Nuclear magnetic resonance approach to properties of poly(ethylene oxide)–poly(methyl methacrylate) blends:
1. Chain dynamics and free volume

C. Brosseau*, A. Guillermo and J. P. Cohen-Addad
Laboratoire de Spectrométrie Physique†, Université Joseph Fourier, BP 87,
38402 Saint-Martin-d'Hères Cedex, France
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Nuclear magnetic resonance relaxation-time measurements performed on poly(ethylene oxide)–deuteriated poly(methyl methacrylate) blends of low-molecular-weight components were analysed as functions of concentration Φ and temperature T. A number of results can be derived from the homogeneity properties of the transverse relaxation functions $M_x(t, \Phi, T)$. The temperature dependence of poly(ethylene oxide) proton relaxation times in the blend is found to obey a Williams–Landel–Ferry equation with a temperature reference $T^*(\Phi) = T_g(\Phi) + 50$ K, $T_g(\Phi)$ being the glass transition temperature of the blend. It is shown that the transverse magnetization dynamics is concentration-independent at the reference temperature $T^*(\Phi)$. The dependence of transverse relaxation upon temperature and poly(ethylene oxide) molecular weight provides qualitative information about the terminal relaxation spectrum.

(Keywords: poly(ethylene oxide); poly(methyl methacrylate); blends; polymer dynamics; nuclear magnetic relaxation)

INTRODUCTION

This work deals with the n.m.r. observation of chain dynamics in binary blends formed from poly(methyl methacrylate) and poly(ethylene oxide). The molecular weights of the two species were low enough to ensure a fast relaxation of disentanglement of polymer chains in molten mixtures observed within the temperature interval 300–400 K. More precisely, the motional averaging of spin–spin interactions of protons was observed; this effect was supposed to result from small values of the lifetime of the temporary network structure that exists in a melt even though its exact definition in a mixture is still unknown. Poly(methyl methacrylate) (PMMA) chains were characterized by a weight-average molecular weight equal to 5.1×10^4 g mol^{-1}, while the value of the average molecular weight M_e^A that defines the mean spacing between entanglements is equal to 9.1×10^3 g mol^{-1}. The number of subchains is thus equal to about 6; it corresponds to the onset of a temporary network structure in pure molten PMMA. The value of the average molecular weight M_e^B that defines the mean spacing between entanglements in a pure poly(ethylene oxide) (PEO) melt is equal to 2.2×10^3 g mol^{-1}. Mixtures were formed from PEO chains characterized by a weight-average molecular weight ranging from 10^4 to 6.5×10^4 g mol^{-1}. Such molecular weights correspond to a well defined network structure in pure PEO. N.m.r. observations were made from protons attached to PEO chains, while PMMA chains were deuteriated. Consequently, the random motion of PEO chain was clearly discriminated from that of PMMA chains.

The description of molecular properties of miscible polymers in a melt parallels that of dynamic properties observed in a pure molten polymer. It concerns mainly the local friction coefficient, the effect of temporary elasticity and the exact nature of the terminal relaxation process.

Considering two miscible polymers A and B, which are used to form a blend, it is of interest to know how the resulting dynamic properties of the mixture are connected to those of pure polymers A and B. A law of mixing must apply to the friction coefficient ζ_0 associated with the translational random motion of a few skeletal bonds; this basic parameter governs all dynamic fluctuations. This coefficient normally exhibits a free-volume dependence upon temperature variations in a pure polymer.

A law of simple linear addition of the relaxation moduli of the pure components has been proposed to express the relaxation modulus $G_T(t)$ of a blend:

$$G_T(t) = \Phi_A G_A(t) + (1 - \Phi_A) G_B(t) \qquad (1)$$

where Φ_A is the volume fraction of polymer A, and $G_A(t)$ and $G_B(t)$ are relaxation moduli of A and B, respectively. Formula (1) includes the moduli of temporary elasticity G_N^A and G_N^B when the numerical value of the time variable is equal to zero[1]. This law, however, is inconsistent with many experimental results, and a detailed analysis of the dynamics of polymers in a binary blend has recently been proposed to interpret rheological properties[1].

The modulus of relaxation of a blend is expressed as:

$$G(t) = [\Phi_A m(t/\tau_A) + (1 - \Phi_A) m(t/\tau_B)]\Phi(t) \qquad (2)$$

where $\Phi(t)$ represents the effect of the tube renewal[2,3] and $m(t/\tau)$ is calculated according to the reptation model[2,3].

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* To whom correspondence should be addressed
† Laboratoire associé au CNRS

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The purpose of the present work was to study the effect of polymer mixing upon the chain dynamics observed from the transverse magnetic relaxation of protons linked to PEO chains in full miscibility with PMMA chains. Such n.m.r. observations are sensitive to the local friction and/or to the terminal relaxation of polymer chains[4].

PROPERTIES OF POLY(ETHYLENE OXIDE)–POLY(METHYL METHACRYLATE) BLENDS

The binary system under investigation here, PEO–PMMA, was chosen because its properties of miscibility have been extensively studied.

PEO and PMMA have very different glass transition temperatures; for PEO $T_g \approx 218$ K while for PMMA $T_g \approx 378$ K. This value corresponds to syndiotactic PMMA and is much different from the corresponding isotactic T_g value, which is about 328 K. The addition of PEO to PMMA induces a glass transition temperature of the mixture that is lower than that of PMMA; this effect corresponds to an increase of the free-volume fraction of the mixture, a result typically observed in polymer solutions[5]. Several observations about the phase diagram of the PEO–PMMA system have been in relatively good agreement with one another. From calorimetric studies and with reference to the single glass transition temperature criterion, total miscibility has been shown to occur above the melting point of PEO ($T_m = 338$ K). Below the melting temperature and for values of the PEO concentration higher than 20–30% (w/w), PEO crystallization takes place, amorphous PMMA being incorporated between the PEO lamellae[6]. The crystallization process of the mixture has been widely studied[7]. It is worth noting that the transition between homogeneous and heterogeneous blends corresponds to the appearance of PEO crystallinity in the mixture. The PEO–PMMA system is homogeneous up to a value of the PEO concentration equal to 20–30% (w/w). This point has been shown previously by Liberman *et al.*[8] using differential scanning calorimetry (d.s.c.) (i.e. changes in the glass transition temperature and depression of the melting point) and refractometry techniques (i.e. changes in the refractive index), by Li and Hsu using infrared vibrational spectroscopy[7].

