Nuclear Magnetic Resonance Study of the Segmental Motion of Poly(ethylene oxide) 2000 Grafted on Silica

Louis Facchini and André Pierre Legrand*

Laboratoire de Physique Quantique, ERA 676, E.S.P.C.I., 75231 Paris Cedex 05, France.

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ABSTRACT: The segmental motion of poly(ethylene oxide), with an average molecular weight of 2000, grafted on silica gel, in contact with benzene has been investigated by ^{13}C and ^{1}H magnetic resonance. A two-phase system is observed in the temperature range 10–70 °C, with a population ratio of about one at 65 °C. Analysis of the spin–lattice and spin–spin relaxation times provides evidence for strongly anisotropic segmental motion in each phase. The trend of the Fourier transform of the autocorrelation function is deduced. The monomer unit motion is described as the combination of the fast modes of reorientational segmental motion parallel to the surface of silica and the slow mode of reorientational motion along an axis perpendicular to the surface.

Introduction

Polymers or short molecular chains adsorbed on the surface of a solid, or localized at an interface, contribute by their behavior (conformation, mobility, etc.) to strongly modifying the properties of the media. Applications of such systems for chromatography, stabilization of emulsion, and supported catalysis are of interest.

The case of grafted chains on a solid support has given rise to theoretical[1] and experimental studies.[2-4] Simplifying hypotheses concerning the interpretation or prediction of the behavior of chains need more experimental results in order to be tested. Different assumptions may be proposed. Rubin[5] considers that monomer units are only in interaction with the surface when they are in close contact with the surface whereas one could extend the influence of the surface depending on the range of the interaction. Homogeneous or heterogeneous structure of the adsorbed layer could consequently be inferred. Thus, it appears to be important to observe structure and dynamic behavior on a local scale, i.e., at the monomer unit scale. EPR, using an additional spin label grafted to the free end part of the polymer, is a typical way of obtaining this kind of information. An objection may be made concerning the influence of the label on the behavior of the chain itself.[6] NMR of ^{1}H and ^{13}C of the monomer units, although less sensitive than the previous method, is not subject to this objection.

The grafting of an isolated ideal chain on solid surface does not affect the components of the random walk parallel to the surface.[7] Experimentally the highest value of the grafted ratio is about $S/\pi R_F^2$, where S is the surface of the solid and R_F is the Flory radius of the macromolecule.[8] From the dynamic point of view, one can imagine that the diffusion of the monomer units along the axis perpendicular to the surface is more perturbed than the diffusion of the monomer units parallel to the surface. Thus the grafting of a macromolecule on a solid surface must introduce a significant anisotropy in the segmental motion. On the other hand, it is known that a macromolecule has a complex motion even in solution. It is schematically characterized by a slow process of subchain motion superimposed on a local fast process of monomer unit motion.[9] One can postulate that the subchain motion is more disturbed by the grafting than the fast motion of monomer units. So it seems to us that the analysis of the modification of the anisotropy of the segmental motion is a powerful tool of investigation for studying polymers grafted on a solid surface. NMR is a technique which can study a system with different motions on time scales in a range of 10^4 to 10^{11} Hz. It is known that the spin–lattice relaxation time is only sensitive to characteristic motion frequencies on the order of the Larmor frequency, whereas spin–spin relaxation time is also sensitive to the slow processes of motion.

In this work, we describe the analysis of relaxation times of poly(ethylene oxide) (PEO) with an average molecular weight of 2000, grafted on silica gel and immersed in benzene. In this system, polymer–surface interaction seems greater than the solvent–surface interaction.[10] From the point of view of NMR, PEO is a very simple system since all the CH_2 groups are chemically identical (except the terminal groups). Thus, the NMR spectrum of the polymer solution is a simple line for the high value of molecular weight.

Experimental Section

PEO with a molecular weight of 2000 ($M_n = 1760$, $M_w = 1870$, $P = 1.06$) was grafted on dehydrated silica by means of a hydroxyl group by Lecourtier.[11] The silica was silica gel 60 Merck used for chromatography. The particles were in the range of 0.04–0.06 mm in diameter. Its specific surface, measured by adsorption of nitrogen, was about 350 m^2/g. PEO supplied by Merck was poly(ethylene glycol) 2000 for synthesis. The ratio of grafting is about 20% by weight. As a solvent, deuterated benzene is used in order not to produce a ^{1}H NMR signal and in order to decrease the dipolar interaction between the nuclei of benzene and the nuclei of the polymer. The sample is sealed under vapor pressure of C_6D_6 in an NMR tube after repeated freeze–pump–thaw cycles.

The ^{13}C NMR spectra are recorded on a Varian FT 80 spectrometer at an operating frequency of 20 MHz under conditions of complete decoupling of protons over a temperature range of 27 to 65 °C. ^{1}H NMR spectra were recorded on Varian XL 100 and Bruker SXP spectrometers at operating frequencies of 100 and 90 MHz, respectively, over the temperature range 10–70 °C. At room temperature a Bruker BKR 302S was used at operating frequencies of 6 and 60 MHz.

