

# N.m.r. and macromolecular migration in a melt or in concentrated solutions

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A procedure of analysis of n.m.r. measurements is proposed as an approach to the observation of a single chain diffusion in a melt. The dynamic screening effect is applied to the definition of a temporary submolecule; this is used as a semi-local probe to investigate collective motions of all parts of a polymer chain. Measurements performed on  $^{13}\text{C}$  nuclei or protons lead to similar conclusions. The best agreement with experimental results is obtained by combining a  $M^3$  dependence of the terminal relaxation time ( $M$  is the chain molecular weight) with a multiple-mode relaxation spectrum; all modes have the same statistical weight.

(Keywords: nuclear magnetic resonance; macromolecules; migration; chain diffusion)

## INTRODUCTION

The purpose of this paper is to analyse the migration process of long polymer molecules in a melt or in concentrated solutions as it may be observed from the dynamics of the transverse magnetization of nuclear spins linked to these chains.

The low frequency viscoelastic relaxation of polymer systems is known to be controlled mainly by the mechanism of dissociation of topological constraints exerted on chains and which are called entanglements<sup>1,2</sup>. This mechanism exhibits a strong dependence upon the chain molecular weight.

These topological constraints also govern the diffusion process of polymer chains<sup>3</sup>. Therefore, the accurate description of the diffusion motion of a chain may be a convenient method of characterizing disentanglement processes which are necessarily involved in any model proposed to explain viscoelastic effects.

Therefore, it is worth trying to define an experimental procedure giving a direct observation of the diffusion of a single chain on a molecular scale although it interacts dynamically with all surrounding chains.

Two problems are encountered in attempting to observe the diffusion of a chain on a molecular scale.

### Space-scale of measurements

One of these problems is that of space-scale of measurement. This is due to a dynamic screening effect induced by topological constraints and characterized by a correlation length  $\sigma_e \lesssim 20 \text{ \AA}$ . Within a space domain defined by  $\sigma_e^3$ , dynamical fluctuations are concerned with short chain segments only (the number of skeletal bonds  $N_e$  is  $\sim 2 \times 10^2$ ); they correspond to high relaxation frequencies ( $\approx 10^8 \text{ Hz}$ )<sup>4</sup>. These motions do not depend upon the molecular weight of polymer chains. There are no correlations between fluctuations of these short segments with one screening domain to another. Therefore, to observe a significant displacement of a long chain, it is necessary to have a space-scale of measurement larger

than  $\sigma_e$ ; otherwise, only local motions will be perceived. This difficulty could be overcome by performing light scattering or neutron scattering experiments. However, there is also a problem with the time scale of the measurement.

### The time scale of measurement

The time interval  $T_{\text{rep}}$  required to observe the diffusion of a chain over its own dimension,  $R_G$ , is about 1 s for a chain of molecular weight  $M \sim 10^6$  and  $R_G \sim 2 \times 10^2 \text{ \AA}$ ; this corresponds to a diffusion coefficient  $D_{\text{self}} \sim 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ . The time interval is approximately equal to 0.1 ms for a displacement over a distance smaller than  $\sigma_e \approx 20 \text{ \AA}$ . These time scales are not appropriate for light scattering or neutron scattering experiments.

### Diffusion coefficient measurements

The difficulties about time scales and space scales have been overcome in two ways. The first was to observe the diffusion of a chain on a macroscopic scale and not a molecular one. Early measurements were made using chains labelled with radio-tracers<sup>5</sup>. Deuterated chains moving through a protonated matrix were observed by infra-red spectroscopy<sup>6</sup>; the diffusion coefficient of polyethylene chains measured according to this experimental procedure was found to vary as the inverse of the square of the chain molecular weight to within a reasonable accuracy.

