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Study by ^{1}H NMR of motion time correlation of monomer units on polymer/solid interface: application to PEO grafted on silica

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Abstract

The ^{1}H NMR technique is used to study the motion of monomer units on the interface poly(ethylene oxide) chains grafted on silica. The NMR line narrowing effect by high speed rotation of the specimen is observed in samples of different molecular weight. Our experiments allow us to determine two correlation times: τ_c, characteristic of the fast motion and τ_l, characteristic of the slow motion corresponding, respectively, to intra- and inter-monomer units. τ_c and τ_l are determined for all the samples of different molecular weight. This procedure is also applied at different temperatures for the same molecular weight. Results are coherent with linewidth and relaxation times measurements.
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1. Introduction

The ^{1}H NMR is used to study the motion and the behaviour of poly(ethylene oxide) (PEO) chains. Polymers adsorbed or grafted on the surface of a solid contribute, by their behaviour (conformation, mobility, etc.) to strong modifications in the properties of the media. The main practical applications of such systems include chromatography [1], colloid stabilisation [2], adhesion of biocompatible materials [3] and reinforcement of elastomers [4].

For grafted polymers the dipolar interaction is an important factor in the spin–spin relaxation process. This interaction, which depends on the local monomer-unit concentration, allows an approach to polymer motion and conformation at the interface [5–7]. This interaction is not completely averaged. The consequence of this is a partially solid-like behaviour of the relaxation function.

It is possible to remove the dipolar interaction by rotating the specimen very rapidly about an axis inclined to the direction of the applied magnetic field B_0 [10,18]. The maximum narrowing effect is achieved at the magic angle $54°44'$ between the direction of B_0 and the rotation axis. The dipolar Hamiltonian is now a periodic function of time and generates satellite lines at a distance $n\omega_r$ on either side of the central spectrum [11]; ω_r being the rotation frequency of the specimen.

MAS technique is used to study the dipolar interaction [12,13]. In the present study we consider the sample rotation effects on the proton in polymer grafted on silica where the static resonance line is already partially narrowed by some restricted molecular motions.

PEO is a simple model system, in which all the CH_2 are chemically identical (with the exception of the terminal group), and the NMR spectrum of the polymer has one simple line. The solid support is silica (Aerosil) with a high degree of chemical purity. The relevant parameters to be considered are the molecular weight and temperature.

2. Experimental

2.1. Material and grafting method

The silica is pyrogenic, Aerosil A300 (from Degussa), prepared through a hydrogenation process. This material was selected because it has a high degree of chemical purity and is not porous. The polymer was poly(ethylene oxide) (PEO). Molecular weight and polydispersity were controlled by gel permeation chromatography and are described extensively in Ref. [9].

The grafting reaction has been explained previously

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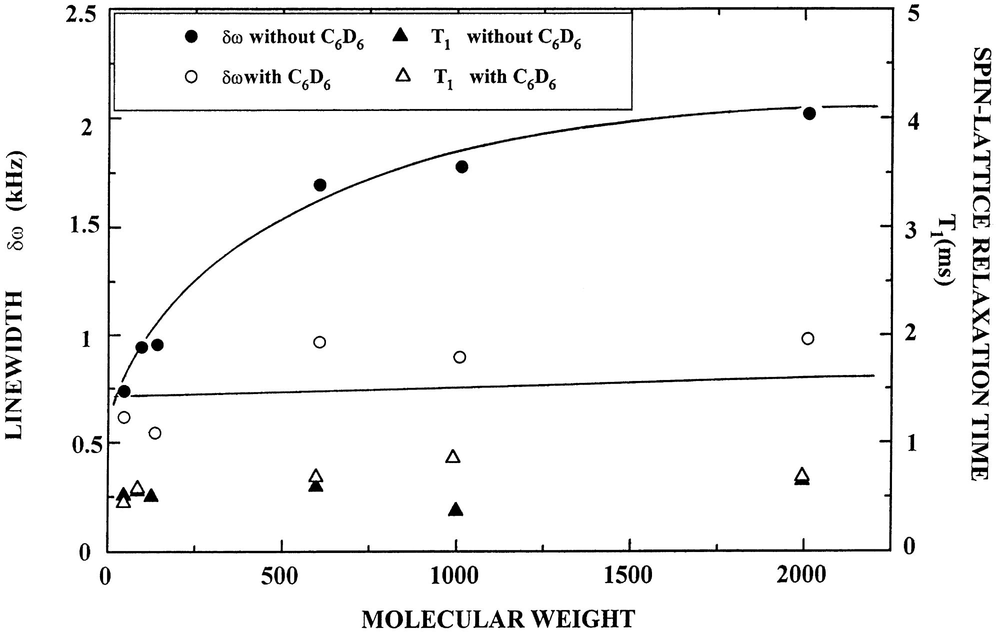