Compatibility in the melt state has also been probed by ^{13}C n.m.r. spectroscopy[9] (from spin–lattice relaxation-time measurements).

The thermodynamic properties of these blends have already been analysed by using the Sanchez–Lacombe equation of state[10]; corresponding values of the Flory interaction parameter χ_{AB} between the monomers have been determined. On performing small-angle neutron scattering measurements, a change of sign of χ_{AB} has been observed[11,12] when the value of the concentration of PMMA becomes higher than 80% (w/w).

As pointed out by Ito *et al.*[12], the enthalpic contribution to χ_{AB} is much smaller than the entropic one: the observation of the thermal dependence of χ_{AB} has shown that the value of χ_{AB} remains constant, i.e. $\chi_{AB}(T = 353\text{ K}) = -10^{-3}$ over the temperature range (353–433 K) when the monomer fraction of PMMA is equal to 0.74.

The importance of tacticity of PMMA on the blend properties is also to be noted: PEO is compatible with syndiotactic PMMA in the amorphous and melt state but not with isotactic PMMA[7,13]. This point was elaborated by Silvestre *et al.*[14] using small-angle X-ray scattering, and further by Marcos *et al.*[6] using infrared spectroscopy.

Many methods have been used to investigate experimentally the dynamic properties of polymer blends depending on the timescale governing the chain motions: a review with a wide spectrum of measurement techniques is given in ref. 15. However, the main ambiguity about the property of polymer–polymer compatibility arises from the space scale of observation that is chosen. The sensitivity of a probe technique to a given space scale can greatly affect the conclusions that one can draw from experiments[15].

NUCLEAR MAGNETIC RESONANCE APPROACH

It is now well established that the transverse magnetic relaxation of protons attached to long polymer chains in a melt exhibits a pseudo-solid behaviour[16]. This behaviour is closely related to the existence of a temporary network structure, which is used to represent polymer melts. The mesh size of the network structure is determined from the modulus of temporary elasticity. G_N^0. By analogy with permanent polymeric gels, the mean molecular weight M_e of active chain segments is expressed as:

$$M_e = \rho RT/G_N^0 \tag{3}$$

ρ being the pure polymer density. The mean spacing between two entanglements along one long chain is defined as one segment, which is also characterized by the molecular weight M_e. The average length L_e of such a segment is given by $L_e = aM_e/M_b$; a and M_b are the mean length and the mean molecular weight of one skeletal bond, respectively. It is now currently considered that L_e represents the curvilinear distance of dynamic screening. More precisely, long-range fluctuations that occur in one chain are screened when observations are made within one chain segment determined by a contour length shorter than L_e.

Condition of full motional averaging

It has long been considered that a scaling invariant can be defined for n.m.r. properties when the lifetime T_R of the temporary network structure of a molten polymer is long enough. The estimate of the lifetime T_R can be obtained from the value of the terminal relaxation time η_0/G_N^0; η_0 is the zero-shear-rate viscosity of the melt. The introduction of a scaling invariant relies upon the following analysis. On the one hand, the condition of motional averaging of spin–spin interactions is defined by the inequality:

$$|\mathscr{H}_T| T_R < 1 \tag{4}$$

where $|\mathscr{H}_T|$ represents the strength of dipole–dipole interactions of protons in the glassy state (typically $|\mathscr{H}_T| = 10^5$ rad s^{-1}). The above condition is not fulfilled when one long chain is considered as a whole; its full random motion is characterized by T_R. A typical value of G_N^0 is 10^5 Pa; therefore, the condition for motional averaging reads:

$$\eta_0 < 10\text{ P} \tag{5}$$

This small numerical value of the viscosity η_0 corresponds to very short chains only.

On the other hand, a partial motional averaging of tensorial interactions of spins must result from internal fluctuations that occur in one chain in a melt.

Condition of motional averaging of partial interaction

Let $\langle \mathscr{H}_T \rangle$ denote this partial average. It has long been supposed that the partial average can be associated with the existence of a temporary network structure. The residual interaction $\langle \mathscr{H}_T \rangle$ is analogous to that observed in permanent polymeric gels. Its order of magnitude is usually equal to 10^3 rad s^{-1}. A rough estimate of the expression for $\langle \mathscr{H}_T \rangle$ is given by $\langle \mathscr{H}_T \rangle = a|\mathscr{H}_T|/L_e$; L_e is the mean contour length between two entanglements along one chain. The motional averaging condition for $|\mathscr{H}_T|$ is now expressed as:

$$\langle \mathscr{H}_T \rangle \eta_0 M_e / \rho RT < 1 \qquad (6)$$

This is fulfilled for $\eta_0 < 5 \times 10^3$ P. This condition applies to short chains that are still entangled. The presence of a residual interaction is well evidenced from the spectrum-narrowing effect induced by sample rotation. It is also well observed from spin echoes specific to the presence of a residual interaction[17].