Another method was to shorten the time scale of chain diffusion by considering short chains in concentrated solutions or long chains in semi-dilute solutions. The diffusion coefficient of polystyrene chains labelled with a photochromic probe and moving through a pulsed pattern of interference fringes was shown to obey the predicted formula<sup>3</sup>:

$$D_{\text{self}} \propto M^{-2} C^{-1.75} \quad (1)$$

where  $C$  is the polymer concentration<sup>7</sup>. A pulsed field

gradient n.m.r. technique<sup>8</sup> was recently used to measure the diffusion coefficient in the concentration range  $0.04 < C < 0.16$  (W/W) for chain molecular weights lower than  $3 \times 10^5$ .

It will be shown in this paper that quantum coherence properties of nuclear spins may be used to investigate a chain diffusion process, not by measuring any diffusion coefficient  $D_{\text{self}}$ , but by adjusting and comparing the chain relaxation spectrum characterized by:

$$T_{\text{Rep}}^{-1} \propto D_{\text{self}} / \langle R_G^2 \rangle \quad (2)$$

to an internal n.m.r. reference frequency much lower than the Larmor frequency.

The adiabatic relaxation of the transverse nuclear magnetization  $M_x(t)$ :

$$M_x(t) = \langle M_x(0)M_x(t) \rangle \quad (3)$$

is known not to depend upon any exchange of energy between the spin-system and the thermal bath; therefore, there is no resonance condition to be fulfilled with the Larmor frequency and this is the reason why slow diffusional processes can be observed.

## TWO BASIC N.M.R. RESULTS

Two basic n.m.r. results are used to investigate the diffusion process of a chain in a melt.

### *The solid-like spin-system response*

(1) When the temperature of a polymer system is raised starting from its glassy state, the resonance line-width of nuclear spins is found to rapidly decrease through the glass transition temperature; then two cases must be considered. For a polymer system composed of short chains, where the spin-system made of short chains, then the spin-system has a liquid-like response (narrow line analogous to that observed for conventional liquids). Whereas for a polymer system composed of long chains the spin-system exhibits a solid-like response; the resonance line ( $\sim 5 \times 10^2$  Hz) is of course much narrower than that observed in the glassy state. This is the first basic n.m.r. result. The solid-like response is easily controlled from a spectrum narrowing effect induced by a sample rotation around an axis perpendicular to the direction of the steady magnetic field<sup>9</sup>.

### *The disentanglement n.m.r. transition curve*

(2) At a given temperature, a transition of n.m.r. properties from a solid-like spin-system response to a liquid-like response is induced by decreasing the chain molecular weight; correspondingly, the resonance line-width is found to decrease from about  $5 \times 10^2$  Hz to about 10 Hz according to a reasonably sharp curve which we called a disentanglement n.m.r. transition curve because the strong chain length dependence of the resonance line-width is necessarily associated with an increase in the rate of dissociation of entanglements<sup>10</sup>. This is the second basic n.m.r. result (*Figure 1*).

## RESIDUAL DIPOLE-DIPOLE INTERACTIONS

Before explaining how the chain migration process may be involved in these basic n.m.r. properties, it is worth

emphasizing that magnetic relaxation processes observed in most polymer systems are induced by dipole-dipole interactions of nuclei; they are tensorial functions of nuclear coordinates; they strongly depend upon the distance  $|\vec{r}|$  between two nuclei and also upon the angle between this vector and the direction of the steady magnetic field. For the sake of simplicity, the energy of the dipole-dipole interaction is written as:

$$W \propto (3 \cos^2 \theta - 1) / r^3 \quad (4)$$

where  $\theta$  is one of the angular coordinates of  $\vec{r}$ .

Most polymer chains are composed of proton pairs and methyl groups. Within a proton pair or a  $\{-\text{CH}_3\}$  group, the distance between nuclei is a constant and only angular properties are observed.

