end-to-end vectors of submolecules are supposed to be slowly fluctuating time functions $\vec{r}_e(t)$ associated with the $\Omega_2(M)$ dispersion. Throughout the present paper, we are mainly interested in collective motions of all end-to-end vectors along a given chain.

III. Experimental Section

Fractionated PDMS samples were prepared to eliminate possible effects of polydispersity on NMR properties.

A. Fractional Precipitation. Three commercially available polymer samples, called PDMS 4, PDMS 6, and PDMS 9, were supplied by Rhône-Poulenc Recherches, with the following specific characteristic parameters: $\bar{M}_w = 0.12 \times 10^6$ ($I = 1.78$), $\bar{M}_w = 0.67 \times 10^6$ ($I = 1.67$), and $\bar{M}_w = 2.8 \times 10^6$ ($I > 2$), respectively (I is the polydispersity ratio). We measured the following intrinsic viscosities in toluene $[\eta] = 0.44$, 1.32, and 3.54 dL·g^{-1}, respectively.

Fractional precipitation of poly(dimethylsiloxane) chains was performed by using benzene or toluene as good solvents while acetone or methanol was added as a nonsolvent. The successive fractions were obtained from dilute solutions by stepwise decrease of the temperature from 310 to 292 K. The three polymer samples were separated into about 10 fractions; fractions weights lay between 0.1 and 2.5 g; the total recovery of the polymer weight was about 90%. Fractionation results corresponding to the three original samples are shown in the form of three cumulative weight distribution curves vs. the intrinsic viscosity (Figure 3).

A Schott-Geräte capillary viscosimeter (Ubbelohde type) with an automatic dilution device was used to carry out intrinsic viscosity measurements in dilute toluene solutions at 298 K.

B. Elastic Light Scattering. Light scattering measurements were performed by using an atomatic Fica 50 photometer; data corresponding to 11 scattering angles going from 50° to 150° were obtained at 298 K with an unpolarized light of wavelength 546 nm; the specific index increment was given the known value $dn/dc = 0.093$ mL·g^{-1}. The weight-average characterization $\bar{M}_w$ and the root mean square radius of gyration R_G were obtained from a Zimm graphical plot. Figure 4 shows the log–log plot of the intrinsic viscosity $[\eta]$ in toluene vs. the average molecular weight $\bar{M}_w$, obtained from light scattering data. The set of data corresponding to fraction molecular weights lying from 1.2×10^5 to 3.0×10^6 was found to fit a straight line, yielding the following equation:

$$[\eta] = 12.4 \times 10^{-3}(\bar{M}_w)^{0.70\pm0.06}$$

Also, the root mean square radius of gyration R_G in toluene is represenced as a function of the average molecular weight $\bar{M}_w$ in Figure 5; the log–log plot was found to fit a straight line corresponding to the power law:

$$R_G = 0.27(\bar{M}_w)^{0.55\pm0.06}$$

The two foregoing power laws are in reasonable agreement with the dependences upon chain molecular weight predicted from usual descriptions of properties of dilute polymer solutions in good solvents.[23]

It is seen from Figures 4 and 5 that the best fits were obtained from fractions prepared from the commercial polymer sample called PDMS 4 and corresponding to the lowest average molecular weight (0.12×10^6); we consider that narrower fractions were prepared from this sample than from the two other ones. All NMR measurements were performed on fractions fitting the linear log–log plot, with polydispersity ratios determined from gel permeation chromatography and lying from 1.25 to 1.4.

C. NMR Measurements. Proton spectra were run on a Jeol spectrometer and a WP 100 Bruker spectrometer operating at

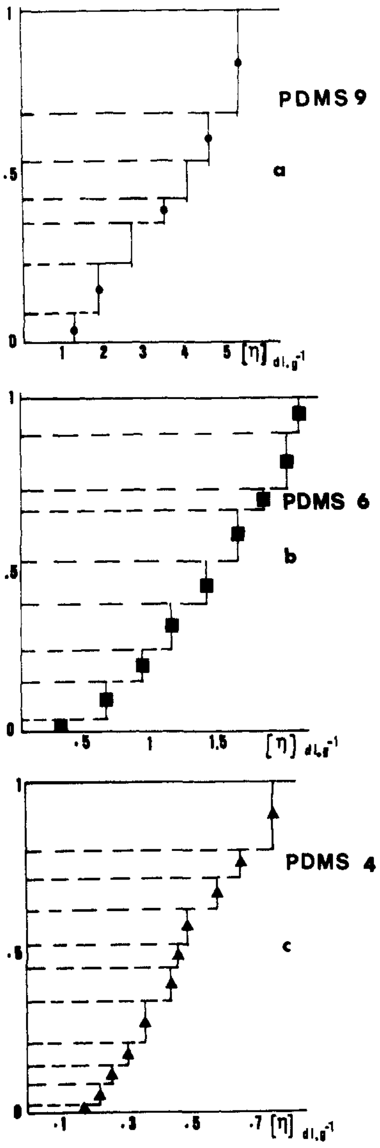

Figure 3. Cumulative weight distribution curves vs. the intrinsic viscosity [η]: (a) PDMS 9; (b) PDMS 6; (c) PDMS 4.