Residual interaction of spins

Neglecting non-adiabatic terms, the residual dipole–dipole interaction associated with all nuclear spins located on a given chain segment is expressed as[18]:

$$\langle \mathscr{H}_T \rangle_L^e = \tfrac{3}{5}[(3\cos^2\theta_e - 1)\langle \boldsymbol{r}_e \rangle^2 \Lambda a^2 \langle (\boldsymbol{r}_e)^2 \rangle_0^{-2}] \times \left(\sum_{k,k'} A_{kk'} \{3\cos^2[\theta(\boldsymbol{b}_{kk'})] - 1\} \right) \qquad (7)$$

The chain segment is characterized by its end-to-end vector $\langle \boldsymbol{r}_e \rangle$; the double sum is extended over all proton pairs along the chain segments. Angular coordinates of the vector $\boldsymbol{b}_{kk'}$ joining two nuclei k and k' are expressed in a reference frame associated with monomeric units. The above expression applies in the laboratory reference frame associated with the steady magnetic field $\boldsymbol{B}_0$; θ_e is one of the angular coordinates of $\langle \boldsymbol{r}_e \rangle$ in this reference frame. The mean-square distance $\langle (\boldsymbol{r}_e)^2 \rangle_0$ is calculated in the absence of any constraint. Finally, Λ is the orientational correlation function involving three skeletal bonds; it is called the parameter of second-order stiffness. When the transverse relaxation mechanism is entirely governed by the residual interaction $\langle \mathscr{H}_T \rangle_L^e$, the magnetic relaxation function $M_x^e(t)$ has a simple expression in the rotating frame:

$$M_x^e(t) = \mathrm{Tr}\{\exp(\mathrm{i}\langle \mathscr{H}_T \rangle_L^e t)\mathscr{M}_x \times \exp(-\mathrm{i}\langle \mathscr{H}_T \rangle_L^e t)\mathscr{M}_x\}/\mathrm{Tr}\{\mathscr{M}_x^2\} \qquad (8)$$

where $\mathscr{M}_x$ represents the total transverse component of the nuclear magnetization operator; $\mathrm{Tr}\{\mathscr{A}\}$ means trace of the operator $\mathscr{A}$. It is seen from formulae (7) and (8) that the timescale of evolution of $M_x^e(t)$ is a function of the ratio $\langle \boldsymbol{r}_e \rangle^2 \Lambda a^2 \langle (\boldsymbol{r}_e)^2 \rangle_0^{-2}$. It is considered that the width of the Gaussian distribution of vectors $\langle \boldsymbol{r}_e \rangle$ throughout the polymer melt is proportional to $\langle (\boldsymbol{r}_e)^2 \rangle_0^{1/2}$; then, the timescale of evolution of $M_x^e(t)$ is given by:

$$\tau \approx \Delta_G^{-1} \langle (\boldsymbol{r}_e)^2 \rangle_0 / a^2 \Lambda \qquad (9)$$

with Δ_G the dipole–dipole interaction associated with the glassy state and with $\langle (\boldsymbol{r}_e)^2 \rangle_0 = \lambda L_e$; λ is the Kuhn step length. The quantity $a^2\Lambda/\lambda L_e$ can be considered as a scaling invariant. It plays the role of a reference frequency to characterize the terminal relaxation spectrum of one chain in a melt.

The relaxation function expressed by formula (8) has already been calculated in the case of one proton pair. It has been shown to apply to the analysis of n.m.r. properties of swollen polymeric gels formed from end-linked PEO chains[18].

Magnetic relaxation functions

Here the n.m.r. results are discussed in the case where the motional averaging condition is progressively fulfilled. Consequently, the relaxation function is assumed to be expressed as usual as:

$$M_x^e(t) = \exp\left(-\int_0^t (t - \tau)\Gamma(\tau)\,\mathrm{d}\tau \right) \qquad (10)$$

where $\Gamma(t)$ is the correlation function of $\langle \mathscr{H}_T \rangle_L^e$, considered as a random time function. Likewise $\Gamma(0) = M_2^M$ is the second moment of the resonance spectrum and is given by[4]:

$$M_2^M = \int_{\boldsymbol{r}_e} (\langle \mathscr{H}_T \rangle_L^e)^2 \mathscr{P}(\boldsymbol{r}_e)\,\mathrm{d}\boldsymbol{r}_e \qquad (11)$$

where $\mathscr{P}(\boldsymbol{r}_e)$ is the probability distribution function of vectors $\boldsymbol{r}_e$. The time evolution of the random variable $\langle \boldsymbol{r}_e \rangle$ can be described within the framework of terminal chain relaxation.

Whatever the complexity of the chain relaxation spectrum, all characteristic times that determine this spectrum are related to a single basic dynamic parameter, which is the friction coefficient ζ_0 (ref. 19). It will be shown hereafter that the transverse magnetization dynamics (equation (10)) is sensitive to this coefficient ζ_0. For illustration, it is instructive to consider the Rouse model for chain dynamics. Within the framework of this model the correlation function is[4]:

$$\Gamma_r(t) = \frac{M_2^M}{N_S^2} \sum_{p,q=1}^{N_s} \exp\left[-t\left(\frac{1}{\tau_p} + \frac{1}{\tau_q} \right) \right] \qquad (12)$$

and when the motional averaging of spin interactions is achieved for all the N_S normal modes (i.e. $\tau_p(M_2^M/N_S)^{1/2} \ll 1$), then the relaxation rate can be written as[4]:

$$1/T_2 = (M_2^M/N_S^2) \sum_{p,q}^{N_s} (\tau_p^{-1} + \tau_q^{-1})^{-1} \qquad (13)$$

with τ_p proportional to ζ_0/p^2kT. It follows from equation (13) that $1/T_2 \sim \zeta_0$ in accordance with our previous remark.