Fig. 1. Evolution of the linewidth and the spin–lattice relaxation time as a function of the molecular weight, for a grafted poly(ethylene oxide): (●) without deuterated benzene, (▲) with deuterated benzene. Data obtained from ^{1}H NMR spectroscopic measurements at 300 MHz.

[9,21]. Molecular weight M varies from 44 (oligomer) to 2000.

2.2. NMR technique

Experimental measurements of $T_1(^{1}\mathrm{H})$ were carried out on a Bruker Fourier transform NMR spectrometer operating at 300 MHz by using the inversion-recovery pulse sequence ($\pi-\tau-\pi/2$). The $\pi/2$ pulse width is less than 1.5 μs which corresponds to B_1 a rotating field of more than 60 Gauss. The dead time of the detection is less than 4 μs. The spectrometer was equipped with “double bearing” probe allowing the magic-angle (54°44′) at a spinning rate of 0–4 kHz. Rotation rates at room temperature are achieved by an air-driven turbine in which the rotor is supported by a gas bearing.

Experiments at low temperature were done by using cold nitrogen gas as the propulsor. Experiments were carried out over the temperature range 260–360 K, with the temperature being controlled by a variable temperature regulator.

3. Effect of dipolar interaction in PEO grafted on silica

All the ^{1}H NMR spectra exhibit a single line for different molecular weight samples. Results obtained for both spin–lattice relaxation time, T_1, and the linewidth (spin–spin relaxation) as a function of molecular weight are shown in Fig. 1.

The analysis of the spin–spin relaxation time of ^{1}H shows that an interaction of the ^{1}H of different monomer-units is introduced. So, the T_2 (T_2 is related to the inverse of the linwidth $\Delta\nu$ ($T_2 = 1/\pi(\Delta\nu)_{1/2}$)) of the proton is sensitive to the local concentration of monomer-units. Reorientation motion of the monomer-units relative to one another is a very slow process, since the spin–lattice relaxation time of ^{1}H is not sensitive to this interaction [8,10].

The slow reorientation process of the units suggests that there exists a static dipolar interaction between the nuclei of different monomer-units. However, it is possible that the reorientation of subunits is very fast relative to the laboratory frame and it is the cause of the narrow line observed with the PEO44 or the PEO2000 immersed in solvent (benzene).

For the PEO2000, if the sample rotates at the magic angle as shown in Fig. 2, the linewidth is about 500 Hz as for PEO44 or for PEO2000 immersed in benzene showing that there exists a residual dipolar interaction which was not averaged in a time shorter than the spin–spin relaxation time.

The line narrowing caused by sample rotation, due in part to the removal of the chemical shift anisotropy, reveals the existence of residual dipolar interaction on PEO grafted on the silica system.

The Hamiltonian which describes the dipolar interaction can be written as [6,16,21]:

$$H_\mathrm{D} = H_\mathrm{D}^\mathrm{intra} + H_\mathrm{D}^\mathrm{inter}$$

where $H_\mathrm{D}^\mathrm{intra}$ is the contribution of all the protons in a monomer-unit and $H_\mathrm{D}^\mathrm{inter}$ is the dipolar interaction between the nuclei of different monomer-units.

The spin–lattice relaxation time is only sensitive to a characteristic motion frequency on the order of the Larmor frequency (300 MHz in our experiments), whereas the linewidth is also sensitive to the slow processes of the motion [14,15]. So, the spin–lattice relaxation time and the linewidth could not identically reveal the two contributions of H_D, because the scale time characteristic of the fluctuation of H_D^{intra} and H_D^{inter} may be very different.