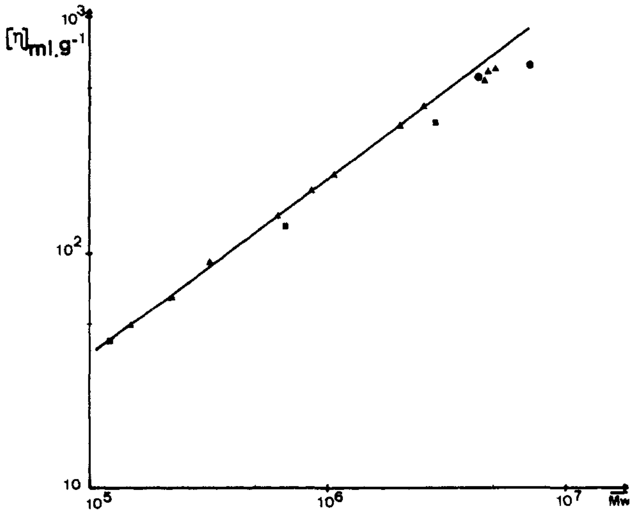

Figure 4. Intrinsic viscosity of fractionated samples (key to points is the same as in Figure 3) vs. the weight-average molecular weight M_w.

60 and 100 MHz, respectively; ^{13}C NMR spectra were run on a WP 100 Bruker spectrometer; they were accumulated about 10^4 times, with heteronuclear gated decoupling.

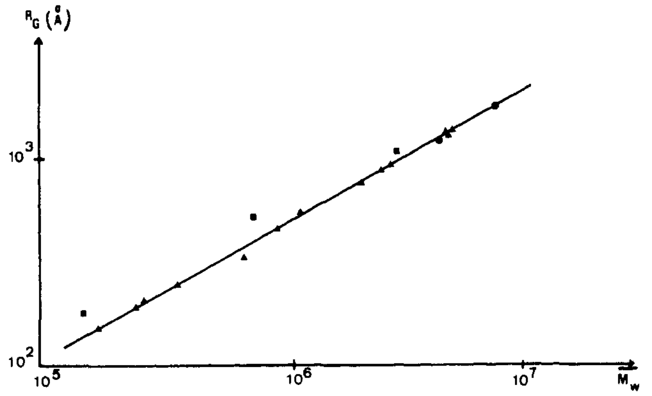

Figure 5. Radius of gyration of fractionated samples (key to points is the same as in Figure 3) vs. the average molecular weight $\bar{M}_w$.

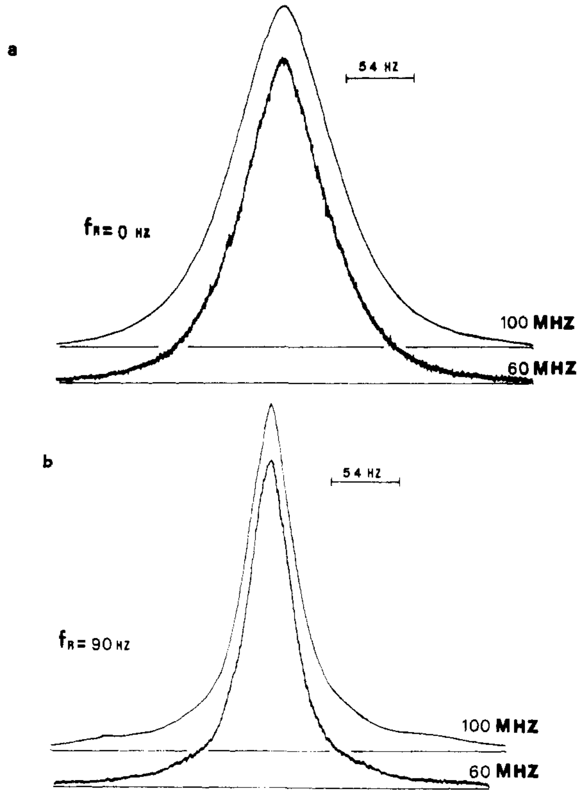

Figure 6. Proton spectra observed on PDMS ($\bar{M}_w = 1.5 \times 10^6$), at 310 K, at 60 and 100 MHz, respectively: (a) without sample rotation, (b) during sample rotation.

IV. Disentanglement NMR Curves

A. Slow Disentanglement Kinetics. The average residual energy $\hbar\Delta_e$ of dipole–dipole interactions was determined from the half-width at half-height of the resonance line observed on high chain molecular weight fractionated sample ($M_w \simeq 2.5 \times 10^6$) at 310 K: $\Delta_e/2\pi = 56.0$ Hz. The pseudosolid response of proton spins was characterized from a spectrum-narrowing effect induced by the rotation of the sample at a frequency $f_R = 90$ Hz. The cylindrical sample was rotating around an axis perpendicular to the steady magnetic field direction. This non-magic angle rotation is known to divide the dipole–dipole interaction strength by two instead of reducing it to zero (Figure 6a,b). Proton spectra observed without sample rotation were recorded at 60 and 100 MHz; they were found to be identical; also, spectra recorded at 60 and 100 MHz during sample rotation are similar. This result clearly proves that no diamagnetic effects due to possible sample inhomogeneities govern the spin-system response.

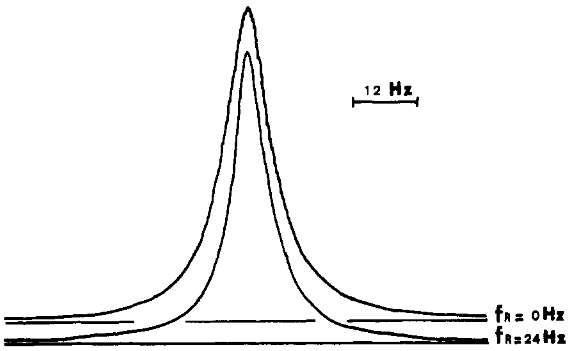

Figure 7. Proton spectra observed on PDMS ($\bar{M}_w = 7 \times 10^4$), at 310 K, at 60 MHz with or without sample rotation.