EXPERIMENTAL

Materials and preparation of blends

Deuteriated poly(methyl methacrylate) (PMMA(D), component 1) and hydrogenated poly(ethylene oxide) (PEO, component 2) were used as the two pure components of the blends. All the polymers were commercial products purchased from Polymer Laboratories and were used as received from the manufacturers. Data relating to the molecular characteristics of the polymer samples are listed in *Table 1*. Prior to use, all polymers were dried overnight under vacuum at 50°C.

Binary blends of monodisperse PMMA and PEO of

Table 1 Some physical characteristics of the polymers used in this work[a]

	T_g (K)	M_e (g mol^{-1})	M_c (g mol^{-1})	ρ (g cm^{-3})
PEO	218	2.2×10^3	3.6×10^3	1.08
PMMA	378	9.1×10^3	3.1×10^4	1.14

[a] Values for M_e are from ref. 24; other values are from ref. 25

various compositional ratios were prepared by solution casting from benzene. The solvent was allowed to evaporate slowly at room temperature. The mixture was then dried in a vacuum oven at 70°C for two days to complete removal of solvent.

The blend was transferred into a n.m.r. sample tube, which was sealed after prolonged evacuation to avoid any chemical degradation. The following compositions (in per cent) were investigated: PEO/PMMA 10:90, 15:85, 20:80, 25:75 and 40:60 (w/w).

Before each n.m.r. test, samples were annealed at a temperature equal to 80°C in order to erase all memory effects and to give all samples the same thermal history. Experiments were all run in decreasing order of temperature.

We found by differential scanning calorimetry that the T_g of the blends obtained with the above preparation take similar values to those reported by Li and Hsu[7]. The tacticity of PMMA samples was determined from dilute solution ^{1}H n.m.r. spectra. Analysis of the integrals of the corresponding resonance lines gives 68% syndiotactic, 28% heterotactic and 4% isotactic triad concentrations.

N.m.r. measurements

The transverse magnetic relaxations of the protons linked to PEO were measured through multiple spin–echo sequences using a pulsed spectrometer (Bruker CXP) operating at 36.0 MHz. Transverse magnetization was obtained by using a Carr–Purcell sequence to overcome the usual inhomogeneity problems and other off-resonance effects. A pseudo-solid echo sequence as previously described in several papers[16,17] was also employed to probe dipolar tensorial interaction of nuclear spins through their characteristic properties of symmetry and intersection. The sample temperature was kept constant with ±1 K.

NUCLEAR MAGNETIC RESONANCE OBSERVATION OF POLY(ETHYLENE OXIDE) CHAIN DYNAMICS

Transverse magnetic relaxation functions of protons attached to PEO chains were recorded at several values of the temperature within the range 293 K $\leqslant T \leqslant$ 410 K and at several values of the PEO weight fraction Φ. They were analysed according to the following method.

Property of time–temperature superposition

It was first attempted to show that relaxation functions obey a superposition property by changing the timescales of representation of experimental curves. This property, illustrated by *Figures 1a* and *1b*, is observed for each PEO concentration and $T > T_g(\Phi)$. As a consequence, the n.m.r. relaxation function can be written as:

$$M_x(t, \Phi, T_j) = M_x(a_{ij}(\Phi)t, \Phi, T_i) \qquad (14)$$

where $a_{ij}(\Phi)$ denotes the shift factor of the relaxation timescale between temperatures T_i and T_j. Values of a_{ij} are plotted in a semi-logarithmic scale on *Figure 1c*. This graph shows a non-linear dependence with respect to $1/T$ and therefore cannot be described by an Arrhenius relationship.

As a consequence of the superposition property, all relaxation functions can be characterized by a single time