Fourier transform spectra obtained from $(180,t,90,\mathrm{FID})_N$ (where FID is the free induction decay and N is the number of scans) are reported in Figure 1 (^{13}C) and Figure 2 (^{1}H) for different values of the time t. Over the temperature range 10–70 °C, the existence of a two-phase system characterized by different mobilities of the monomer units characterized by different relaxation times is clearly demonstrated. The population ratio is determined from the ^{1}H and ^{13}C FID, but the precision is missing because the dead time of the receiver is of the order of 20 μs (principally for the less mobile phase nuclei). However, the spin–spin relaxation times are not too much modified because they are very long relative to the dead time. Nevertheless, we had been able to estimate that the less mobile phase population is about 90% of the total at room temperature and 50% at 340 K. The fact that one can distinguish spin–lattice relaxation times on the order of 0.5 s implies that the lifetime in each phase is much greater than 0.5 s.[12]

In the assumption that the evolution of the nuclear magnetization after a pulse is described by Bloch equations for each phase, there exists a time such that the spectrum of the other phase is null. Thus the spin–spin relaxation time is deduced from the line width of the Fourier transform of the FID obtained in the sequence $(180,t_0,90,\mathrm{FID})_N$. As the line width is relatively

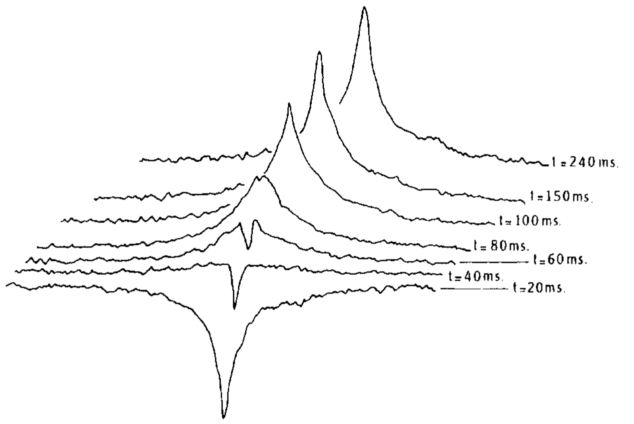

Figure 1. Inversion–recovery experiments on ^{13}C at 20 MHz, at 300 K, under conditions of complete decoupling of ^1H. The delay t between the 180° and 90° pulses is indicated.

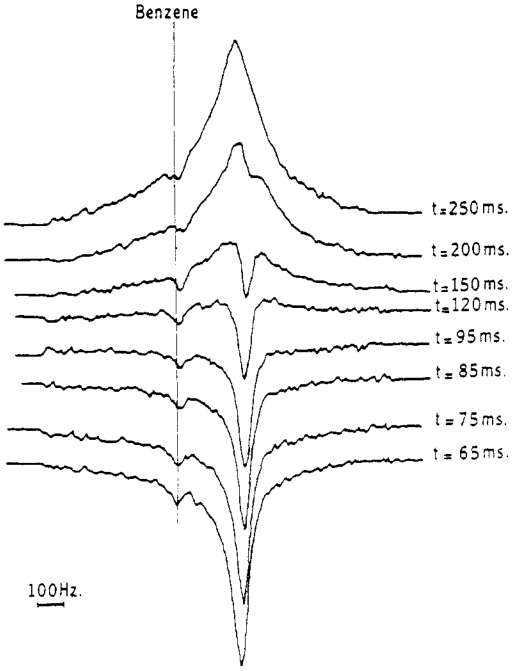

Figure 2. Inversion–recovery experiments on ^1H at 100 MHz at 300 K. The delay t between the 180° and 90° pulses is indicated.

broad, the inhomogeneity of the static magnetic field was neglected. The spin–lattice relaxation time is deduced from t_0 by the relation

$$T_1 = t_0/\ln 2$$

The phase where T_1 and T_2 are longest is the most mobile phase (mmp), which we associate with segments far from the surface, whereas the phase with smaller T_1 and T_2 is the less mobile phase (lmp), which we associate with segments near the surface. The values of T_1 and T_2 for each phase and each nucleus, as a function of temperature, are shown in Figures 3 and 4. The experimental results which were published for the first time[13] are slightly modified because the precision of our measurements has been improved (in particular for the spin–spin relaxation times).

Preliminary EPR measurements of silica have shown that paramagnetic centers are present in very low quantities. Thus, in our analysis the influence of paramagnetic centers is neglected.

The nuclear Overhauser enhancement (NOE) is also measured from ^{13}C NMR measurements and is equal to 3 only at a temperature of 65 °C. Thus, for this temperature we deduce that NOE is 3 for each phase. The experimental NOE can be written

$$(\mathrm{NOE})_{\mathrm{exptl}} = p(\mathrm{NOE})_{\mathrm{lmp}} + (1 - p)(\mathrm{NOE})_{\mathrm{mmp}}$$

where $(\mathrm{NOE})_{\mathrm{lmp}}$ is the NOE of the less mobile phase, $(\mathrm{NOE})_{\mathrm{mmp}}$ is the NOE of the most mobile phase, and p is the relative population of the less mobile phase. Unfortunately, we cannot deduce p with a good precision for temperatures lower than 65 °C, so we cannot deduce the NOE of each phase at temperatures lower than 65 °C.

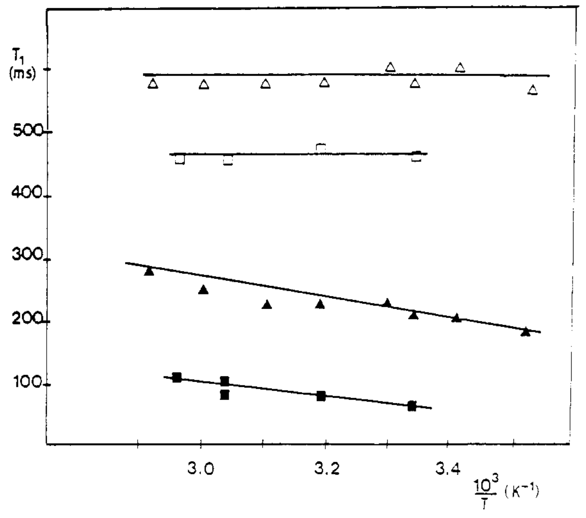

Figure 3. ^{13}C at 20 MHz and ^1H at 100 MHz spin–lattice relaxation times as a function of temperature: for the less mobile phase, (▲) ^1H, (■) ^{13}C; for the most mobile phase, (△) ^1H, (□) ^{13}C.