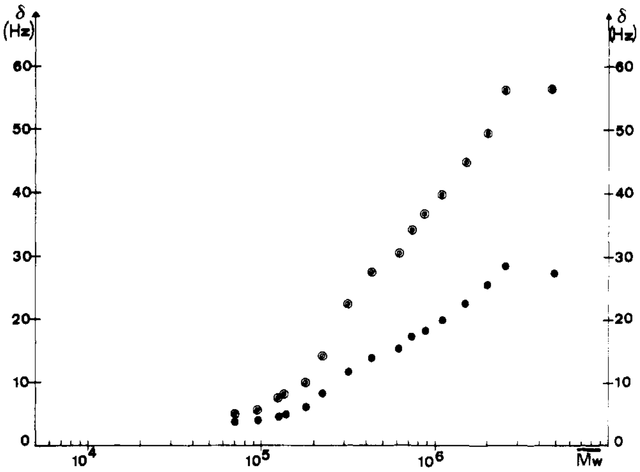

Figure 8. Disentanglement NMR curve observed from proton spectra at 310 K as a chain molecular weight function: (●) during sample rotation, (⊙) without sample rotation.

Therefore, it is concluded that the terminal relaxation spectrum $\Omega_2(M)$ is somehow longer than the inverse of the residual energy measured in angular frequency units:

$$T_\nu = (2\pi\Delta_e)^{-1} = 2.9 \times 10^{-3} \text{ s}$$

B. Fast Disentanglement Kinetics. Then, a low chain molecular weight fractionated sample ($M_w = 7 \times 10^4$) was observed at 310 K. The half-width at half-height of the resonance line was found to be equal to $\delta_l = 5$ Hz; no spectrum-narrowing effect could be detected upon sample rotation at a frequency $f_R = 24$ Hz (Figure 7). This result now shows that the chain relaxation spectrum $\Omega_2(M)$ is entirely shorter than T_ν, whatever its exact structure. A liquidlike response of the spin system was observed.

The purpose of the present paper is to analyze the transition of NMR properties from a pseudosolid spin-system response to a liquidlike one, in order to characterize the chain relaxation spetrum $\Omega_2(M)$.

C. Disentanglement NMR Curve. Figure 8 illustrates the progressive narrowing effect of proton resonance lines obtained by observing several molten polymer samples made of shorter and shorter PDMS chains; this narrowing effect necessarily reflects a shift of the terminal-chain relaxation spectrum toward shorter values, induced by decreasing the average chain molecular weight $\bar{M}_w$ from about 2×10^6 to about 10^5; correspondingly, the rate of dissociation of chain entanglements is considerably increased since it is predicted to vary as a $(\bar{M}_w)^3$ function. This is the reason that the curve represented in Figure 8 was called a disentanglement NMR curve. It is worth emphasizing that this curve not only describes a quantitative spectrum-narrowing effect from about 60 to 5 Hz but also corresponds to a qualitative change of the spin-system properties going from a pseudosolid response to a nearly liquidlike one. Figure 8 also shows the spectrum-narrowing effect observed upon rotation of the sample tube at a frequency faster than Δ_e. The factor of line-width reduction starts being smaller than 2 from an average chain molecular weight M_w smaller than about 6×10^5.

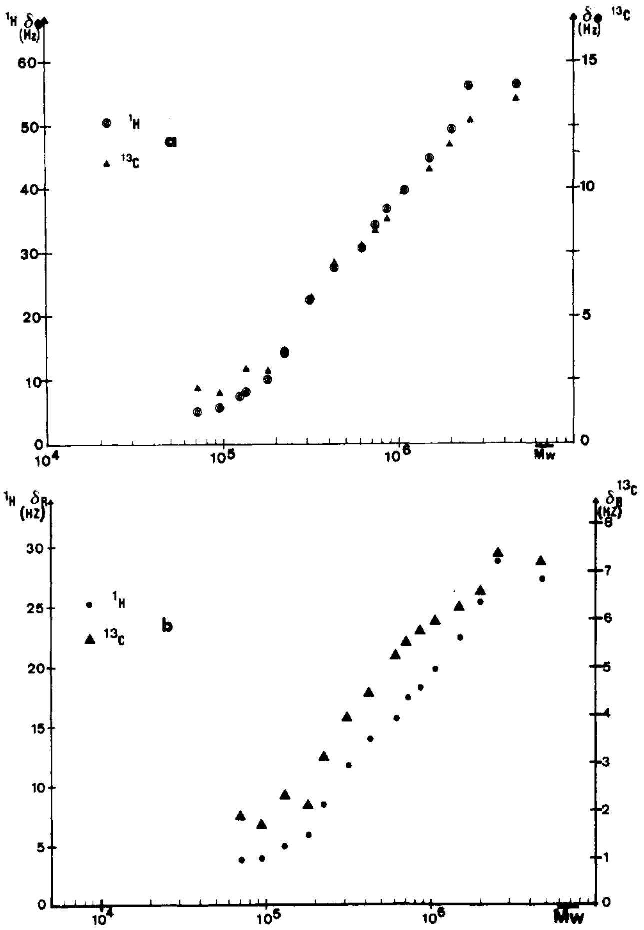

Figure 9. Disentanglement NMR curves observed from ^{13}C nuclei and protons are brought into coincidence by adjusting the line-width frequency scale: (a) without sample rotation, (b) during sample rotation.