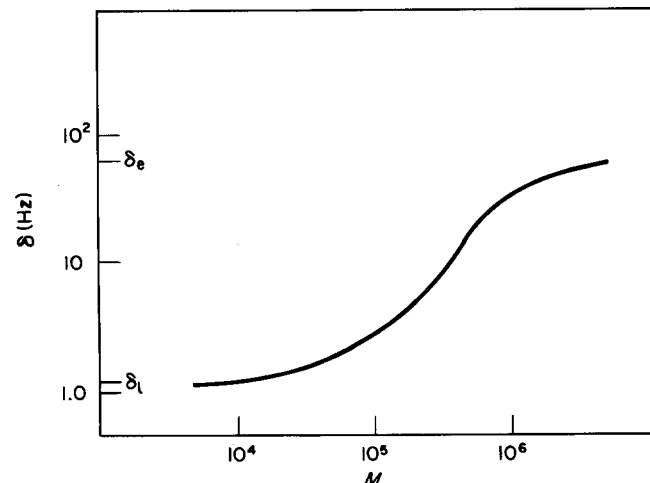
We consider that the solid-like response reflects a residual energy of dipole-dipole interactions because a partial spectrum narrowing effect only, is induced by macromolecular motions. Although the chain diffusional motion is isotropic, it is similar to observing an apparent non-isotropic motion because the diffusion of a chain over its own dimension is only achieved in a time interval which is longer than the n.m.r. time scale.

## A BASIC ASSUMPTION: A TWO-STEP MOTIONAL AVERAGING

### *Two dispersions*

The only basic assumption necessary to account for the solid-like response and the disentanglement n.m.r. transition curve is to consider that there is a two-step motional averaging of spin-spin interactions; this is supposed to result from a wide chain relaxation spectrum consisting of two well separated parts<sup>11</sup>: two dispersions  $\Omega_1$  and  $\Omega_2$ . This hypothesis is in agreement with general viscoelastic properties and with the dynamic screening effect: that the cut in space correlations also corresponds to a cut in the time correlations.

$\Omega_1$  is called the transition spectrum; it is associated with local motions of short segments and it may be studied from the nuclear magnetic spin-lattice relaxation. While  $\Omega_2(M)$  is called the terminal spectrum; it is associated with the collective diffusion of all parts of a chain and it strongly depends upon the chain molecular weight.



**Figure 1** Schematic disentanglement n.m.r. transition curve

$$N_e \propto C^{-1} M^0 \quad (9)$$

(b) its life-time identified with the relaxation time of disentanglement

$$T_{\text{Rep}} \propto CM^3 \quad (10)$$

For polymer systems made of long chains, we only observe n.m.r. properties of the temporary network structure, while for polymer systems made of short chains we observe the dynamical dissociation of the network structure.

Characteristic n.m.r. properties of this network structure must be now determined.

### RESIDUAL DIPOLE-DIPOLE ENERGY WITHIN A SUBMOLECULE

#### Temporary average orientational order

Whatever the complex nature of all topological constraints exerted on a submolecule, we suppose that it is fully characterized at any time,  $t$ , by its temporary end-to-end vector  $\vec{r}_e(t)$ ; it is supposed to be the only relevant thermodynamic variable describing a submolecule. The residual energy of the dipole-dipole interaction corresponding to a given end-to-end vector,  $\vec{r}_e(t)$ , can be calculated for a proton pair or a methyl group<sup>12,13</sup>:

$$E(\vec{r}_e) = |\langle \mathcal{H}_D \rangle_{\Omega_1}| \propto \langle 3 \cos^2 \theta - 1 \rangle_{\vec{r}_e} \quad (11)$$

$$E(\vec{r}_e) \propto \vec{r}_e^{-1} (3 \cos^2 \theta - 1) \vec{r}_e / N_e^2 \quad (12)$$

The non-zero end-to-end vector  $\vec{r}_e(t)$ , induces a reduction of the chain entropy; which is similar to considering that every monomeric unit experiences an additional potential energy hindering its isomerization process. This entropy reduction effect can be observed on polymeric gels<sup>14,15</sup> and on polymer systems with surface interactions also.

Formula (12) actually describes a transfer of localization of n.m.r. properties from a local space scale to a semi-local one defined by  $\vec{r}_e(t)$ : there is a temporary average orientational order of monomeric units. This order is a small effect since it reflects a strength of correlation equal to about  $10^2$  Hz while the strongest correlation or orientation (in a glass) is about  $10^5$  Hz. We are no longer interested in the memory or orientation of a monomeric unit but in the loss of memory of orientation of  $\vec{r}_e(t)$  vectors.