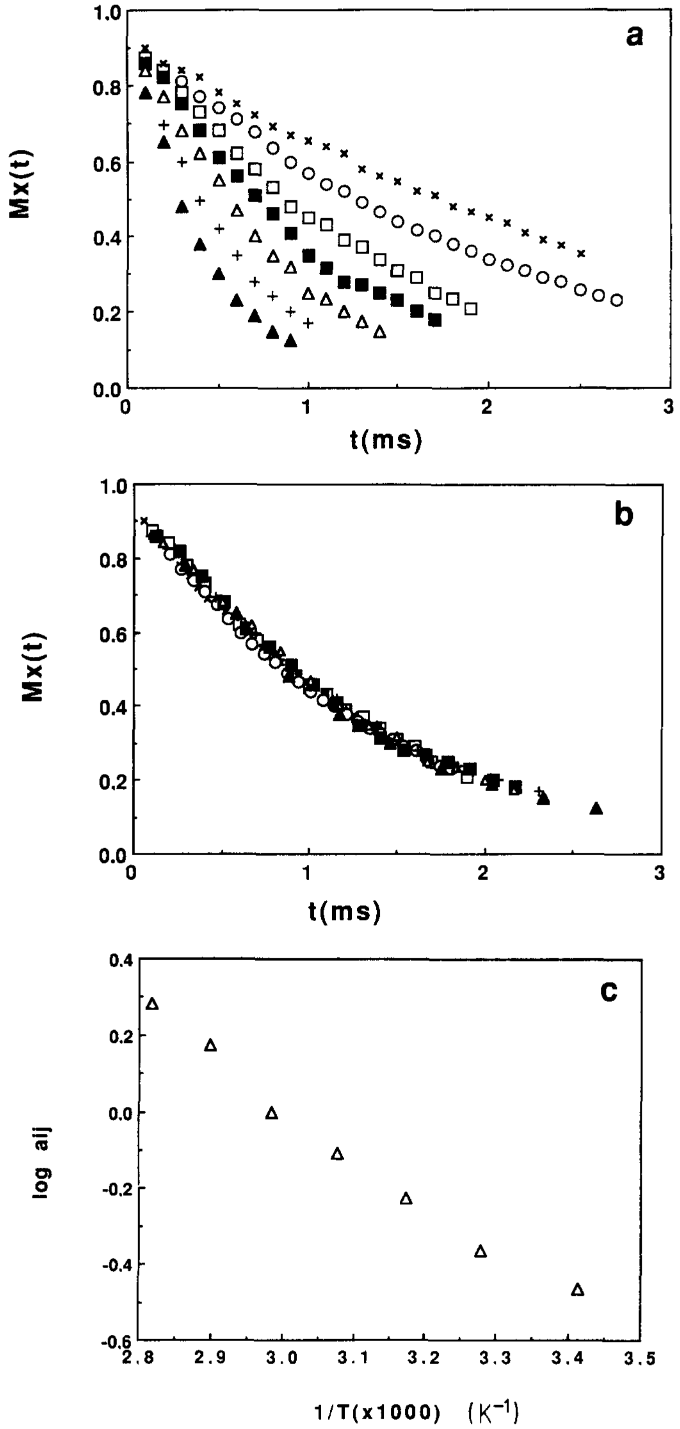


Figure 1 (a) Transverse magnetization relaxation for PEO in B-type blend (Φ_{PEO} = 0.37 w/w): (×) T = 355 K, (○) T = 345 K, (□) T = 335 K, (■) T = 325 K, (△) T = 315 K, (+) T = 305 K and (▲) T = 293 K. (b) Relaxation function shifted to the reference temperature T = 335 K. Timescale shift factors are: 1.9 (T = 355 K), 1.5 (T = 345 K), 0.78 (T = 325 K), 0.6 (T = 315 K), 0.43 (T = 305 K) and 0.34 (293 K). (c) Arrhenius plot of timescale shift factors a_{ij} corresponding to (b)

parameter $t_{0.6}$ corresponding to 60% of the decay of the initial value, whatever the complex mathematical structure of these functions.

It is worthwhile to note from the timescale of the relaxation signal shown in *Figure 1* that no crystallized PEO domains are observed.

Partial motional averaging regime

A specific pulse sequence was applied to the transverse magnetization to attempt to form pseudo-solid spin echoes; they are specific to the presence of a residual interaction of spins[17]. Typical pseudo-solid echoes observed from PEO chains are shown in *Figure 2*; they correspond to a PEO concentration $\Phi = 0.20$ and temperature values equal to 336, 376 and 396 K ($M_w = 2.2 \times 10^4$ g mol^{-1}).

Pseudo-solid echoes observed at $T_g + 10$ K are well defined (*Figure 2a*) and obey characteristic properties[17] of a relaxation mechanism fully governed by the residual dipolar interaction. One of these properties concerns the slope of the echo function $E(t, \tau)$ at the time $t = \tau_+$, which must be exactly the opposite of the slope of the relaxation function at $t = \tau_-$:

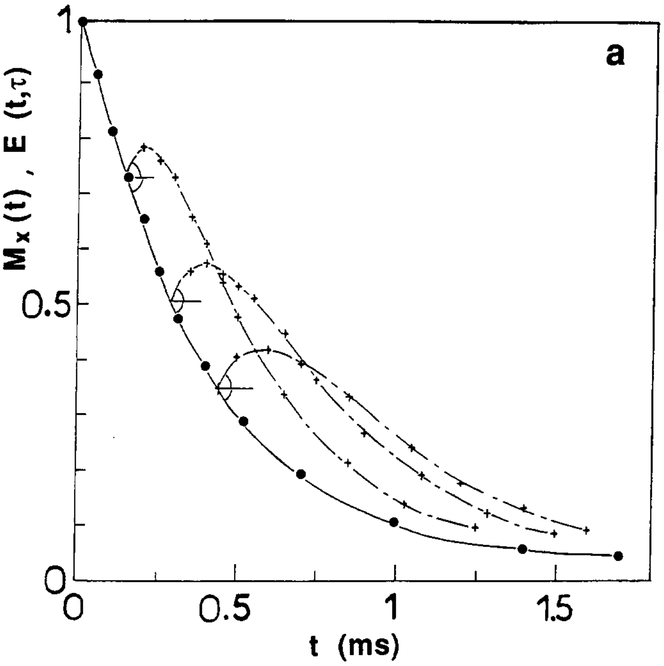
$$\left(\frac{\mathrm{d}E(t,\tau)}{\mathrm{d}t}\right)_{t=\tau_+} = -\left(\frac{\mathrm{d}M_x^e(t)}{\mathrm{d}t}\right)_{t=\tau_-} \qquad (15)$$

At $T_g + 50$ K the shape of the pseudo-solid echoes becomes distorted and flattens (*Figure 2b*). For higher temperatures, echoes are hardly distinguished from the relaxation function (*Figure 2c*) and present a strong deviation from condition (15).

The presence of pseudo-solid echoes shows that polymer chains are subjected to topological constraints. The relaxation rate of these constraints is shorter than or equal to the residual dipolar interaction. It is shown next that the relaxation rate is governed by a basic dynamic parameter.