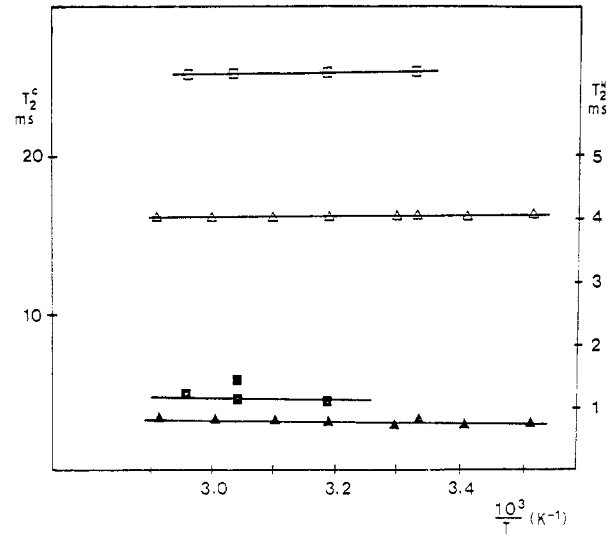

Figure 4. ^{13}C at 20 MHz and ^1H at 100 MHz spin–spin relaxation times as a function of the temperature: for the less mobile phase, (▲) ^1H, (■) ^{13}C; for the most mobile phase, (△) ^1H, (□) ^{13}C.

Table I
Calculated and Experimental Relaxation Times, at 300 K, in the Assumption of Two Modes Acting in the Same Motion Process[a]

	calcd, ms	exptl, ms
T_1^H (100 MHz)	202	220 ± 22
T_1^H (60 MHz)	106	110 ± 30
T_1^H (6 MHz)	10	30 ± 9
T_2^H	0.75	0.75 ± 0.05
T_1^C (20 MHz)	32	73 ± 7
T_2^C	4.8	5.2 ± 0.5

[a] $t_{c1} = 3.05\mathrm{E}{-8}$ s, $w_1 = 0.7_{12}$; $t_{c2} = 1.4\mathrm{E}{-9}$ s, $w_2 = 0.2_{88}$.

At room temperature, the population of the most mobile phase is on the order of 10% of the total population and one can only determine the relaxation time of ^1H at low Larmor frequencies (6 and 60 MHz) for the less mobile phase. The spin–lattice relaxation time as a function of frequency for this phase is given in Table I. One notes the great dependence on T_1^H with the Larmor frequencies, whereas Figures 3 and 4 show that the spin–lattice and spin–spin relaxation times are not very dependent on temperature. Since the ^1H FID of the less mobile phase is not dependent on frequency from 6 to 100 MHz, one can conclude that magnetic shielding interaction is not a cause of relaxation.

Analysis of Relaxation Times

We have shown[13] that the motion of monomer units is very perturbed by grafting, as has been shown by EPR of a spin-labeled chain grafted on silica.[14,15] From NMR measurements we have shown that its motion is very anisotropic. More than 1 order of magnitude is observed between characteristic times of fast and slow processes of motion. As Hermann et al.[9] observed with poly(oxymethylene) in solution, we observed that the process of motion is apparently not discerned identically by ^{13}C and ^{1}H. In the present paper we show that the motion discerned by ^{13}C and ^{1}H is correlated and that the apparent difference between the two nuclei is caused by the nonisolated CH$_2$ groups from the point of view of proton dipolar interaction.

To analyze the relaxation, the first question is: What is the interaction which is the cause of the relaxation? Since (1) the paramagnetic impurities can be neglected, (2) the ^{1}H spin–spin relaxation time of the less mobile phase at room temperature is not dependent on frequency, and (3) NOE is 3 at 65 °C for both phases, we conclude that only the dipolar interaction between the nuclei is the cause of the relaxation.

For PEO in solution in benzene, Heatley et al.[16] have shown that the contribution of the solvent to relaxation can be neglected. Since in our system we have taken deuterated solvent, and the average distance between the grafted macromolecules is approximately the Flory diameter of polymer in solution, one can assume that only the nuclei of the single chain are a cause of relaxation. Since the effect of the dipolar interaction between two nuclei decreases with r^{-6}, it stands to reason that the interaction H^c, which causes the ^{13}C relaxation, is restricted to the two ^{1}H's of the CH$_2$ group. On the other hand, the distance between ^{1}H's of two CH$_2$ groups can be approximatively the same order of magnitude as the H–H distance between two geminal protons. Thus, for protons the dipolar interaction can be written

$$H^{\mathrm{H}} = H_0 + H_1 + H_2$$

where H_0 is the dipolar interaction between two geminal protons. H_1 is the dipolar interaction between two adjacent CH$_2$ groups in the monomer unit. H_2 is the dipolar interaction between nuclei of different monomer units of the chain.