#### Calibrated gels: superposition n.m.r. property

N.m.r. properties may be shown to obey the key formula (12) by observing the progressive swelling process of elementary chains in calibrated covalent gels. End-to-end vectors are identified with vectors joining two consecutive crosslink points; they hardly vary with time in a covalent gel corresponding to a permanent network structure. The characteristic dependence of  $E(\vec{r}_e)$  with respect to the submolecule (elementary chain) end-to-end vector  $\vec{r}_e$  is observed by swelling the covalent gel. Applying a packing condition to partly swollen elementary chains,  $|\vec{r}_e|$  may be expressed as a function of the swelling ratio,  $q$ , according to the formula:

$$|\vec{r}_e| \propto q^{2/3} \quad (13)$$

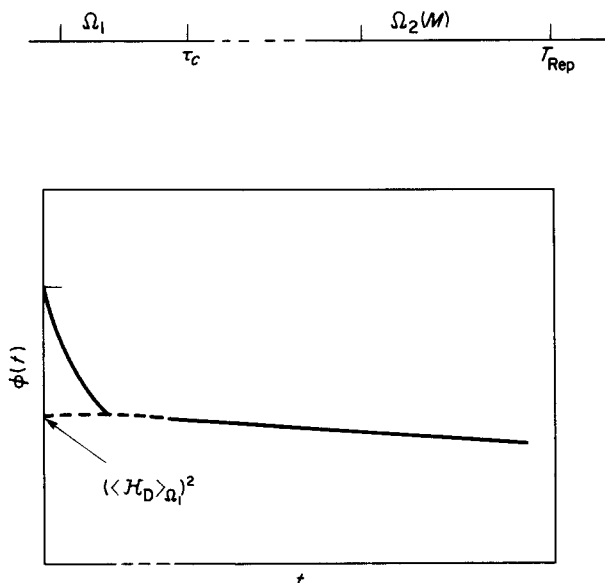


Figure 2 Two-part correlation function of dipole-dipole interactions, associated with the two-dispersion chain relaxation spectrum

#### Loss of memory of orientations

The memory of orientations of a given monomeric unit observed through dipole-dipole interactions,  $\mathcal{H}_D$ , is lost in two steps; the memory function:

$$\phi(t) = \langle \mathcal{H}_D(t) \mathcal{H}_D(0) \rangle \quad (5)$$

is split in two parts, with:

$$\phi(0) = \langle \mathcal{H}_D(t) - \langle \mathcal{H}_D \rangle_{\Omega_1} \rangle_{\Omega_1}^2 + (\langle \mathcal{H}_D \rangle_{\Omega_1})^2 \quad (6)$$

(i) There is a fast decay of the memory function associated with the  $\Omega_1$  spectrum; this leads to a residual energy  $\langle \mathcal{H}_D \rangle_{\Omega_1}$ , calculated within a dynamic screening domain, i.e. over short segment motions corresponding to the  $\Omega_1$  spectrum (Figure 2).

(ii) There is a long decay of  $\phi(t)$  associated with the  $\Omega_2(M)$  spectrum.

#### Spectrum narrowing conditions

Two conditions must be fulfilled to observe a complete spectrum narrowing effect:

$$(i) \quad \mathcal{H}_D(t) - \langle \mathcal{H}_D \rangle_{\Omega_1} | \tau_c \lesssim 1, \text{ for the } \Omega_1 \text{ spectrum} \quad (7)$$