D. ^{13}C Disentanglement Curve. Before we give a numerical analysis of the disentanglement NMR curve drawn from measurements performed on proton spectra, it is of interest to show that a similar curve may be obtained from the resonance line width of ^{13}C nuclei belonging to methyl groups attached to PDMS chains. The two disentanglement NMR curves observed from protons and ^{13}C nuclei, respectively, were brought into coincidence with each other by adjusting the linear frequency scale of ^{13}C resonance line widths of the scale of proton line widths (Figure 9a); ^{13}C nuclei were observed in natural abundance (1%); therefore, we consider that the spin-system response corresponding to a carbon nucleus attached to a given methyl group is mainly governed by the dipole–dipole interaction it has established with the nearest neighboring proton located on the same methyl group. No magnetic interactions between nuclei located on different chain segments are expected to significantly determine the carbon nucleus magnetic relaxation. Single-chain magnetic properties are perceived from ^{13}C spectra. The main feature derived from the striking coincidence of the proton and ^{13}C disentanglement NMR curves is that the proton spin-system response can be only sensitive to dipole–dipole interactions between nuclei located within a given chain segment. Although dipolar interactions between protons attached to different chain segments also exist, they have a negligible effect on the transverse nuclear magnetization dynamics which is mainly determined from the residual energy already introduced in section II. This property may be explained in the following way. Dipolar interactions between protons located on different chain segments are very sensitive to the distance r joining two nuclei because of their r^{-3} dependence upon this variable; this distance is a rapidly fluctuating time function associated with fast short segment motions occurring within temporary submolecules. The time average of these interactions is zero and their second-order contribution to the transverse magnetization relaxation rate has an order of magnitude close to that of the spin–lattice relaxation rate ($\simeq 1$ s^{-1}), whereas the distance between nuclei located within a proton pair or within a methyl group is a constant. Then the spin-system response only depends upon orientational effects of proton groups; it is very sensitive to symmetry properties of their diffusional motions. The resulting residual fine structures of proton spectra averaged within temporary submolecules are much stronger than the spin–lattice relaxation rate; they mainly govern the relaxation process of the transverse magnetization.

Accordingly, we consider that we observe single-chain proton magnetic properties although all chains are in dynamical interactions with one another.

Proton and ^{13}C disentanglement NMR curves observed during sample rotation are reported in Figure 9b.

V. Analysis of Disentanglement NMR Curves

The purpose of the present paper is not to give an exact time dependence of the transverse magnetic relaxation function associated with a given specific chain diffusion model. The aim of this section is only to estimate the time scale of the nuclear magnetic relaxation process by using two main models of terminal diffusional mechanisms of polymer chains. The ways these models are involved in nuclear spin dynamics have been extensively discussed in several papers previously published; they will be briefly evoked further.

The three assumptions underlying the numerical analysis of the disentanglement NMR curves are as follows:

(i) A two-step average of dipole–dipole interactions of nuclei exists. It is closely associated with the two-dispersion spectrum of chain relaxation times.

(ii) The contour length $L_e \propto N_e$ of temporary submolecules is independent of the chain molecular weight M_w; N_e is derived from the apparent molecular weight M_e between coupling junctions, $N_e = M_e/m_0$; $2m_0$ is the monomer unit molecular weight; M_e values have been tabulated for various polymers,[24] $M_e = 8800$ for PDMS.

(iii) Finally, within a given polymer chain, submolecules are labeled by an index n running from 1 to $N_S = M/M_e$; it is supposed that any submolecule is fully characterized by its end-to-end vector $\vec{r}_e{}^n(t)$, at any time t.

Consequently, the residual dipole–dipole frequency $\Delta_{re}{}^n(\vec{r}_e{}^n,L_e)$ within methyl groups is considered as one of several possible physical quantities characterizing the partial equilibrium of the temporary physical system associated with any submolecule; $\Delta_{re}{}^n$ is expressed from formula 7 as

$$\Delta_{re}{}^n(\vec{r}_e{}^n,N_e) = 0.67\beta\Delta_G{}^n\vec{r}_e{}^n \begin{bmatrix} 1 & & \\ & 1 & \\ & & -2 \end{bmatrix} \vec{r}_e{}^n/N_e{}^2\sigma_e{}^2 \quad (8)$$

$\sigma_e{}^2$ is the mean square end-to-end distance of any submolecule; the parameter β accounts for flexibility properties of real PDMS chains; the average Δ_e of $\Delta_{re}{}^n(\vec{r}_e,N_e)$ over all submolecules will serve as an internal reference frequency to investigate properties of the terminal relaxation spectrum $\Omega_2(M)$:

$$\Delta_e = 0.55\beta\Delta_G{}^r/N_e \quad (9)$$

$(\Delta_G{}^r)^2$ is the second moment that would be observed on real PDMS chains in the glassy state. The three foregoing assumptions are in full agreement with common descriptions of viscoelastic properties of a polymer melt. Two main types of models have been suggested until now to describe chain diffusional processes in a melt or in concentrated solutions and corresponding to collective motions of $\vec{r}_e{}^n(t)$ vectors within a given chain. According to the first model, proposed by Rouse, any macromolecule is supposed to lose the memory of its organization in space at every submolecule of the chain, at any time; such a mechanism leads to a multiple-mode relaxation spectrum $\Omega_2(M)$. According to the reptation mechanism, corresponding to the second class of models, the memory of chain orientation is lost only at submolecules located at the chain ends. The resulting relaxation spectrum also consists of many modes; however, in calculations of practical interest there is a weight factor which eliminates all modes except the longest one; this is illustrated by formula 2.

These two models applied to NMR properties will now be compared with each other by calculating fluctuations of $\Delta_{re}{}^n$ quantities induced by random time-dependent variations of $\vec{r}_e{}^n(t)$ vectors.

A. Multiple-Mode Relaxation Spectrum. Correlation functions of submolecule end-to-end vectors $\vec{r}_e{}^n(t)$ derived from the Rouse model are known; they are calculated from time-dependent coupled Gaussian distribution functions. The multiple-mode relaxation spectrum associated with this model determines the transverse magnetic relaxation function of protons attached to PDMS chains according to the following normalized expression:[14]

$$M_M(t) = \prod_{p,q=1}^{N_S} h_M(t\tau_{p,q}{}^{-1}) \quad (10)$$

with

$$h_M(t/\tau_{p,q}) = \exp\{-2(\Delta_e\tau_{p,q})^2[\exp(-t\tau_{p,q}{}^{-1}) + t\tau_{p,q}{}^{-1} - 1]/N_S{}^2\} \quad (11)$$

$$\tau_{p,q}{}^{-1} = \tau_p{}^{-1} + \tau_q{}^{-1} \quad (12)$$

while the $\Omega_2{}^M(M)$ dispersion is determined by[13]

$$\tau_p{}^{-1} = (\tau_1{}^\nu)^{-1}(2N_S + 1)^2 \sin^2\left(\frac{\pi p}{2N_S + 1}\right) \quad (13)$$

$p = 1, 2, ..., N_S$.