For polymers in solution H_2 is always negligible. It is only in very concentrated polymer solutions that this term appears.[17] In a large number of papers, the second term H_1 is also neglected.[16] In ref 18 this term is introduced. From the coordinate of nuclei for the different configurations, the authors deduced that the order of magnitude of H_1 is 20% of H_0 on the assumption of fast exchange between all the trans, gauche, and gauche prime configurations of oxygen atom.

The second question is how do these different interactions H_0, H_1, and H_2 for ^{1}H, and H^c for ^{13}C reveal the reorientation process? For example H^c is sensitive to the reorientational process of the C–H direction of geminal protons. On the other hand, H_1 is sensitive to the motion of an axis which is quasi-perpendicular to the CH$_2$ plane (the reorientation process of the C–C bond). If the motion is anisotropic, it is far from obvious that the correlation functions are the same to describe the fluctuation of the different interactions.

It is often claimed that in polymer solutions, ^{13}C observes a more isotropic motion than the ^{1}H. The study of poly(oxymethylene) (POM) offers an example of that analysis.[9] In that case H_1 is neglected because the CH$_2$ groups are isolated from one another by an oxygen atom. It is clear, considering the values of $T_1^{\mathrm{H}}/T_2^{\mathrm{H}}$ above the T_1^{H} minimum, that the proton relaxation cannot be satisfactorily described in terms of a simple isotropic motion of a CH$_2$ unit. On the other hand, the NOE is equal to 3, and T_1^{C} is practically equal to T_2^{C}, whatever the temperature, showing an apparently isotropic motion. Indirect measurements of the spin–lattice relaxation time measurements were carried out on the monodeuterated POM. In that case the quadrupolar interaction with the local electric field gradient is the main cause of the relaxation. Since the electric field gradient axis has the same direction as the C–H bond, the motion observed by ^{13}C and ^{2}H must be the same. The authors concluded contrarily to a more anisotropic motion from the ^{2}H point of view. These puzzling results might be reexamined taking into account the H_2 term, because the distance between deuterium of substituted CH$_2$ unit and protons of an other monomer unit can be short.

Cohen-Addad has taken account of the H_2 term for a very concentrated solution.[19] In this case H_2 is not averaged by the motion, whereas H_0 is averaged; this clearly shows that the reorientation process of these two interactions is very different.

The motion of monomer units of PEO can be broken down into a reorientation of the C–C bond and an intramonomer unit motion around the C–C axis. The later motion can be a jump between the three different rotameric states: trans, gauche, and gauche prime of the oxygen atom.[18] The activated energy of this jump is 4 kcal/mol, which implies a relatively significant variation of relaxation times with temperature. The fact that relaxation times of grafted PEO depend little or not at all on temperature implies that this jump is not a preponderant cause of relaxation. Thus the average of H_0, H_1, and H^c is governed by the *same reorientation motion which is characteristic of the global motion of the monomer unit.*

Assuming that the entire interaction is averaged in a time which is shorter than spin–spin relaxation times (i.e., shorter than 1 ms), one can write[20]

$$1/T_1^{\mathrm{H}} = aA(2j_1(f) + 8j_2(2f)) + A'(2j_1'(f) + 8j_2'(2f))$$

$$1/T_2^{\mathrm{H}} = aA(3j_0(0) + 5j_1(f) + 2j_2(2f)) + A'(3j_0'(0) + 5j_1'(f) + 2j_2'(2f))$$

$$1/T_1^{\mathrm{C}} = B(3j_1(f) + j_0(f_{\mathrm{H}} - f_{\mathrm{C}}) + 6j_2(f_{\mathrm{C}} + f_{\mathrm{H}}))$$

$$1/T_2^{\mathrm{C}} = (B/2)(4j_0(0) + 3j_1(f_{\mathrm{C}}) + j_0(f_{\mathrm{H}} - f_{\mathrm{C}}) + 6j_2(f_{\mathrm{H}} + f_{\mathrm{C}}))$$

$$\mathrm{NOE} = 1 + (\gamma_{\mathrm{H}}/\gamma_{\mathrm{C}})(6j_2(f_{\mathrm{H}} + f_{\mathrm{C}}) - j_0(f_{\mathrm{H}} - f_{\mathrm{C}}))/(3j_1(f_{\mathrm{C}}) + j_0(f_{\mathrm{H}} - f_{\mathrm{C}}) + 6j_2(f_{\mathrm{H}} + f_{\mathrm{C}}))$$

A is deduced from the interaction of two geminal protons, multiplied by a factor a to take into account dipolar interaction between two CH$_2$'s of a monomer unit.

$$A = 3\gamma_{\mathrm{H}}^4\hbar^2/(40r_{\mathrm{H-H}}^6) = 1.4 \times 10^9\ \mathrm{s}^{-2} \qquad r_{\mathrm{H-H}} = 1.8\ \text{Å}$$

a has been estimated to an average value of 1.2. B is deduced from the interaction between ^{13}C and the two geminal protons of an isolated CH$_2$ group.

$$B = \gamma_{\mathrm{H}}^2\gamma_{\mathrm{C}}^2\hbar^2/(10r_{\mathrm{C-H}}^6) = 2.1 \times 10^9\ \mathrm{s}^{-2} \qquad r_{\mathrm{C-H}} = 1.1\ \text{Å}$$

$j_q(f)$ is the Fourier transform of the autocorrelation function $g_q(t)$ characteristic of the global monomer unit motion.

$$g_q(t) = \langle H^q(t'-t)H^{-q}(t')\rangle / \langle (H^q(t'))^2\rangle$$

$H^q(t')$ is the fluctuating magnetic dipole field defined in ref 20. A' is related to the H_2 interaction between the protons of different monomer units. $j_q'(f)$ is the Fourier transform of $g_q'(t)$ characteristic of the reorientation process of the monomer unit relative to the other.