and

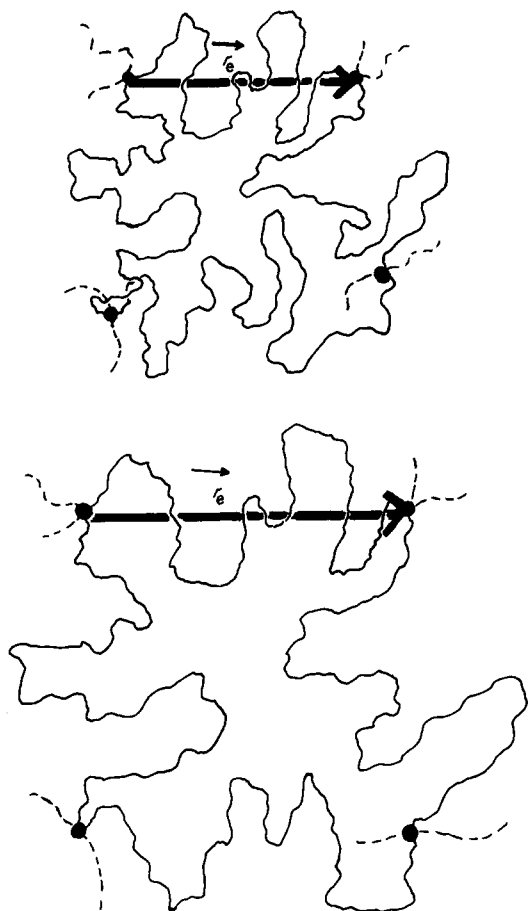
$$(ii) \quad \langle \mathcal{H}_D \rangle_{\Omega_1} T_{\text{rep}} \lesssim 1, \text{ for the } \Omega_2(M) \text{ spectrum} \quad (8)$$

where  $\tau_c$  is the longest relaxation time of  $\Omega_1$ ; and  $|\langle \mathcal{H}_D \rangle_{\Omega_1}|$  plays the role of an internal n.m.r. reference frequency which can be used to monitor the terminal relaxation spectrum  $\Omega_2(M)$ .

#### A temporary network structure

Finally, all these properties may be pictured by considering the existence of a temporary network structure made of temporary submolecules. A submolecule is a temporary object characterized by:

(a) its size defined from the dynamic screening length  $\sigma_e \propto N_e^{1/2}$ , with:



**Figure 3** Schematic progressive swelling of elementary chains in a covalent gel

$q$  is defined as the ratio of the volume  $V$  of the swollen gel over the volume  $V_0$  of the dry gel ( $q = V/V_0$ ) (Figure 3).

To observe the characteristic dependence of  $E$  with respect to the number of bonds of a submolecule (elementary chain),  $N_e$  is varied by changing the concentration of synthesis,  $v_c$ , of covalent gels<sup>15</sup>:

$$N_e \propto v_c^{-5/4} \quad (14)$$

Combining equations (13) and (14), the residual energy of dipole-dipole interaction should vary as

$$E \propto q^{2/3} v_c^{5/3} \quad (15)$$

Using the reduced variable  $q^{2/3} v_c^{5/3}$ , transverse relaxation rates measured on calibrated poly(dimethylsiloxane) gels have been shown to obey a superposition property<sup>15</sup>. Several concentrations of synthesis  $v_c = 0.84, 0.74$  and  $0.46 \text{ g cm}^{-3}$  and two swelling agents (toluene and chloroform) were used. The methyl group is appropriate in studying submolecule properties because the fast rotation around its C-axis eliminate most of the dipole-dipole interactions. The remaining part only depends upon the orientation of the  $\bar{C}$ -axis, i.e. orientation of skeletal bonds.

#### Entangled chains: a superposition property

N.m.r. properties may also be shown to obey formula (12) by increasing the mesh size of the temporary network structure. The number of bonds,  $N_e$ , in a submolecule is increased by slightly diluting concentrated solutions of

long polymer chains according to formula (9); while the rate of dissociation of entanglements is not sufficiently high to induce the second step of motional averaging process. Therefore, by increasing the mesh size we can expect to only observe a reduction of the residual energy of spin-spin interactions, reflecting more freedom given to isomerization processes of monomeric units. The relaxation function of the transverse magnetization is expected to keep its mathematical structure (Figure 4).