The spin-system response (10) was calculated from a second-order cumulant expansion; it represents a spectrum-narrowing effect occurring step by step when the chain molecular weight of polymer samples is decreased; each relaxational frequency $\tau_{p,q}{}^{-1}$ progressively contributes to the motional averaging of a reduced average residual fine structure Δ_e/N_S. Attention will be now paid to the terminal relaxation time $\tau_1{}^\nu$. It must be first emphasized that the Rouse Model of chain motion is not considered as appropriate to the description of viscoelastic properties of long polymer chains entangled in a melt, whereas it applies rather well to the interpretation of short-chain viscoelastic behavior ($M \lesssim 5 \times 10^4$). An arbitrary factor Q_e was usually introduced in the Rouse model to account for the observed molecular weight dependence of the zero-shear rate viscosity, commonly $\eta_0 \propto M^{3.4}$ ($M \gtrsim 5 \times$

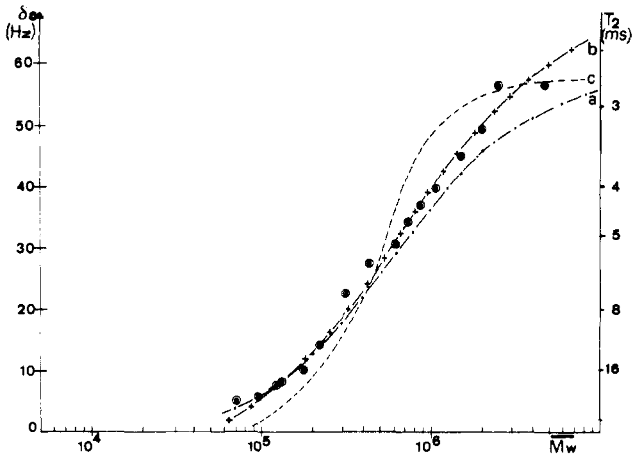

Figure 10. Experimental results compared with dinsentanglement NMR curves calculated from two possible chain relaxation spectrum models and two possible molecular weight dependences of the terminal relaxation times, τ_1^{ν} or T_{Re}: (a) from formula 10, with $\Delta_e/2\pi = 56$ Hz, $\tau_1^{\nu} \propto (\bar{M}_w)^3$, $\tau_1^{\nu} = 5$ s for $\bar{M}_w = 10^6$; (b) from formula 10, with $\Delta_e/2\pi = 66$ Hz, $\tau_1^{\nu} \propto (\bar{M}_w)^3$, $\tau_1^{\nu} = 3.3.$ s for $\bar{M}_w = 10^6$; (c) from formula 14, with $\Delta_e/2\pi = 56$ Hz, $\tau_{Re} \propto (\bar{M}_w)^2$, $T_{Re} = 3 \times 10^{-2}$ s for $\bar{M}_w = 10^6$.

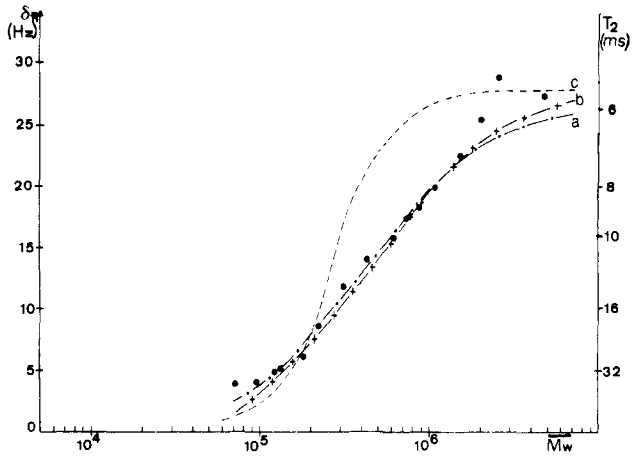

Figure 11. Experimental results observed during sample rotation are compared with disentanglement NMR curves calculated in the same way as in Figure 10: (a) from formula 10, with $\Delta_e/2\pi = 27$ Hz, $\tau_1^{\nu} \propto (\bar{M}_w)^3$, $\tau_1^{\nu} = 14$ s for $\bar{M}_w = 10^6$; (b) from formula 10, with $\Delta_e/2\pi = 28$ Hz, $\tau_1^{\nu} \propto (\bar{M}_w)^3$, $\tau_1^{\nu} = 11.6.$ s for $\bar{M}_w = 10^6$; (c) from formula 14, with $\Delta_e/2\pi = 28$ Hz, $T_{Re} \propto (\bar{M}_w)^2$, $T_{Re} = 2 \times 10^{-2}$ s for $\bar{M}_w = 10^6$.