The results obtained for both T_1 and the linewidth as a function of molecular weight are shown in Fig. 1. The linewidth increases with molecular weight M. This effect disappears when the compound is immersed in deuterated benzene, and does not exist when we observe the evolution of the spin–lattice relaxation time.

From these results, we may consider that not only the relaxation is sensitive to the dynamics of the segment which causes a fluctuation of H_D, but also that the intensity of the two different contributions of H_D are modified.

In fact, H_D is averaged by the fluctuation caused by the motion of the segment, so we can separate H_D in two parts:

$$H_D = H_D^1 + H_D^2$$

where H_D^1 is a fluctuating interaction, ($\bar{H}_D^1 = 0$) and H_D^2 is a static interaction, $H_D^2 \neq 0$.

The latter interaction depends on the local density of the monomer-unit. It is not averaged because the motion of segments relative to one another is strongly hindered. The local motion of a segment is rapid enough to average Hamiltonian $\bar{H}_D^1$.

The effects of these two terms on T_1 and T_2 of the spin system are very different. The spin–lattice relaxation depends only on H_2 whereas the spin–spin relaxation function depends on both H_1 and H_2.

4. Effect of macroscopic and microscopic motions on dipolar interaction

From the above considerations, we can assume that in our system the macroscopic and microscopic effects coexist. We

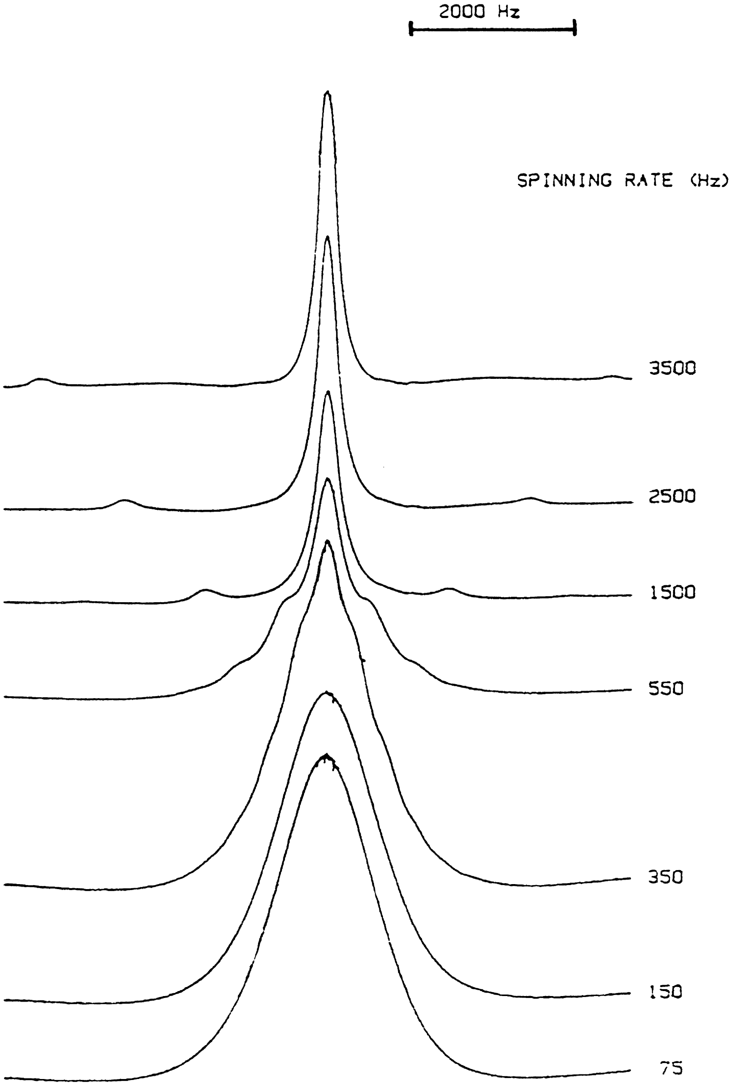

Fig. 2. Effect of sample rotation on narrowing central line and apparition side band at different spinning rates. Example of grafted poly(ethylene oxide) (molecular weight $M = 2000$) at room temperature.