Relaxation functions of protons recorded on five concentrated solutions ( $0.45 < C < 0.9 \text{ g cm}^{-3}$ ) of long poly(isobutylene) chains ( $M \sim 10^6$ ) in carbon disulphide, have recently been shown to obey a superposition property, by applying a suitable shift factor to the time scale<sup>16</sup>. All relaxation functions correspond to a solid-like response; the superposition property reflects less average order of monomeric units; the chain entropy is increased within submolecules.

### CHAIN DYNAMICS

#### Internal reference frequency

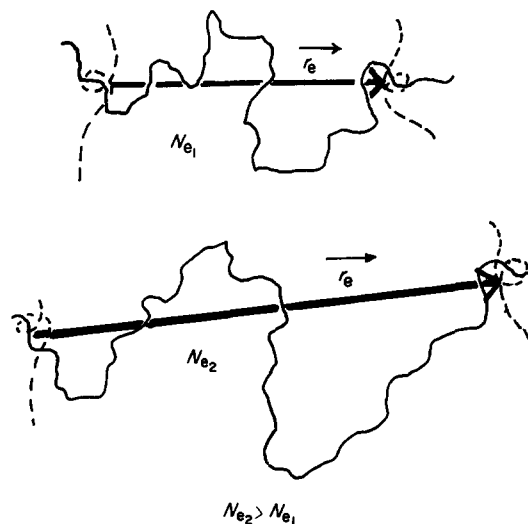
We now have a quantitative method of characterizing n.m.r. properties of the temporary network structure, from the residual energy of dipole-dipole interactions:

$$\overline{\langle \mathcal{H}_D \rangle_n}^2 \propto E^2(r_e) = T_v^{-2} \quad (16)$$

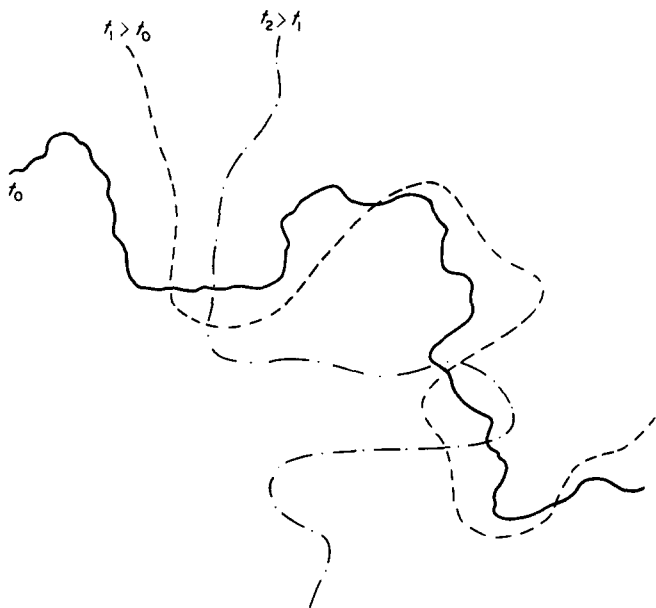
$T_v^{-1}$  serves as an internal reference frequency.

A submolecule is then considered as an ephemeral element which will be used as a probe to analyse long range fluctuations in a chain. We suppose that the two-step motional averaging process still applies when the network structure dissociates quickly enough to induce a complete spectrum narrowing effect. The second step of this effect is closely related to the loss of memory of orientation not of a monomeric unit but of an end-to-end vector of a submolecule.

When the chain molecular weight is decreased, the mesh size is kept constant but the rate of dissociation of the network structure is increased. The residual energy of dipole-dipole interactions is now considered as a time



**Figure 4** Mesh size of the temporary network structure is increased by slightly diluting the polymer system; the number of bonds  $N_e$  in a submolecule is increased



**Figure 5** According to the Rouse model, the memory of position of a chain is lost in each of its points at any time

function,  $E(\vec{r}_e(t))$ , obeying the obvious condition:

$$\overline{E^2(r_e(t))} = T_v^{-2} \quad (17)$$

at any time  $t$ . The description of the network at any time,  $t$ . The description of dynamical fluctuations of the network structure is a complex problem which has been solved until now within a mean field approximation. The dissociation process of the network structure is supposed to be closely reflected by the diffusive motion of a single chain in dynamical interactions with all surrounding chains. Therefore, it is considered that the loss of memory of orientation of a submolecule end-to-end vector may be associated with the  $\Omega_2(M)$  terminal spectrum of a chain. Two main models have been proposed until now to describe diffusional motions of a chain in a melt.