10^4); this factor Q_e yielded a molecular weight dependence of the terminal relaxation time, $\tau_1^{\nu} \propto M^{4.4}$. The present discussion is restricted to the investigation of collective motions of all parts of a chain using a Rouse model but ignoring the exact way it could be related to viscoelastic properties of a melt. Consequently, the τ_1^{ν} dependence upon the chain molecular weight was arbitrarily set equal to $\bar{M}_w^3$. Then, disentanglement NMR curves were simulated by considering β in Δ_e and τ_1^{ν} as adjustable parameters; calculated curves are compared with experimental points in Figure 10. Curve a was obtained with the values $\Delta_e/2\pi = 56$ Hz and $\tau_1^{\nu} = 5$ s for $\bar{M}_w = 1.0 \times 10^6$, while curve b was obtained with the values $\Delta_e/2\pi = 66$ Hz and $\tau_1^{\nu} = 3.3$ s for $\bar{M}_w = 1.0 \times 10^6$. We consider that curve b fits experimental results in a better way than curve a. Also, Figure 11 shows the disentanglement NMR curve calculated by taking sample rotation effects into consideration; for the sake of simplicity NMR effects of the competition of the macroscopic rotation of polymer chains with their own self-diffusion process were calculated by dividing the residual fine structure $\Delta_e/2\pi$ exactly by 2; the corresponding terminal relaxation time $\tau_1^{\nu\prime}$ was found to be equal to 11 s; the discrepancy between τ_1^{ν} and $\tau_1^{\nu\prime}$ comes from the fact that rotational effects were not calculated for each relaxational mode, separately; the exact but tedious calculation will be described in a subsequent paper; however, the agreement with the experimental disentanglement NMR curve is still satisfactory.

An estimate of the terminal relaxation time can be obtained from viscoelastic measurements. Tabulated values of G_N^0 are $10^{6.3} \sim 10^{6.4}$ dyn/cm^2, while $\eta_0 \simeq 7 \times 10^6$ P for $M_w = 1.0 \times 10^6$ (ref 25); therefore, $\eta_0/G_N^0 \simeq 3.1$ s.[24] The comparison of this ratio with the NMR results is not actually significant because the two types of measurements were performed on samples probably too different from each other; η_0/G_N^0 only gives an order of magnitude. Also, the value of the second moment ΔH^2 of proton resonance lines measured on PDMS samples at temperatures lower than 100 K has been reported in several previous papers; from one of them[25] $\Delta H^2 = 6$ G^2 or $(\Delta H^2)^{1/2} \simeq 6 \times 10^4$ rad·s^{-1}; this values gave an order of magnitude of the parameter β in formula 9 equal to 3 to simulate the disentanglement NMR curve drawn in Figure 10b; this value also gives an estimate of the contribution of steric factors, including the chain flexibility to the residual fine structure. The reduction factor of dipole–dipole interactions induced by chain entanglements mainly comes from the entropic contribution associated with the number of skeletal bonds N_e.

It is not the purpose of the present paper to give an extensive description of ^{13}C resonance spectra observed on molten poly(dimethylsiloxane) samples; however, it is worth emphasizing that the coincidence of disentanglement NMR curves of protons and ^{13}C nuclei was obtained by reducing the frequency scale f proton line widths by a factor equal to 4. This value is also equal to the ratio $\gamma_p/\gamma_{^{13}C} = 3.98$, where γ_p and $\gamma_{^{13}C}$ are the gyromagnetic ratios of protons and ^{13}C nuclei, respectively. Accordingly, we consider that the reduction factor of the proton linewidth frequency scale is also a measure of the ratio of the residual proton dipole–dipole interaction strength over the ^{13}C–proton residual interaction strength.

Finally, the exponent value ϵ characterizing the chain molecular weight dependece of the terminal relaxation time $T_{Re} \propto \bar{M}_w^{\epsilon}$ was varied from about 2.5 to 3.5; the best agreement with experimental results is obtained for ϵ values within the range 3 ± 0.3.

To conclude this section, it is noted that the terminal-chain diffusional model analogous to the Rouse model is compatible with the interpretation of NMR properties if it is assumed that the molecular weight dependence of the terminal relaxation time is arbitrarily set proportional to $\bar{M}_w^3$ instead of $\bar{M}_w^2$, as should be predicted from the model proposed by Rouse.

B. Single-Mode Relaxation Spectrum. When the terminal diffusional process of a chain is supposed to result from a single-mode relaxation spectrum because of weight factors eliminating all relaxational frequencies but one, the corresponding normalized relaxation function of protons may be expressed as[14]

$$M_R(t) = \exp\{-(2^{1/2}\Delta_e)^2 T_{Re}^2[\exp(-tT_{Re}^{-1}) + tT_{Re}^{-1} - 1]\} \tag{14}$$

T_{Re} is the terminal relaxation time; there is a single motional averaging condition, $\Delta_e T_{Re} \lesssim 1$.

The reptation model underlying the calculation of the spin-system response (14) deals with the diffusion of a primitive chain built from $N_S = M/M_e$ steps with constant step length σ_e^1; the primitive chain can be pictured as a random-walk sequence of N_S submolecules represented by segments of equal length σ_e; since the length of any submolecule end-to-end vector $\vec{r}_e^{\,n}(t)$ is supposed to be constant, the only property inducing a possible nuclear magnetic relaxation mechanism is the loss of orientation of step vectors of the primitive chain. The disorientation of all parts of a chain is completed within the time interval T_{Re} defined by

$$T_{Re} = N_S^3\sigma_e^3/l^3\nu_R \qquad (15)$$

$l \ll \sigma_e$ is a characteristic length of an elementary diffusional process of defects within submolecules while ν_R is a characteristic jump frequency of this process; T_{Re} is the time interval required by the primitive chain to randomly move forward or backward along its whole own "tube" of contour length $N_S\sigma_e$; the hypothesis of a tube was introduced to account for dynamical interactions of a given chain with its neighboring chains; the tube prevents the chain from exploring laterally. The curvilinear diffusion constant of the primitive chain is

$$D_{C\nu} = \frac{N_S^2\sigma_e^2}{\pi^2 T_{Re}} = \frac{l^3\nu_R}{\pi^3 N_S\sigma_e} \qquad (16)$$

