

Quantitative NMR Characterization of Long-Range Chain Dynamics prior to Reptation: Polyethylene-Oxide

Jean-Pierre Cohen Addad and Armel Guillermo

Laboratoire de Spectrométrie Physique, associé au CNRS (UMR C5588) Université Joseph Fourier, Grenoble I, BP 87, 38402 St. Martin d'Hères Cedex, France

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The thorough analysis of the transverse magnetic relaxation of protons, attached to highly entangled polyethylene-oxide chains in the melt, reveals two striking chain-length dependent properties; these are interpreted from the description (reminiscent of the Rouse model) of the long-range chain dynamics supposed to occur prior to the reptation motion. Experimental results are well matched by this specific NMR approach which accounts for the novel properties and provides the monomeric friction coefficient and the terminal relaxation time, over the molecular weight range 65K to 760K.

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The reptation theory of dynamics of one linear macromolecule (of mass M) moving through cross-linked chains, originated by De Gennes [1] and extended to highly entangled chains by Doi and Edwards [2] predicts a long-range relaxation process which takes place prior to the reptation motion [3]; the spectrum of relaxation times which characterizes this process is reminiscent of the Rouse model and the molecular weight dependence of the terminal relaxation time, τ_R , is M^2 , while the terminal time of the reptation, T_r , varies as M^3 ($M^{3.4}$ for the zero-shear rate viscosity [4]). In this Letter, we report on the quantitative NMR characterization of the long-range dynamic fluctuations which occur prior to the reptation movement; this novel approach is illustrated from molten polyethylene-oxide (PEO) ($65K \leq M \leq 760K$) ($1K = 1000$ g/mol).

Attention is focused on the time average of dipole-dipole interactions of protons attached to one chain; it results from the polymer molecule tumble and monomeric unit random rotations which can be considered as isotropic only after the terminal time interval of the reptation, T_r , has elapsed; consequently, this is the time interval required to observe nuclear magnetic interactions averaged to zero. Furthermore, let $|\mathbf{H}_D|$ denote the strength of proton dipole-dipole interactions; the basic description of any motional averaging effect of magnetic interactions requires the rotational correlation time of observed molecules be equal to or shorter than $1/|\mathbf{H}_D|$ [5]. For example, for one proton pair like $-\text{CH}_2$, $1/|\mathbf{H}_D| \approx 2 \times 10^{-6}$ s; this time scale is much shorter than the relaxation time interval allotted to the renewal process of one chain conformation, except for short polymers ($M \leq 12K$ for PEO) [6]. Consequently, the time average of dipole-dipole interactions is not achieved during NMR observations. It is the purpose of this Letter to show that the resulting residual magnetic interactions induce a set of striking relaxation properties that are specific to high polymer melts.

NMR observations.—Polymer samples were bought from Polymer Laboratories and proton relaxation curves

were recorded using a Bruker MSL spectrometer operating at 60 MHz. At first glance, proton transverse relaxation curves shown in Fig. 1(A) seem to exhibit a single property, i.e., the strong molecular weight dependence; they actually contain hidden properties that are revealed from the following multiple-step analysis of relaxation curves. Let $M_x^T(t, M)$ denote the molecular weight dependent relaxation function represented by curves drawn in Fig. 1(A); it is now well established that the description of the relaxation can be based on the existence of two stochastically independent processes; correspondingly, $M_x^T(t, M)$ is necessarily the product of two contributions called $M_x^R(t, M)$ and $\Phi_R(t)$, hereafter; $M_x^T(t, M) = M_x^R(t, M) \cdot \Phi_R(t)$, where $M_x^R(t, M)$ is chain length dependent and governed both by residual magnetic interactions and by long-range chain fluctuations, whereas $\Phi_R(t)$ is independent of M and describes the relaxation process induced by fast but nonisotropic random motions of monomeric units [7]. Residual dipole-dipole interactions confer a pseudosolid behavior on $M_x^R(t, M)$ which is well detected from the formation of spin-echoes specific to solid state NMR. This time reversal effect cannot be observed from short chains ($M \leq 12K$ for PEO) [6] because they move rapidly and the characteristic time of their displacement is short compared with $1/|\mathbf{H}_D|$. Recently, we have developed an experimental procedure which provides us with the logarithmic derivatives of $M_x^R(t, M)$ and $\Phi_R(t)$, respectively. Shortly, the procedure is based on the time reversal effect which applies to $M_x^R(t, M)$, while $\Phi_R(t)$ is insensitive to this effect; it has been described elsewhere [8] [$M_x^R(t, M)$ is then determined as a numerical integral].