In our experiments, $f = 100$ and 90 MHz. Since as we shall see, $j_q(f)$ depends little or not at all on f frequency of 100 MHz, we shall take $f = 100$ MHz. For ^{13}C, the Larmor frequency f_C is 20 MHz; thus $f_H = 80$ MHz. For the less mobile phase, at room temperature, we have also the values of T_1^H and T_2^H for 6 and 60 MHz.

For each phase, in the temperature range 10–70 °C, for ^{13}C and ^{1}H, the spin–spin relaxation times are much shorter than the spin–lattice relaxation times. Thus, only the term at zero frequency in the formula of T_2^H and T_2^C is kept. The simple expression of spin–spin relaxation times is obtained.

$$1/T_2^C = 2Bj_0(0)$$

$$1/T_2^H = 3aAj_0(0) + 3A'j_0'(0)$$

In the particular case where $A' = 0$, we obtain $T_2^C/T_2^H = a = 1.2$. The experimental value $T_2^C/T_2^H = 6$ shows that *H_2 is a significant cause of proton spin–spin relaxation time.*

Spin–spin relaxation times do not depend on temperatures from 10 to 70 °C, so $A'j_0'(0)$ does not depend on temperatures for each phase. For the less mobile phase, $A'j_0'(0) = 390$ s^{-1}, and for the most mobile phase, $A'j_0'(0) = 70$ s^{-1}. Since A' is certainly smaller (or of the same order) than A, one can deduce that the characteristic time of $j_0'(f)$ is greater (or of the same order) than 5×10^{-8} s, i.e., $j_0'(f)$ is very dependent on f for frequencies greater than 20 MHz. Thus we can assume that the effect of H_2 can be neglected in determining the spin–lattice relaxation times of ^{1}H at 100 MHz. We shall see that this assumption is true for the most mobile phase from 10 to 70 °C and can be confirmed by measurements at 6 MHz for the less mobile phase.

At 65 °C, the nuclear Overhauser enhancement is 3 for the two phases. NOE = 3 implies that $j_q(f)$ does not depend on f from f_C to $f_C + f_H$, i.e., from 20 to 100 MHz. Thus the expressions of spin–lattice relaxation times are

$$1/T_1^C = 10Bj_0(f)$$

$$1/T_1^H = aA(2j_0(f) + 8j_2(2f))$$

where $f = 100$ MHz.

On the assumption that $j_q(f)$ does not depend on q, one can deduce $j_0(f)$ and $j_0(2f)$ from the experimental values of T_1^H and T_1^C. The value of $j_0(0)$ is obtained from T_2^C. The results are given in Figure 5.

Note that the value of $j_0(f)$ does not depend on f from 20 to 200 MHz for the most mobile phase. This is equivalent to saying that T_1^H can be obtained from T_1^C in the apparent condition of extreme narrowing; consequently, $T_1^H/T_1^C = B/(aA) = 1.25$, which is in good agreement with the experimental value of 1.25 ± 0.1, for this phase.

The relaxation times of the most mobile phase do not depend on temperature; so $j_0(f)$ is described from 10 to 70 °C by the curve of Figure 5. $j_0(f)$ is characteristic of a very anisotropic motion of the monomer units. The simplest description of this motion is the combination of fast and slow modes of motion characterized by short and long correlation times. Unfortunately, one necessarily has three parameters: short correlation time, long correlation time, and the weight of each mode of the segment motion, whereas we have only two values $j_0(0)$ and $j_0(20 \text{ MHz} < f < 200 \text{ MHz})$ deduced from the experimental results. Thus, one cannot describe quantitatively the reorientation process of the most mobile phase.

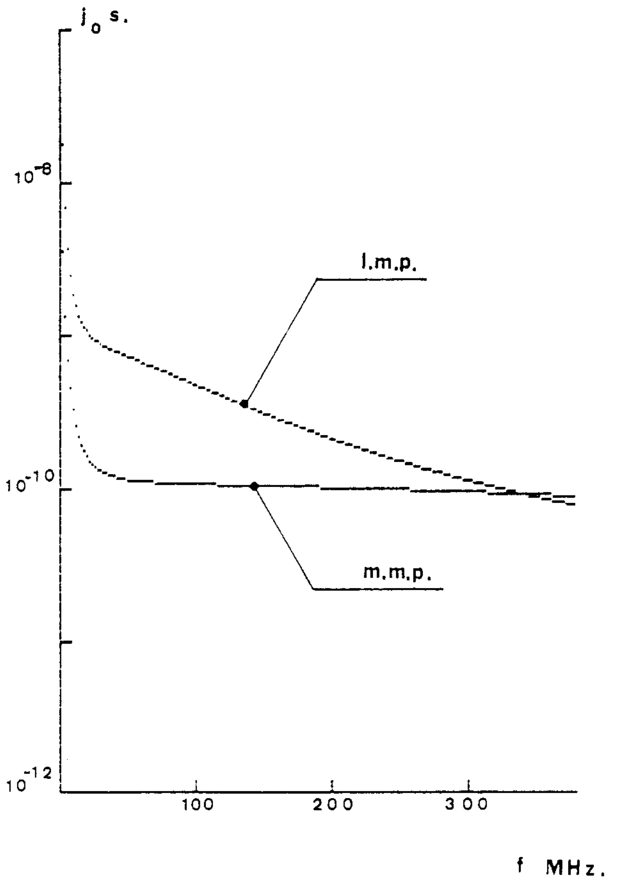

Figure 5. Schematic Fourier transform of the autocorrelation function characteristic of motion processes at 65 °C, with the values deduced from the experimental relaxation times: for the less mobile phase, (- -); for the most mobile phase, (– –).