Note that the displacement $N_S\sigma_e$ of the primitive chain along the tube gives rise to a mean square displacement in space equal to

$$\sigma_e(N_S\sigma_e) = \sigma_T^2$$

The main problem encountered in choosing a single-relaxation-mode process to interpret NMR results is that the $\bar{M}_w^3$ dependence of the relaxation time T_{Re} leads to a change of NMR properties of a solidlike spin-system response to a liquidlike one, far too sharp when it is compared with experimental results. The disentanglement NMR curve c shown in Figure 10 was computed by assuming a chain molecular weight dependence $T_{Re} \propto \bar{M}_w^2$; correspondingly T_{Re} was found to be equal to 3×10^{-2} s for $\bar{M}_w = 1.0 \times 10^6$ while $\Delta_e/2\pi = 56$ Hz. Figure 10c shows that even the $(\bar{M}_w)^2$ dependence of the relaxation time T_{Re} is in disagreement with experimental results. Furthermore, the $(\bar{M}_w)^2$ dependence predicted from the reptation diffusion of a chain concerns the equilibration time T_d of defects along the primitive chain; the curvilinear displacement of the primitive chain occurring along its tube during the time interval T_d is only a very small fraction of the whole contour length $N_S\sigma_e$: $(l/N_S\sigma_e)^{1/2}$; this induces a mean square displacement in space equal to $\sigma_T^2(l/N_{Se})^{1/2} \ll \sigma_T^2$; consequently the corresponding disorientation of any step vector of the primitive chain is too small to govern the transverse nuclear magnetic relaxation process of protons attached to polymer chain.

To conclude this section, it is considered that any single-mode chain relaxation process is not compatible with the interpretation of NMR experimental results, except if the characteristic time involved in the transverse magnetic relaxation is supposed to have a dependence upon the chain molecular weight $\bar{M}_w^{\epsilon}$ with a low power ($\epsilon < 1$); such a power law has not be given any physical meaning until now. The foregoing analysis does not eliminate the reptation mechanism from possible models describing long-range collective motions of a polymer chain in a melt; it only raises probable difficulties concerning the exact description of chain diffusional effects upon NMR properties; this will be discussed in the next section.

C. Discussion. We consider from analyses given in sections VA,B that the chain diffusional model in best agreement with experimental results is characterized by (i) a terminal relaxation time depending upon the chain molecular weight $\bar{M}_w$, according to the relationship $T_{Re} \propto (\bar{M}_w)^{3.\pm 0.3}$, in agreement with the reptational model, and (ii) a broad terminal spectrum, a uniform statistical weight being assigned to each relaxation mode.

Such a spectrum is contrasted to the stress relaxation modulus calculated by Doi and Edwards (formula 2) which practically depends upon a single relaxation mode, but this does not necessarily question the reptational model. This point may be analyzed in the following way. The first question arising from a study of the dependence of diffusional properties upon the chain molecular weight, $\bar{M}_w$, concerns the estimate of polydispersity effects on NMR. In this respect it is worth emphasizing that polydispersity effects are negligible in the plateau region of the disentanglement NMR curve because the residual energy of dipole–dipole interactions of nuclei is determined by the mesh size of the temporary network built from entanglements, only; this was observed on several molten polymers. Furthermore, the recent study of calibrated polystyrene samples analogous to the present study leads to a characterization of chain diffusional properties similar to that of PDMS chains, determined in the present paper; the polydispersity ratio of polystyrene samples was less than 1.1, except in the plateau region of the disentanglement NMR curve.[12,13] Also, a similar result was reached by studying the dynamics of polyisobutylene chains while the polydispersity ratio of samples was about 1.4. On the other hand, if the disentanglement NMR curve were described from a single-chain relaxation time $T_{Re} \propto \bar{M}_w^3$, it would look like almost a step function (it is much sharper than curve c in Figure 10); consequently, it should be very sensitive to polydispersity effects closely associated with the peculiar preparation of samples, instead of giving a standard disentanglement NMR curve. It is considered that the absence of strong polydispersity effects on the transferse magnetization dynamics reinforces the hypothesis of a multiple-mode chain relaxation spectrum.

Such a hypothesis may be given the following support. The first point is that the position vector $\vec{R}_n(t)$, the stress relaxation modulus $G(t)$, and the spin-system response $M(t)$ correspond to observables very different from one another; consequently, average values of these observables do not necessarily obey the same differential equations and the same initial conditions defined to solve these equations; therefore, for example, initial conditions which originate the relaxation spectrum of formula 1 do not necessarily apply to the description of the nuclear magnetization dynamics. The present study indicates tht more details are necessary to calculate the entire relaxation process of nuclear spins attached to a chain than to predict macroscopic properties such as a chain diffusion coefficient or the viscoelastic behavior of a melt. For example, the constant length of submolecule end-to-end vectors without any lateral exploration is probably an oversimplified hypothesis.

VI. Conclusion

The purpose of the present study was to investigate reptational effects on the dynamics of the transverse nuclear magnetization rather than to evaluate the validity of the reptation model. PDMS fractionated samples were used although the polydispersity is worse than that of polystyrene standards; however, a methyl group is a NMR probe much more convenient than any proton attached to polystyrene chains.