Minimum property: Whether their expression results from a cumulant expansion or not, relaxation curves may be conveniently represented as the ratio $\ln[M_x^R(t, M)]/t$; corresponding relaxation curves are drawn in Fig. 1(B). It is seen that all curves exhibit a minimum occurring at t_m which is nearly independent of chain length; this novel property gives evidence for the existence of two contributions, called $M_x^1(t, M)$ and $M_x^{11}(t, M)$ hereafter.

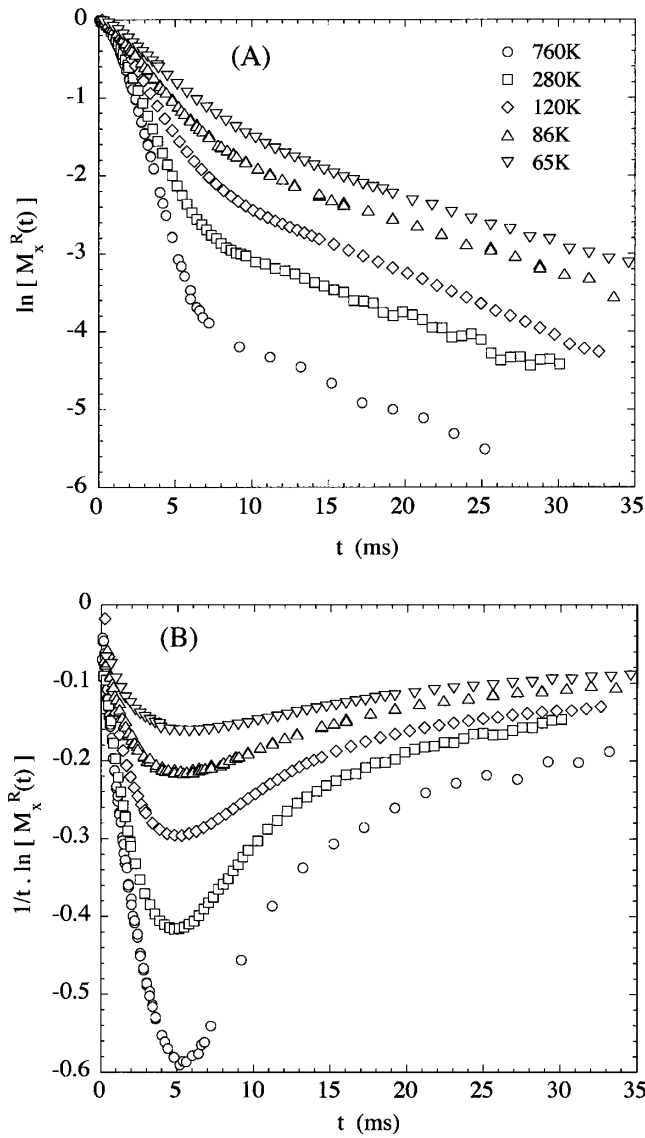


FIG. 1. (A) Molten PEO at 343 K; proton transverse relaxation curves drawn after eliminating the function $\Phi_R(t)$ for several molecular weights. (B) Illustration of the minimum property of the $\ln[M_x^R(t, M)]/t$ representation.

No minimum can be mathematically interpreted unless $M_x^R(t, M)$ is considered as the sum of at least two functions: $M_x^R(t, M) = M_x^I(t, M) + M_x^{II}(t, M)$. It is seen from the semilogarithmic plot in Fig. 1(A) that the tail of each relaxation curve is an exponential time function: $M_x^{II}(t, M) = (1 - A_1) \exp(-t/T_2)$; experimental values of the relaxation rate $1/T_2$ and the amplitude A_1 of $M_x^I(t, M)$ are reported in Table I.

Intersection property: $M_x^{II}(t, M)$ was subtracted from $M_x^R(t, M)$ to obtain $M_x^I(t, M)$; all resulting curves drawn in Fig. 2 obey an intersection property at the well defined time: $t_i = 1.6 \pm 0.05$ ms. This second novel property shows that both the amplitude of $M_x^I(t, M)$ and the molecular random movements responsible for the magnetic relaxation are molecular weight dependent.

Theoretical.—The novel striking properties of $M_x^R(t, M)$ and $M_x^I(t, M)$ are now interpreted and simulated using a model of long-range chain dynamics reminiscent of the Rouse model built in terms of the coupled motions of submolecules.