Free-volume dependence of n.m.r. relaxation time

The transverse magnetic relaxation functions of PEO chains possess a remarkable property, which has been elaborated upon by inspection of their concentration dependence. We found that the magnetization decays were in good coincidence whatever the concentration value when an appropriate reference temperature $T^*(\Phi)$



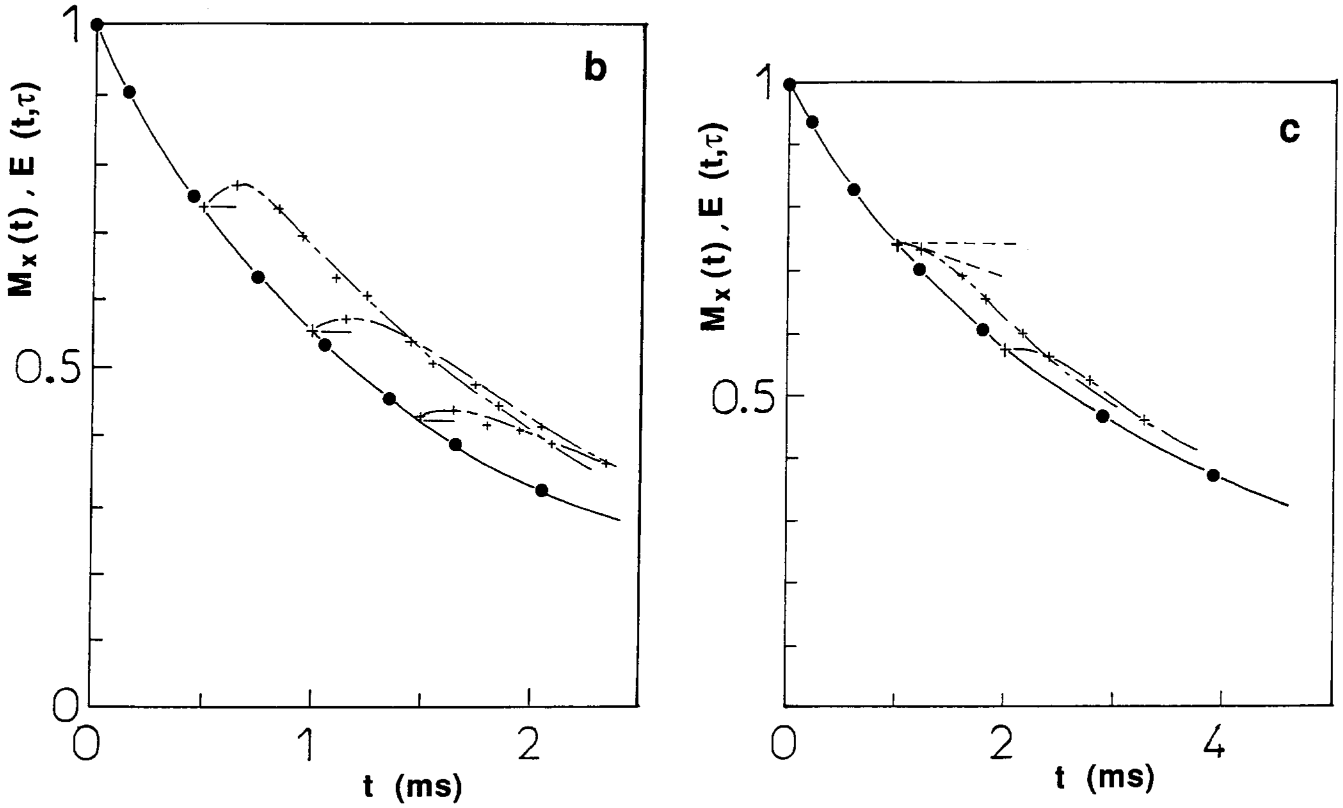


Figure 2 Relaxation function (●) and pseudo-solid echoes (+) observed for PEO in B-type blend ($\Phi_{PEO} = 0.20$ w/w) at different temperatures: (a) $T = 336$ K, (b) $T = 376$ K, (c) $T = 396$ K

was chosen. This can be seen on *Figure 3* corresponding to the B-type blend. The key point here was to recognize that the reference temperature was $T_g(\Phi)$ shifted of a value $C(\Phi)$. Values of $C(\Phi)$ are explicitly given in *Figure 3* and are around 50 K.

Consequently, the n.m.r. relaxation function is expressed as:

$$M_x(t, \Phi, T) = M_x(a_T(\Phi)t, \Phi, T^*(\Phi)) \qquad (16)$$

where $a_T(\Phi)$ represents the timescale shift factor with reference to the temperature $T^*(\Phi)$. For illustration, the graph of $a_T(\Phi)$ is displayed in *Figure 4* for the B-type blend.

As already shown in *Figure 1c*, the shift factors $a_T(\Phi)$ do not satisfy an Arrhenius temperature dependence. They can be fully accounted for by assigning a Williams–Landel–Ferry (WLF) free-volume equation. The free-volume analysis is illustrated in *Figure 5* for the different values of the PEO weight fraction. The best fit was obtained for the above defined $T^*(\Phi) = T_g(\Phi) + C(\Phi)$.

The relaxation time–temperature shift factor a_T is given by equation (16) and yields:

$$\{\log[t_{0.6}(T)/t_{0.6}(T^*)]\}^{-1} = (\log a_T)^{-1}$$
$$= C_1 + C_2/(T - T^*) \qquad (17)$$

where C_1 and C_2 are related to the free-volume fraction $f = C_1/2.303$ and to the thermal coefficient of expansion of free volume $\alpha = C_1^2/2.303C_2$ at $T = T^*$.