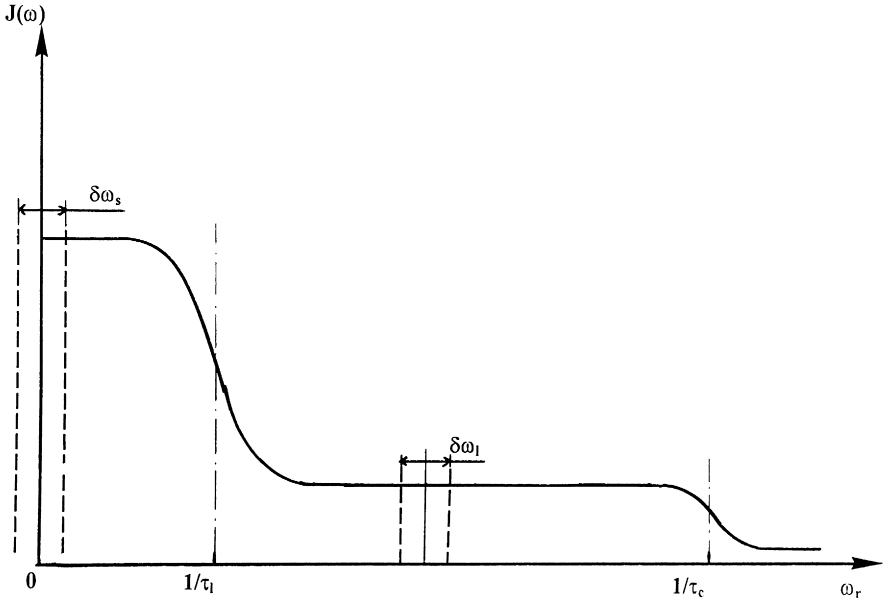

Fig. 3. Effects of sample rotation on linewidth $\delta\omega$, when two molecular motions τ_c and τ_l are present in a sample.

assume that the fluctuations of local dipolar field arise from two contributions:

- local motion of the monomer-units which is relatively fast and described by H_D^{intra} Hamiltonian and characterised by short correlation time τ_c.
- reorientation motion of monomer-units relative to one another described by H_D^{inter} Hamiltonian and characterised by a relatively longer correlation time τ_l.

In this situation the rigid lattice second moment $(\delta\omega_0)^2$ [17,20] results from two contributions:

$$(\delta\omega_0)^2 = (\delta\omega_l)^2 + (\delta\omega_c)^2$$

where $(\delta\omega_c)^2$ corresponds to the intra-molecular part averaged by random microscopic motion characterised by a correlation time τ_c and $(\delta\omega_l)^2$ corresponds to the inter-molecular part removed by the macroscopic motion characterised by a correlation time τ_l. We can assume $\tau_c \ll \tau_l$.

5. Effect of molecular motion on line narrowing

In the absence of macroscopic motion when only the internal microscopic motions are present in the sample, the static linewidth $\delta\omega_{st}$ arises from the low frequency contribution of the spectral density of motion $J(\omega)$ [14]:

$$(\delta\omega)^2 = (\delta\omega_0)^2 \int J(\omega)\, \delta\omega$$

When the sample is spinning at ω_r, we may consider the components near $\pm\omega_r$ of $J(\omega)$ as secular terms, and the linewidth is found to be:

$$(\delta\omega)^2 = (\delta\omega_0)^2 \int_{-\omega_r}^{\omega_r} J(\omega)\, \delta\omega$$

For isotropic random motion of the lattice, one generally uses the BPP relaxation model of $J(\omega)$ [14]. $J(\omega)$ is the normalised spectral density function, which for a random motion characterised by a single correlation time is given by:

$$J(\omega) = \frac{\tau}{\pi(1 + \omega^2\tau^2)}$$

where τ represents the correlation time of thermal motion. We notice that line narrowing will be effective for rotation rates comparable with $1/\tau$.