Evidence for NMR submolecules: The interpretation relies on the partition of one chain into appropriate submolecules. The strong evidence for the existence of submolecules is given from the amplitude $(1 - A_1)$ of $M_x^{II}(t, M)$; the product $(1 - A_1)M = (22 \pm 2)K$, found to be nearly independent of chain length, is considered as equal to twice the molecular weight of one end-submolecule m_s in any chain. End-submolecules are well distinguished from the remaining part of the chain because their proton relaxation rate ($\approx 0.07 \text{ ms}^{-1}$) is much smaller than the approximate relaxation rate ($\approx 0.7 \text{ ms}^{-1}$) corresponding to $M_x^I(t, M)$; the NMR distinction originates from the qualitative difference between movements of end-submolecules which are necessarily less anisotropic and faster than movements of internal submolecules. The model is based on the assumption that the size of one end-submolecule is also the size of any submolecule located along one chain; the definition of one submolecule is reinforced from the pure liquid behavior of the proton relaxation observed from low molecular weight PEO, for $M \leq 12K$; proton relaxation rates of end-submolecules ($\approx 70 \text{ s}^{-1}$) and of short free chains (12K) in the melt ($\approx 20 \text{ s}^{-1}$) have about the same order of magnitude. The actual physical meaning of the submolecule concept, involved in NMR, will be given in the next section; the average molecular weight of each submolecule is set equal to $11K$ and each submolecule is comprised of $n \approx 750$ skeletal bonds. The number N_s of submolecules in one chain is M/m_s ; the correlation between experimental and theoretical amplitudes, A_1 and $(1 - 2/N_s)$, respectively, is clearly seen in Table I. An end-to-end vector is assigned to each submolecule along one chain and the collective motions of end-to-end vectors are described according to the Rouse model. The main features about this model applied to NMR are only recalled here.

Proton transverse relaxation: Starting from $|\mathbf{H}_D|$, the residual dipole-dipole interaction associated with one Gaussian submolecule is $|\mathbf{H}_D|/n$; for each submolecule, the transverse relaxation function is expressed as

$$M_x^I(t, N_s) = (1 - 2/N_s) \exp \left[-\Delta_T(N_s)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \times \Gamma(|t_1 - t_2|) \right]. \quad (1)$$

$\Delta_T(N_s)^2$ includes both the quantum average of the residual spin-spin interactions and all numerical factors; the correlation function $\Gamma(|t_1 - t_2|)$ has already been exactly calculated [7]:

$$\Gamma(|t_1 - t_2|) = \left[\frac{1}{N_s} \sum_p \exp(-|t_1 - t_2|/\tau_p) \right]^2 \quad (2)$$

TABLE I. Polymer molecular weights and polydispersity indexes. Experimental amplitudes A_1 of $M_x^I(t, M)$ relaxation curves and relaxation rates $1/T_2$ of $M_x^{II}(t, M)$ curves; experimental values of residual magnetic interactions: $\Delta_E(M)^2$. Number of NMR submolecules per chain, N_s , theoretical amplitudes $(1 - 2/N_s)$ of $M_x^I(t, N_s)$ curves and theoretical values of residual magnetic interactions: $\Delta_T(N_s)^2$.

$10^{-3}M$	I_p	A_1	Experimental			Theoretical		
			$1/T_2$ (ms $^{-1}$)	t_m (ms)	$\Delta_E(M)^2$ (ms $^{-2}$)	N_s	$1 - 2/N_s$	$\Delta_T(N_s)^2$ (ms $^{-2}$)
65	1.04	0.69	0.054	5.8	0.27	6	0.66	0.12
86	1.03	0.75	0.06	5.3	0.34	8	0.75	0.24
120	1.02	0.82	0.076	5.0	0.44	11	0.82	0.37
180	1.04	0.87	0.06	4.8	0.48	16	0.875	0.45
280	1.07	0.90	0.071	4.9	0.52	25	0.92	0.50
450	1.03	0.93	0.07	4.9	0.55	41	0.95	0.53
760	1.03	0.97	0.08	5.4	0.61	70	0.97	0.55

with $\tau_{p^{-1}} = \tau_{s^{-1}} \sin^2(\pi p/N_s)$ and $\tau_s = C_\infty b^2 \zeta_0 n^2 / 12kT$; C_∞ is the characteristic ratio of one PEO chain, b is the mean skeletal bond length, and ζ_0 is the friction coefficient corresponding to one skeletal bond. A set of functions is obtained by varying N_s ; for each N_s , the shape of the corresponding curve is governed by the product $\Delta_T(N_s)\tau_s$. The final time scale of this set is given by τ_s .