For the less mobile phases, the situation is different because the values $j_0(0)$, $j_0(f)$, and $j_0(2f)$ are different. Thus, in that case, we can improve our analysis.

Analysis of the Segmental Motion in the Less Mobile Phase as a Function of Temperature

We have shown that $j_0(f)$ is characteristic of a very anisotropic motion. The high $j_0(0)$ value relative to $j_0(f)$ for f greater than 20 MHz implies that $j_0(0)$ is only sensitive to the slow mode of motion. This slow mode may be characterized by a weight, w_1, relatively to the other modes, and by a mean correlation time, t_{c1}. Thus the reduced spectral density takes the following value at the origin:

$$j_0(0) = 2w_1t_{c1}$$

A more detailed expression, as a function of the frequency, may be achieved through experimental measurements of relaxation times at low frequencies.

From the nondependence of the spin–spin relaxation time with temperature, one can deduce that w_1 and t_{c1} do not depend on temperature. The effect of the slow mode on the Fourier transform of the autocorrelation function decreases between 0 and 20 MHz. The fact that, at 65 °C, $j_0(f)$ does not depend on frequency from 20 to 100 MHz implies that the effect of the slow mode on $j_0(f)$ can be neglected for f greater than 20 MHz. Since the relaxation time is only slightly dependent on temperature, one can assume that the slow mode of motion has no effect on $j_0(f)$ for f greater than 20 MHz, from 10 to 70 °C.

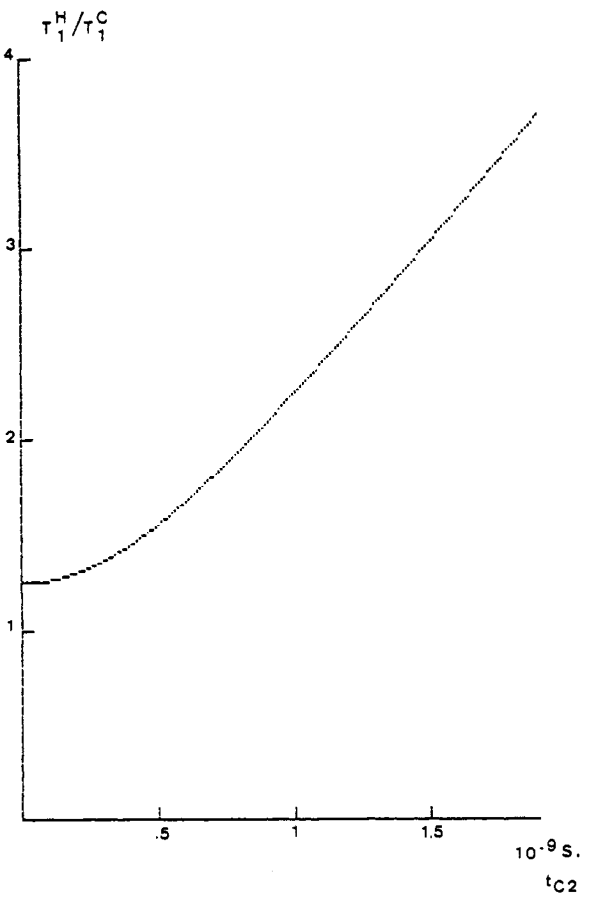

Figure 6. Calculated T_1^H/T_1^C vs. t_{c2} for the frequencies f = 100 MHz and f_C = 20 MHz, assuming that only a main medium mode is acting, with a = 1.2, A = 1.4E+9, and B = 2.1E+9.

For 20 < f < 200 MHz, assuming a main medium mode characterized by a weight w_2 and a correlation time t_{c2}, one can write the following expression for the reduced spectral density:

$$j_0(f) = 2w_2t_{c2}/(1 + (2\pi f t_{c2})^2)$$

Consequently, the expressions of the spin-lattice relaxation times are given by

$$1/T_1^H = 4w_2aA(t_{c2}/(1 + (2\pi f t_{c2})^2) + 4t_{c2}/(4\pi f t_{c2})^2)$$

$$1/T_1^C = 2w_2B(3t_{c2}/(1 + (2\pi f_C t_{c2})^2) + t_{c2}/(1 + (2\pi(f_H - f_C)t_{c2})^2) + 6t_{c2}/(1 + (2\pi(f_C + f_H)t_{c2})^2))$$

One notes that the T_1^H/T_1^C ratio is a function of t_{c2}, which is not dependent on w_2 (Figure 6). Thus, from the experimental curve T_1^H/T_1^C (Figure 7), the evolution of t_{c2} as a function of the temperature T can be deduced (Figure 8). An order of magnitude of the activation energy of the medium mode of the monomer unit reorientation motion in the less mobile phase is deduced: E_2 = 1.2 kcal/mol. From the value of t_{c2} and T_1^H one can deduce w_2 from 10 to 70 °C (Figure 9).