**Rouse model**

According to the Rouse model, the memory of position of a polymer molecule is lost in each of its points, at any time. This model is built from linear thermodynamic fluctuations governed by a free energy:

$$F_{e,j} \propto 3kT r_{e,j}^2 / N_e \quad (18)$$

Associated with the end-to-end vector  $\vec{r}_{e,j}$  of the whole chain is a sum or all elementary free energies  $F_{e,j}$ . Collective motions of submolecule end-to-vectors  $\vec{r}_{e,j}(t)$  are described from normal modes determining the  $\Omega_2(M)$  spectrum. Any relaxation time  $\tau_p^R$  is defined from

$$\tau_p^R \propto \tau_1^R p^{-2}, \quad p = 1, 2 \quad (19)$$

$\tau_1^R$  is the terminal relaxation time; normal modes have a uniform statistical weight;  $\tau_1^R$  is predicted to vary as the square of the chain molecular weight. It is currently considered that this model applies well to short chains in a melt, without any entanglements<sup>1</sup> (Figure 5).

**Reptation model**

The other model proposed to describe the diffusional motion of a chain in a melt is founded on the tube concept and the reptation motion. The tube concept was first introduced by Edwards to describe statistical fluctuations of chains, at equilibrium. The reptation motion of a chain in its surrounding tube was proposed by De Gennes. According to the reptation model, the memory of orientation of submolecules is lost at tube ends only. The memory of orientation is kept in central parts of the tube until these are reached by one of the ends of the chain moving backwards and forwards in a random fashion, along the tube. The  $\Omega_2(M)$  terminal spectrum consists of a series of modes characterized by relaxation times:

$$\tau_p^{Re} \propto T_{Rep} / p^2 \quad p = 1, 3, 5, \dots$$

The terminal relaxation time  $T_{Rep}$  was predicted to vary as  $M^3$  instead of  $M^2$ . The statistical weight of each mode is proportional to  $p^{-2}$ ; this gives a negligible weight to all modes, except for the first one. The reptation model is in reasonable agreement with viscoelastic properties (Figure 6).

**Comparison with n.m.r. results**

The principle of the n.m.r. observation of the diffusion process of a single chain in a melt is to shift the  $\Omega_2(M)$  spectrum through the internal reference frequency  $T_v^{-1}$ . Starting from very long chains  $\Omega_2$  is shifted towards short values of chain relaxation times by decreasing the chain molecular weight<sup>17</sup>. Then, the relaxation rate of the transverse component of the nuclear magnetization is decreased according to the disentanglement n.m.r. transition curve discussed in the Introduction.

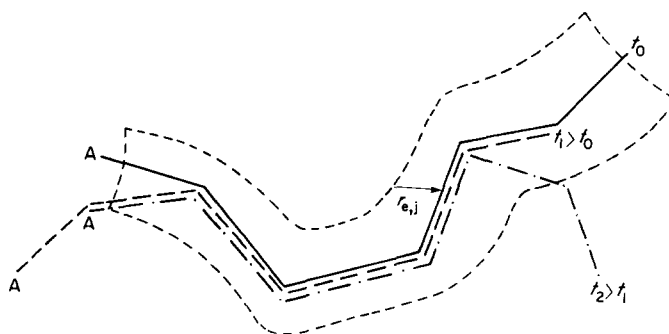
The relaxation function of the transverse magnetization has been calculated according to the formula:

$$M_x(t) = \exp \left\{ -\alpha T_v^{-2} \left( \sum_{p,q} \tau_{p,q}^2 [\exp(-t \tau_{p,q}^{-1}) + t \tau_{p,q}^{-1} - 1] \right) \right\} \quad (20)$$