Minimum and intersection properties: Let $M_x^{\text{Theo}}(t, N_s)$ denote the theoretical relaxation function defined from the equation

$$M_x^{\text{Theo}}(t, N_s) = M_x^I(t, N_s) + 2/N_s \quad (3)$$

in which the exponential function $M_x^{II}(t, M)$ is replaced with the constant amplitude $2/N_s$. The purpose of the following numerical simulation is to prove that the above simple expression of $M_x^{\text{Theo}}(t, N_s)$ and the mathematical structure of $M_x^I(t, N_s)$ account for both the property of intersection of $M_x^I(t, N_s)$ and the existence of the minimum of the $\ln[M_x^{\text{Theo}}(t, N_s)]/t$ representation. The pattern of theoretical curves, $M_x^I(t, N_s)$, corresponding to $N_s = 8,$

11, 25, and 41 is shown in Fig. 3(A); the intersection occurs at $t_i = 1.6$ ms. More generally, any intersection time t_i of all $M_x^{\text{Theo}}(t, N_s)$ curves is associated with a specific set of numerical values of the mean square residual interaction $\Delta_T(N_s)^2$. The intersection time $t_i = 1.6$ ms implies the set of appropriate numerical values, reported in Table I; once these numerical values were chosen, the minimum of the $\ln[M_x^{\text{Theo}}(t, N_s)]/t$ representation was found to occur at 5.1 ms [Fig. 3(B)]. In other words, the intersection property is correlated to the minimum property; it implies the effective dependence of $\Delta_T(N_s)^2$ on N_s according to the equation $\Delta_T(N_s)^2 \approx 0.6 + 1.2 \ln(1 - 2/N_s)$.

Discussion.—Figures 3(A) and 3(B) clearly show that the novel striking NMR properties can be reproduced from Eqs. (1)–(3). Considering Eqs. (1) and (2) and experimental values of the amplitude A_1 , theoretical curves were calculated, using appropriate numerical values of the mean square residual interaction, $\Delta_E(N_s)^2$, to obtain the best fit (Table I); the correlation time, associated with one submolecule, τ_s , was found to be independent of chain length and equal to 1.25 ms; experimental results are well matched by the theory, within an uncertainty smaller than 2% (Fig. 2). The square root of $\Delta_E(N_s)^2$ is about 700 rad s $^{-1}$; this value is close to the estimate $|\mathbf{H}_D|/n = 660$ rad s $^{-1}$, with $|\mathbf{H}_D| \approx 5 \cdot 10^5$ rad s $^{-1}$ and $n \approx 750$. Furthermore, it is worth noting that the value of the basic time which characterizes one submolecule, $\tau_s = 1.25$ ms at 343 K, is not far from the approximate value (≈ 0.6 ms) calculated from its expression $(C_\infty b^2 \zeta_0 n^2 / 12kT)$ with $\zeta_0 = 8 \cdot 10^{-10}$ N s m $^{-1}$ at 343 K, $C_\infty = 5$, $b = 1.5$ Å, and $n = 750$ [9]. Finally, the concept of submolecule is clearly perceived from the value of the product $\Delta_E(N_s)\tau_s \approx 1$; this is the condition which must be obeyed to observe the motional averaging effect on NMR properties. In other words, the statistical break of fluctuations is revealed from the number of skeletal bonds, n , specific to NMR; n is determined when the inverse of residual dipole-dipole interactions, $n/|\mathbf{H}_D|$, matches τ_s which depends on n^2 . The quantity $n/|\mathbf{H}_D|$ is hardly temperature dependent, whereas τ_s depends strongly on T through the friction coefficient ζ_0 . It may be worth emphasizing that this approach applies to PEO (1300 K)

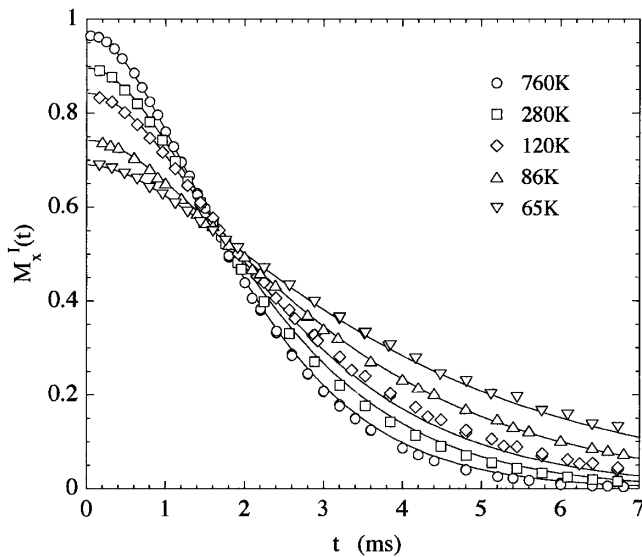


FIG. 2. Illustration of the intersection property of experimental $M_x^I(t, M)$ curves; continuous lines were drawn from Eqs. (1) and (2) using experimental values of parameters reported in Table I.