6. Application to the PEO grafted on silica

It will be assumed that the fluctuation of the local dipolar field arises from the segmental motion characterised by a short correlation time τ_c, and from the reorientational motion of macromolecules relative to each other whose correlation time τ_l could be much longer. The resulting spectral density $J(\omega)$ is illustrated in Fig. 3.

The static linewidth can be written as follows:

$$(\delta\omega_s)^2 = (\delta\omega_c)^2 \int_{-\delta\omega_s}^{\delta\omega_s} J_c(\omega)\, d\omega + (\delta\omega_l)^2 \int_{-\delta\omega_s}^{\delta\omega_s} J_1(\omega)\, d\omega$$

where $J_c(\omega)$ and $J_l(\omega)$ are the spectral densities corresponding to the two motions:

$$J_c(\omega) = \frac{\tau_c}{\pi(1 + \omega^2\tau_c^2)}$$

$$J_l(\omega) = \frac{\tau_l}{\pi(1 + \omega^2\tau_l^2)}$$

If the segmental motion is very fast: $\tau_c\delta\omega_s \ll 1$ (the case of all the molecular weights), $\delta\omega_s$ can be written as the

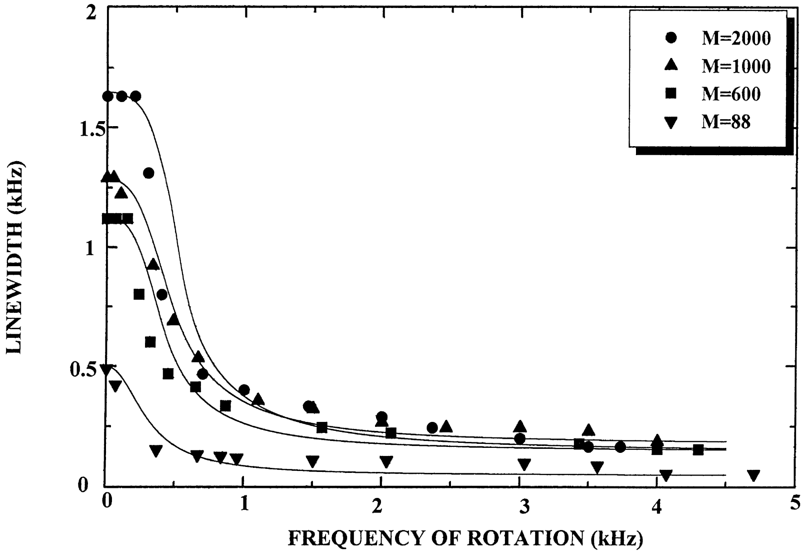

Fig. 4. Evolution of linewidth versus rotation frequency of samples. Different molecular weight *M* at room temperature for grafted poly(ethylene oxide). Data obtained from ^{1}H NMR spectroscopic measurements at 300 MHz.

follows:

$$(\delta\omega_s)^2 = \frac{2}{\pi}(\delta\omega_c)^2\tau_c + \frac{2}{\pi}\frac{(\delta\omega_c)^2}{\delta\omega_s}\ \text{arctg}\ \tau_l\delta\omega_s$$

Information about dynamics of segmental motion cannot be obtained from a study of partially narrowed linewidth of a static sample. The effect of segmental motion is partially masked by inter-molecular broadening. Macroscopic rotation of the sample can then suppress this effect. In fact, the line narrowing occurs when ω_r is comparable to $1/\tau_l$. Starting from $(\delta\omega_s)$ at $\omega_r = 0$, the linewidth reaches a limiting value $(\delta\omega)_{li}$ for $1/\tau_l < \omega_r < 1/\tau_l$. The residual linewidths were independent on the spinning frequency. This behaviour is usually observed in our experiences (Fig. 4).

7. Influence of molecular weight

The experiment has been performed on PEO grafted on silica at room temperature for different molecular weights. Fig. 4 shows the evolution of linewidth versus rate rotation. The same evolution is observed in our experiences. In fact, when the rotation frequency increases, one observes a line narrowing for $\omega_r \approx 1/\tau_l$. After this transition, the linewidth is limited to $(\delta\omega)_{li}$ independent of the rotation rate, because of a very large value of $1/\tau_c$. This behaviour is characteristic of the coexistence of two motions—fast and slow—described, respectively, by H_D^{intra} and H_D^{inter} and characterised, respectively, by correlation times τ_c and τ_l. Study of the NMR linewidth as a function of ω_r would be interesting for evaluating the correlation time τ_c in PEO/silica.