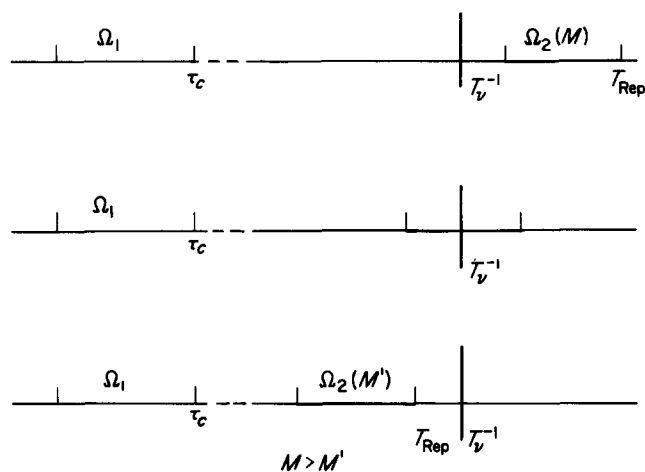
with

$$\tau_{p,q}^{-1} = \tau_p^{-1} + \tau_q^{-1} \quad (21)$$

$\alpha$  is a constant depending upon the chain diffusion model chosen to describe n.m.r. properties<sup>13,17</sup>. The best agreement with experimental n.m.r. results is obtained by combining the chain molecular weight dependence of the



**Figure 6** According to the reptation model the memory orientation is lost at tube ends



**Figure 7**  $\Omega_2(M)$  terminal spectrum is shifted through the internal reference frequency  $T_v^{-1}$  by decreasing the chain molecular weight

terminal relaxation time  $T_{Rep}$  given by the reptation model, with the  $\Omega_2(M)$  relaxation spectrum given by the Rouse model<sup>10,16,18</sup>. Values of the terminal relaxation times obtained from previously reported n.m.r. measurements were  $5 \times 10^{-2}$ ,  $2 \times 10^{-2}$  and  $8 \times 10^{-2}$  s poly(dimethylsiloxane) (PDMS), polystyrene (PS) and poly(isobutylene) (PIB) chains, respectively; the concentrations were 1.0, 0.53 and  $0.47 \text{ g cm}^{-3}$ , respectively; while the molecular weights were  $2.2 \times 10^5$ ,  $2.5 \times 10^5$  and  $2.25 \times 10^5$ , respectively. These relaxation times are about ten times longer than those usually estimated from viscoelastic measurements and defined by the ratio  $\eta_0/G_N^0$ ;  $\eta_0$  is the zero shear rate viscosity and  $G_N^0$  is the plateau modulus. Results observed on protons were found to be similar to those observed on  $^{13}\text{C}$  nuclei in natural abundance. Such a property clearly shows that magnetic interactions between nuclei located on different chain segments have negligible effects. These interactions are averaged to zero by local motions of short segments in dynamic screening domains. Therefore, a linear distribution nuclear magnetization is defined along polymer chains in a melt. Consequently, it is possible to observe dynamical properties of a single chain although it is in dynamical interactions with all other surrounding chains.

## CONCLUSION

Long range fluctuations of polymer chains in a melt observed from n.m.r. correspond to the loss of memory of orientation of temporary submolecules associated with dynamic screening domains. The criterion of isotropy is defined from the residual energy of tensorial interactions of nuclear spins within screening domains. More details about the reptation model would be probably necessary to actually account for all n.m.r. results. Also, a more tedious characterization of the spin-system response would probably lead to a better accuracy in the determination of the chain molecular weight dependence of terminal relaxation times.

Finally, it is worth emphasizing that the n.m.r. approach to the observation of a chain diffusion process necessarily leads to the analysis of the whole terminal relaxation spectrum whereas measurements of a diffusion constant do not give any detailed information about this spectrum.

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