On the assumption that those two slow and medium modes are sufficient to describe the motion process, one can write

$$1 = w_1 + w_2$$

If, moreover, exponential autocorrelation functions ought to describe those modes, the value of t_{c1} is deduced from the ^{13}C spin-spin relaxation time. One sensibly obtains $t_{c1} = 2.9 \times 10^{-8}$ s. ^{1}H spin-lattice relaxation time measurements, at frequencies low enough to be sensitive to the slow mode contribution in the reduced spetral density function, can improve the analysis. Experimental and calculated results are reported in Table I. As it can be observed the fit is relatively good except at low frequency (T_1^H(6 MHz), T_1^C(20 MHz)). This discrepancy is essentially due to the not so fast enough decrease of the slow mode associated with the value of t_{c1}. On the other hand, this cannot be attributed to the contribution of the A' term because it would shorten more again the proton spin-lattice relaxation time.

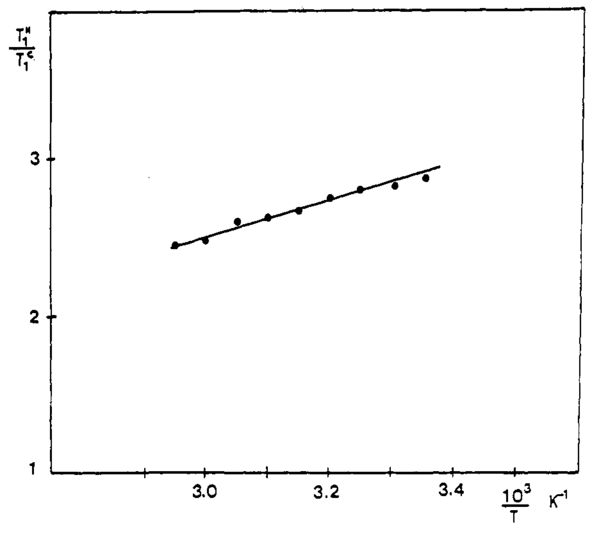

Figure 7. Experimental curve T_1^H/T_1^C vs. $1/T$ for the less mobile phase for the frequencies f = 100 MHz and f_C = 20 MHz.

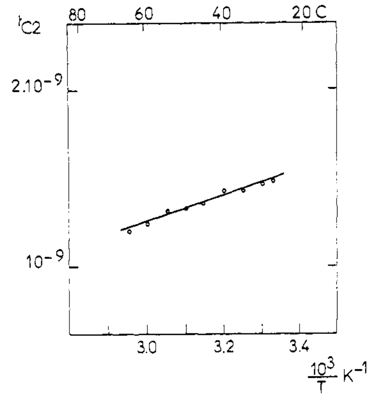

Figure 8. t_{c2} vs. $1/T$ for the less mobile phase, assuming that only a main medium mode is acting.

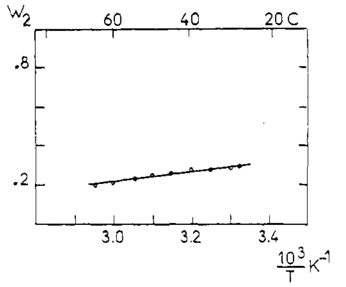

Figure 9. w_2 vs. $1/T$ for the less mobile phase.

At this point of the analysis two possibilities can be looked at.

The first is to consider the slow mode as defined by a nonexponential autocorrelation function. Consequently, this allows a faster decrease in time of the autocorrelation function characteristic of that mode, and an easier analysis and fit, in the assumption of a medium mode as presented above. This is observed in low dimensional diffusion process of motion.[20,21] This needs precise experimental results at very low frequencies.

Table II
Calculated and Experimental Relaxation Times, at 300 K, in the Assumption of Three Modes Acting in the Same Motion Process[a]

	calcd, ms	exptl, ms
T_1^H (100 MHz)	226	220 ± 22
T_1^H (60 MHz)	131	110 ± 30
T_1^H (6 MHz)	39	30 ± 9
T_2^H	0.75	0.75 ± 0.05
T_1^C (20 MHz)	71	73 ± 7
T_2^C	5.1	5.2 ± 0.5

[a] t_{c1} = 1E-7 s, $w_1 = 0.2_{18}$; t_{c2} = 1.4E-9 s, $w_2 = 0.2_{88}$; t_{c3} = 1E-11 s, $w_3 = 0.5_{31}$.

The second is to use an anisotropic motion, as had been done by Woessner.[22] In that case three correlation times have to be taken into account. This ought to preserve the analysis of the slow mode, the t_{c1} and w_1 of which are adjusted in such a way as to cancel its influence in the frequency domain where the medium mode acts, and to fit the experimental results. The third mode is used here to normalize the total reduced spectral density $j_0(f)$, which can be written as

$$j_0(f) = j_0^1(f) + j_0^2(f) + j_0^3(f)$$

where

$$j_0^i = 2w_i t_{ci}/(1 + (2\pi f t_{ci})^2)$$

and

$$1 = w_1 = w_2 + w_3$$

The slow mode $j_0^1(f)$ is the main part of $j_0(f)$ at low frequency, and as the value of the reduced spectral density at the origin is determined via the T_2^C, one can write

$$j_0^1(0) = 2w_1 t_{c1} = j_0(0)$$

varying the value of t_{c1} in such a way as to fit proton spin-lattice relaxation time at low frequency (T_1^H(6 MHz), T_1^C(20 MHz)), one can deduce w_1, and consequently w_3, wince w_2 is kept constant. The extra fast mode characterized by t_{c3} must be of little influence in the frequency range $20 < f < 200$ MHz. By trial and error t_{c3} is estimated so as to obtain a best fit for all the experimental relaxation times (Table II, Figure 10).

From these two analyses, one can deduce two important points.