Behaviors of the longitudinal and the transverse magnetic relaxations of nuclei linked to macromolecules, induced by varying the sample chain molecular weight, are currently found to be very contrasted to each other, in

Macromolecules 1985, *18*, 1109–1116

most polymer melts. The spin–lattice relaxation process of protons in poly(dimethylsiloxane)[27] exhibits no variations when the chain molecular weight is higher than 3 × 10^3, whereas the resonance line width observed on the same polymer may vary from about 1 to about 10^2 Hz when the chain molecular weight goes from 10^3 to 2 × 10^6. More important is the qualitative change of the transverse spin-system response induced by increasing the chain molecular weight and going from a liquid response to a solidlike one, determined by strong entanglement of long chains. The longitudinal relaxation is only sensitive to local motions of monomer units, occurring around the Larmor frequency (2 × 10^8 rad·s^{-1}); these are generally independent of the chain molecular weight. The transverse magnetization dynamics is mainly sensitive to long-range motions involving the terminal chain diffusional spectrum; this corresponds to low relaxational frequencies and strongly depends upon the chain molecular weight. The presence of entanglements originates a residual energy of dipole–dipole interactions of nuclei; this energy expressed in frequency units was used as an internal reference throughout the present paper to characterize the terminal spectrum of chain diffusion in a melt.

Several features result from the present NMR investigation of fractionated PDMS samples:

(i) The best agreement with experimental results is obtained by assuming that a macromolecule in a melt loses the memory of its organization in space at every part of the chain, at any time; the resulting multiple-relaxation mode is characterized by a terminal relaxation time whose molecular weight dependence is proportional to $\bar{M}_w^{3.\pm0.3}$; it is equal to about 3 s for $\bar{M}_w \sim 1.0 \times 10^6$ at room temperature.

(ii) Measurements performed both on ^{13}C and ^{1}H nuclei gave similar results; since ^{13}C nuclei in natural abundance have no interchain interactions, we consider that single-chain magnetic properties are perceived from ^{13}C nuclei, although all chains are in dynamical interactions with one another.

(iii) Finally, high-speed sample rotation clearly shows that effects of the residual dipole–dipole interactions are progressively screened by increasing the rate of chain disentanglement.

Acknowledgment. Poly(dimethylsiloxane) samples were fractionated and characterized by M. Sauviat.

References and Notes

(1) De Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572.
(2) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789.
(3) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1979**, *74*, 1802.
(4) Bueche, F.; Cashin, W.; Debye, P. *J. Chem. Phys.* **1952**, *20*, 1956.
(5) Klein, J. *Macromolecules* **1981**, *14*, 460.
(6) Leger, L.; Hervet, H.; Rondelez, F. *Macromolecules* **1981**, *14*, 1334.
(7) De Gennes, P. G. *Macromolecules* **1976**, *9*, 587.
(8) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1984**, *17*, 431.
(9) Cohen Addad, J. P. *J. Chem. Phys.* **1979**, *71*, 3689.
(10) Cohen Addad, J. P. *J. Phys.* (*Les Ulis, Fr.*) **1982**, *43*, 1509.
(11) Cohen Addad, J. P.; Feio, G. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 957.
(12) Cohen Addad, J. P.; Guillermo, A. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 931.
(13) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(14) Cohen Addad, J. P. *Polymer* **1983**, *24*, 1128.
(15) Graessley, W. W.; Edwards, S. F. *Polymer* **1981**, *22*, 1329.
(16) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 67.
(17) Pake, G. *J. Chem. Phys.* **1948**, *16*, 327.
(18) Andrew, E. R.; Bersohn, R. *J. Chem. Phys.* **1950**, *18*, 159.
(19) Abragam, A. "Principles of Nuclear Magnetism", Oxford University Press: London, 1961.
(20) Cohen Addad, J. P.; Roby, C. *J. Chem. Phys.* **1975**, *65*, 3091.
(21) English, A. D.; Dybowski, C. R. *Macromolecules* **1984**, *17*, 446.
(22) Cohen Addad, J. P.; Domard, M.; Lorentz, G.; Herz, J. *J. Phys.* (*Les Ulis, Fr.*) **1984**, *45*, 575.
(23) De Gennes, P. G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(24) Ferry, J. D. "Viscoelastic Propertis of Polymers", 3rd ed; Wiley: New York, 1980.
(25) Kataoka, T.; Veda, S. *Polym. Lett.* **1966**, *4*, 317.
(26) Powles, J. G.; Hartland, A.; Kail, J. A. E. *J. Polym. Sci.* **1961**, *55*, 361.
(27) Cunniberti, C. *J. Polym. Sci., Part A-2* **1970**, *8*, 2051.

Trends in Molecular Motion for a Series of Glucose Oligomers and the Corresponding Polymer Pullulan As Measured by ^{13}C NMR Relaxation

Alan J. Benesi* and David A. Brant

Department of Chemistry, University of California, Irvine, California 92717.

Received September 28, 1984

ABSTRACT: The dipolar ^{13}C relaxation parameters T_1, T_2, and NOE have been measured at 62.83 MHz for a series of glucose oligomers and the corresponding high molecular weight, linear polymer pullulan. Significant chemical shift differences made it possible to differentiate between ^{13}C atoms in terminal glucose rings, penultimate glucose rings, and interior glucose rings of the oligomers. Terminal and penultimate ring atoms exhibit consistently higher values of T_1, T_2, and NOE than do interior ring atoms. For each type of ring the ^{13}C relaxation parameters approach a characteristic asymptotic limit at about DP = 12. The relaxation parameters of interior ring ^{13}C atoms in the oligomers match those of pullulan at a critical DP = 15. This indicates that the relative angular motion of interior ^{13}C magnetic moments and their directly bonded ^{1}H magnetic moments generates the same electromagnetic power at the pertinent magnetic resonance frequencies, and suggests that the underlying atomic motion is the same in both cases.

Introduction

In addition to its other uses, NMR spectroscopy can serve as a probe of solute motion in liquid solutions. Pulsed-field gradient NMR spectroscopy can be used to measure the translational diffusion coefficients of solute molecules,[1,2] while quadrupolar NMR relaxation measurements and ^{13}C NMR relaxation measurements provide information on the details of the rotational diffusion of

0024-9297/85/2218-1109$01.50/0 © 1985 American Chemical Society