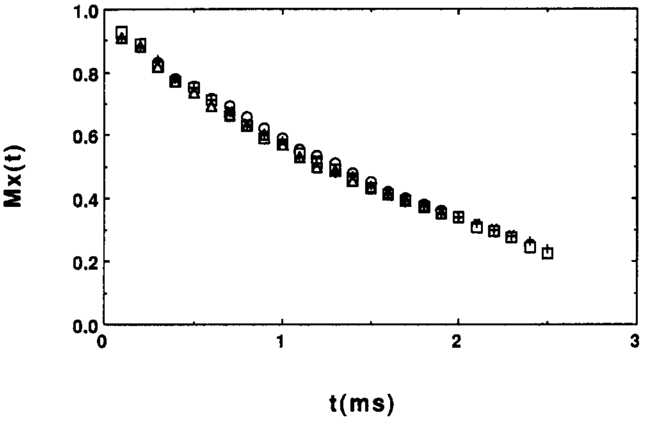


Figure 3 Relaxation functions $M_x(T, \Phi)$ corresponding to PEO in B-type blend: (+) $\Phi = 0.10$ ($T^* = 393$ K, $C = 46$ K); (○) $\Phi = 0.13$ ($T^* = 390$ K, $C = 50$ K); (□) $\Phi = 0.20$ ($T^* = 377$ K, $C = 51$ K); (△) $\Phi = 0.24$ ($T^* = 370$ K, $C = 54$ K); (×) $\Phi = 0.37$ ($T^* = 342$ K, $C = 50$ K)

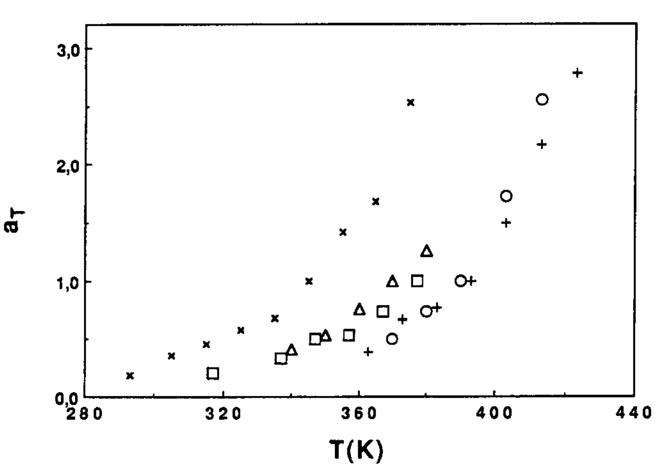


Figure 4 Temperature dependence of time shifts $a_T(\Phi)$ for B-type blend. Same symbols as in *Figure 3*

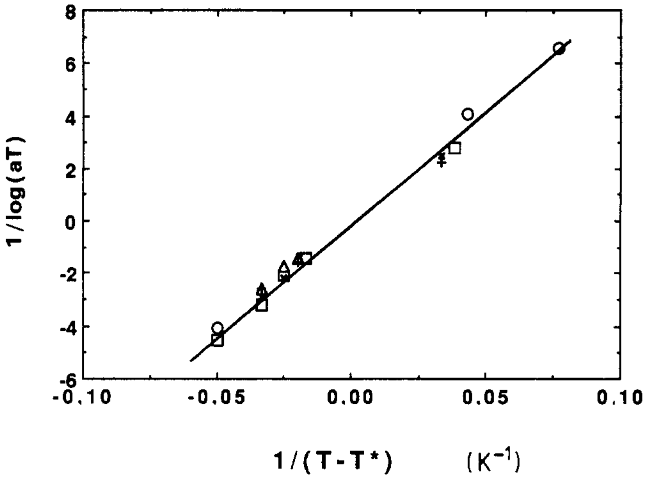


Figure 5 Free-volume plot of the shift factor a_T for B-type blend. The full line represents equation (17)

Table 2 Molecular-weight characteristics of PEO–PMMA blends with their symbols. Polydispersity indices are in parentheses

Blend	M (PEO) ($\times 10^3$ g mol^{-1})	M (PMMA) ($\times 10^3$ g mol^{-1})
A	10 (1.10)	51 (1.04)
B	21.8 (1.09)	51 (1.04)
C	37 (1.07)	51 (1.04)
D	64.7 (1.04)	51 (1.04)

Values of C_1 and C_2 obtained from a least-squares analysis are: $f_T^* = 0.058$ and $\alpha_T = 9.3 \times 10^{-5}$ K^{-1} for B-type blend. Comparison of these data with the values for PMMA(H) reported by Ferry[19] ($f = 0.013$ and $\alpha = 1.7 \times 10^{-4}$ K^{-1}) yields the conclusion that PEO (low-T_g component) plays the role of a solvent in these blends. This conclusion is supported by the high mobility value of PEO reported in the literature[20].

Molecular-weight dependence

We turn now to the discussion of the above results in terms of the chain length. We explored the relaxation behaviour for a wide range of PEO molecular weights (see *Table 2*) from 10^4 to 6.7×10^4 g mol^{-1} and taking the PMMA molecular weight as constant. Our results are summarized in *Figure 6*. Two different behaviours can be distinguished depending on temperature, and are attributed to the lifetime of topological constraints as seen by the PEO chains.

At lower temperature ($T < T^*$), the relaxation times $t_{0.60}$ and $t_{0.25}$ measured at 60% and 25% of the decay amplitude have identical dependence on molecular weight. This indicates that the magnetization decay shapes are molecular-weight-independent. Moreover, for this temperature range, well shaped pseudo-solid echoes are observed (e.g. *Figure 2a*). Consequently, the transverse magnetization dynamics is driven by the residual dipolar interaction $\langle \mathscr{H}_T \rangle_L^c$: the relaxation rate of the constraints is shorter than $\langle \mathscr{H}_T \rangle_L^c$. A slight increase of the relaxation times $t_{0.60}$ and $t_{0.25}$ is observed but is not connected to a weak increase of the deviation $T - T_g$ from T_g