(1) Spin-lattice relaxation time of proton at 6 MHz is sensitive to the slow mode of motion deduced from the measurement of ^{13}C spin-spin relaxation time; this implies that *^{13}C and ^1H reveal the same reorientation motion.*

(2) Reduced spectral density function characteristic of the fluctuation of H_2 can be neglected above about 10 MHz.

Discussion

The two phases thus observed would be localized into two zones. One is proximal of the surface, for the less mobile phase, where the segmental motion is restricted. The remote one, for the most mobile phase, where the motions are more free. The determination of the correlation times reveals an important anisotropy of the monomer unit motion (about 2 orders of magnitude of difference between the characteristic correlation times). This means that the motion process is divided into two main modes. One might be bidimensional, related to the surface, and corresponds to short correlation times, whereas the other evinces a longer correlation time more characteristic of a motion orthogonal to the surface. This remark is compatible with the Rubin's lattice model,[5] where the adsorbed polymer is represented by an overlap of layers parallel to the surface. From this point of view, the diffusion along the axis perpendicular to the solid surface can be described by a jump between these layers. So t_{c1} is the lifetime of a monomer unit in a layer. During a time on the order of t_{c1}, there is bidimensional segmental motion along the layer.

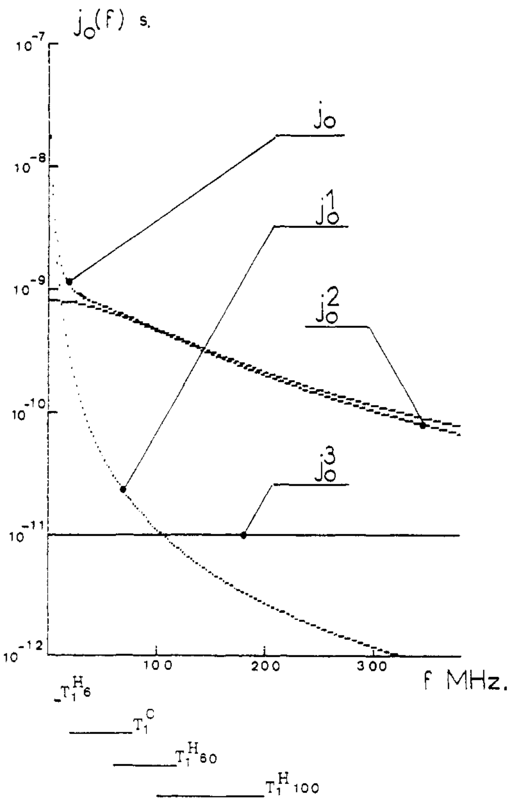

Figure 10. Reduced spectral density functions as a function of the frequency f, calculated so as to fit experimental results, at a temperature of 300 K, for the less mobile phase, in the assumption of the three modes acting in the same motion process.

EPR measurements, although confirming the two-population process, at temperatures lower than NMR ones, evince in the temperature range studied here a different behavior.[14] In effect, no slow population, or less mobile phase, characterized by a correlation time of about 10^{-8} s is observed. The fast population, or most mobile phase, is essentially characterized by one correlation time of about 10^{-10} s, the evolution of which, in the temperature range considered here been very small. This fact corroborates equally the experimental observation on the small evolution of the NMR relaxation times. Nevertheless, one has to note that the spin label is bound to the free end part of the chain by an ester function, which increases the number of degrees of freedom of the spin label itself. Specific behavior of the tails have been observed on terminally anchored PEO on polystyrene latex[23] and theoretically predicted for physically absorbed chains.[24] From the NMR point of view the dangling tails behave like the loops and are not perceived distinctly, in the frequency range of observation.

A similar two-phase model has been previously observed by Spiess[25] on a semicrystalline linear polyethylene. He pointed out that as the data could be analyzed within this simple model, this indicates that the regions of intermediate mobility do not lead to strong effect, as in our case.

In both phases, we must introduce the H_2 term, which indicates that the concentration of local monomer units is greater than in the free polymer solution. The value $A'j(0)$ is more important in the less mobile phase than in the most mobile phase. Since A' and $j'(0)$ increase with the concentration, we deduce that this one is greater in the less mobile phase than in the most mobile phase. Since we have no reason to assume a very high monomer unit concentration along the layers, one might assume there is a great concentration along the axis perpendicular to the surface. From this point of view the characteristic time of H_2 is about t_{c1}, so the order of magnitude of A' for the less mobile phase is the same as A. One has to note that such an important value is not observed with polymer in solution. This might due to the fact that local conformations generally energetically disfavored for the polymer itself would occur for grafted polymer. This implies a very high value of monomer unit concentration perpendicular to the surface. It is clearly a cause of the relatively bidimensional reorientation motion of the monomer units. This implies a flat conformation of the grafted polymer on the solid surface; i.e., the thickness of grafted chain perpendicular to the surface is smaller than the Flory diameter.

Conclusion

The poly(ethylene oxide) grafted on silica, in contact with a solvent, presents a specific behavior due to the chain–solvent–surface interactions.

A two-phase system, characterized by different mobilities of the monomer units, is observed. The less mobile phase might be related to restricted mobility loops or trains and the most mobile phase to the loops and tails.

Explaining the experimental ^{13}C and ^{1}H relaxation measurements using the same reorientation process characteristic of the global motion of the monomer unit, the following had been shown:

(1) The motion of the monomer units is very anisotropic in the two phases.

(2) Proton spin–spin relaxation time is sensitive to the local monomer units concentration. This one is greater in the less mobile phase than in the most mobile phase, while in dilute polymer solution this effect is negligible.

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