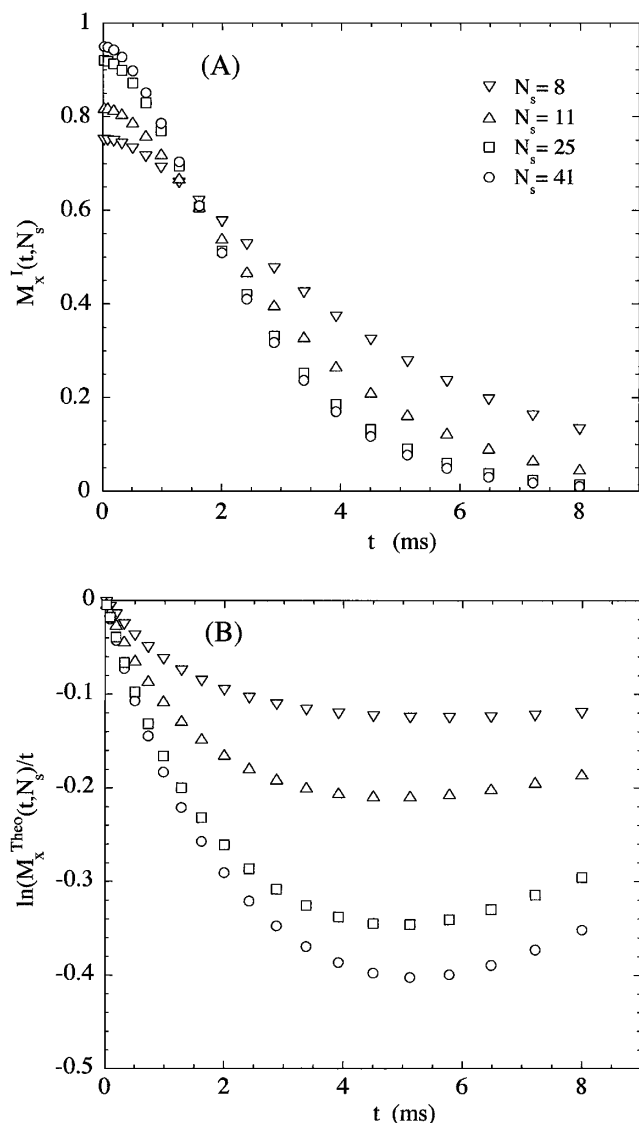


FIG. 3. (A) Illustration of the intersection property of $M_x^I(t, N_s)$ curves, calculated according to Eqs. (1) and (2). (B) Illustration of the minimum property of the theoretical $\ln[M_x^{\text{Theo}}(t, N_s)]/t$ representation, calculated according to Eqs. (1)–(3).

solutions in dimethylformamid, too; Δ_T was found to vary as 0.74 cm s^{-1} , over the PEO concentration range: $0.18 \leq c \leq 1$ (w/w). Consequently, the segmental size of one submolecule varies as $1/c$. Finally, for poly-(butadiene) observed at room temperature, the molecular weight of one submolecule was found to be 4500 g/mol.

Conclusion.—This work shows that the quantitative interpretation of proton magnetic relaxation in molten PEO requires the recorded relaxation curves be thoroughly analyzed according to an experimental procedure which is

specific to highly entangled chains and which reveals hidden striking properties. The interpretation, in very good agreement with experimental results, provides the characterization of long-range chain dynamics supposed to occur prior to the reptation motion. The proposed model requires the partition of one chain into Gaussian submolecules; their segmental size is specific to NMR and depends on the strength of magnetic proton-proton interactions and on the monomeric friction coefficient. The proposed relaxation function accounts for the very specific shape of experimental curves. It is clearly seen that the analysis of relaxation curves can provide the monomeric friction coefficient and the terminal relaxation time associated with this intermediate state of dynamics. Partly averaged magnetic interactions exhibit a chain length dependence which will be subsequently analyzed, taking earlier and recent developments about tube properties into consideration [10–12]. This work shows that the submolecule concept which implies a break in chain dynamics is quite general; however, the actual segmental size corresponding to this dynamic screening effect probably depends on the technique of observation. Results will be compared with properties probed from double-quantum NMR spectroscopy [13].

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