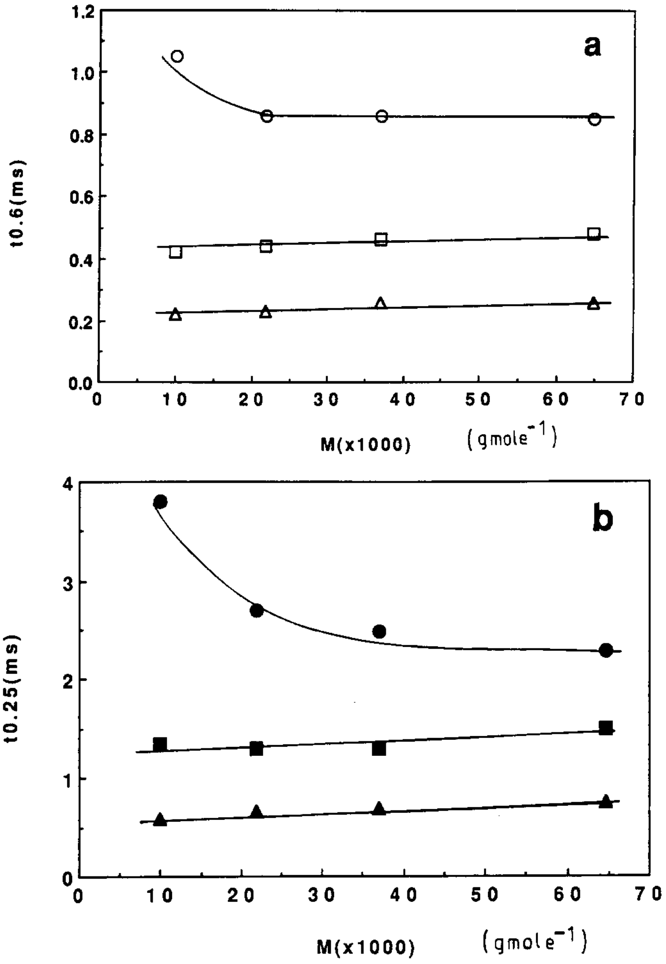


Figure 6 (a) Molecular-weight dependence of relaxation time $t_{0.60}$: (△) $T = 336$ K, (□) $T = 356$ K, (○) $T = 376$ K; full curves are guides for the eye. (b) Same as (a) for the relaxation time $t_{0.25}$

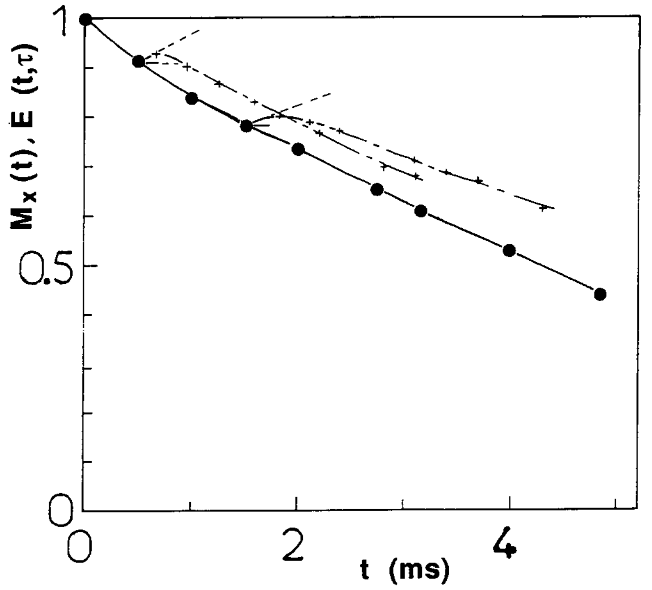


Figure 7 Relaxation function (●) and pseudo-solid echoes (+) observed for PEO in D-type blend ($\Phi_{PEO} = 0.20$ w/w) at $T = 416$ K

because of the usual increase of T_g observed by lengthening polymer chains.

For temperatures higher than T^* the relaxation times $t_{0.60}$ and $t_{0.25}$ vs. molecular weight plots indicate a change of the n.m.r. signal shape, showing that the transverse magnetization relaxation is here sensitive to the relaxation rate of the constraints. The decrease of the magnetic relaxation times is induced by an increasing lifetime of the constraints when the molecular weight is increased. Note that pseudo-solid echoes are still observed (*Figure 7*) for sample D (the highest molecular weight) at 416 K ($T^* + 40$ K), in marked contrast with sample A (the lowest molecular weight), for which such echoes cannot be observed for $T \geqslant T^*$. In addition, it is worth comparing *Figure 2c* and *Figure 7*; the tangents drawn to echoes $E(t, \tau)$ at $t = \tau$ are negative in *Figure 2c* whereas the tangents are positive in *Figure 7*.

CONCLUDING REMARKS

Two main features need to be discussed.

(1) Concerning the reference temperature $T^* = T_g(\Phi) + 50$, we note that a similar value was encountered by Williams *et al.*[21] in a mechanical relaxation study for a variety of polymers (e.g. PMMA, $T_g + 55$; polystyrene, $T_g + 54$; polyisobutylene, $T_g + 41$). A similar property was also found in glassy materials[21]. In the case of polybutadiene, the temperature shift has been observed from two independent experimental investigations: viscoelastic measurements[22] and analysis of spin–lattice relaxation rate of protons and ^{13}C nuclei[23] lead to a shift temperature equal to 55 K.

It would be useful to compare the present n.m.r. relaxation data with the rheological behaviour of these blends at the same iso-free-volume condition. Except for the work of Wu[24], considering high-molecular-weight components in PEO–PMMA blends, no short-chain measurements have been reported in the literature to our knowledge.

(2) Chain dynamics was investigated by varying either the temperature or the molecular weight of PEO. Here the n.m.r. approach permits us to characterize chain dynamics of one component in the blend in a molten state thermodynamically defined by the glass transition temperature of the blend shifted by 50 K. When the properties of pseudo-solid echoes are well verified, the approach reported in this work is relevant to characterize the transient network structure correlated to the temporary elasticity of the blend (low temperature and high molecular weight). Further experiments using a wide range of higher molecular weights are needed. A companion paper will follow to cope with the long-chain behaviour in PEO–PMMA blends.

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