The linewidth, when the sample rotates at ω_r, can be written as [17,18,19]:

$$\begin{aligned}(\delta\omega_r)^2 &= (\delta\omega)_{sc}\\ &\quad\times\left\{\frac{2}{3}\int_{\omega_r-\delta\omega_r}^{\omega_r+\delta\omega_r} J_c(\omega)\,d\omega + \frac{1}{3}\int_{2\omega_r-\delta\omega_r}^{2\omega_r+\delta\omega_r} J_c(\omega)\,d\omega\right\}\\ &\quad+(\delta\omega)_{sl}\\ &\quad\times\left\{\frac{2}{3}\int_{\omega_r-\delta\omega_r}^{\omega_r+\delta\omega_r} J_l(\omega)\,d\omega + \frac{1}{3}\int_{2\omega_r-\delta\omega_r}^{2\omega_r+\delta\omega_r} J_l(\omega)\,d\omega\right\}\end{aligned} \tag{1}$$

In our experiences, we have always $\tau_c\omega_r \ll 1$ and:

$$\begin{aligned}(\delta\omega_r)^2 &= \frac{2}{\pi}(\delta\omega_c)^2\tau_c(\delta\omega_r) + \frac{(\delta\omega_l)^2}{\pi}[\text{arctg}(\omega_r+\delta\omega_r)\tau_l\\ &\quad-\text{arctg}(\omega_r-\delta\omega_r)\tau_l]\end{aligned}$$

For an exact calculation, one must also consider the components near $\pm 2\omega_r$ in the spectral density $J(\omega)$.

By taking account of the terms and in the case when the axis of rotation is inclined at the magic angle, we obtain the following expression:

$$\begin{aligned}(\delta\omega_r)^2 &= \frac{2}{\pi}(\delta\omega_c)^2\tau_c(\delta\omega_r)\\ &\quad+\frac{(\delta\omega_l)^2}{\pi}\left[\frac{2}{3}\text{arctg}(2\omega_r+\delta\omega_r)\tau_l-\text{arctg}(\omega_r-\delta\omega_r)\tau_l\right]\\ &\quad\times\left[+\frac{1}{3}\text{arctg}(2\omega_r+\delta\omega_r)\tau_l-\text{arctg}(2\omega_r-\delta\omega_r)\tau_l\right]\end{aligned} \tag{2}$$

We can notice that the evolution of the linewidth with rotation frequency deduced from expression (2) is in agreement with all our experiences.

Table 1
Correlation times and parameters for PEO grafted on silica for different molecular weight

Parameter	Molecular weight			
	PEO-88	PEO-600	PEO-1000	PEO-2000
Second moment ($\delta\omega_0$) (kHz)^2	45 000	182 130	380 000	415 000
Static linewidth ($\delta\omega_s$) (Hz)	477	1120	1290	1630
Limiting linewidth ($\delta\omega$)$_{li}$ (Hz)	110	240	280	240
Slow correlation time τ_l (ms)		3	2.3	2.2
Fast correlation time τ_c (μs)	3.8	2.07	1.15	0.9

Particularly, when $\omega_r > 1/\tau_l$, the linewidth reaches a limiting value:

$$(\delta\omega)_{li} = \frac{2}{\pi}(\delta\omega_c)\tau_c \tag{3}$$

The residual linewidth must therefore give the fast correlation time of fast internal motion.

From this expression, we can confirm that the faster the segmental motion is, the weaker the linewidth. In order to study this motion, we adopt the Andrew approach [17] introduced above.

Some computing programs are elaborated using the previous expressions. Last relation (2) permits to plot theoretical curves and to fit them by varying τ_c and τ_l, τ_c are deduced from expression (3).

We obtain a good agreement between theoretical curves and experimental results by varying the value of τ_l, τ_c and τ_l are determined. Table 1 shows the experimental results concerning the measurement of these correlation times for different molecular weights *M*.

We have reported the evolution of the correlation time as a function of molecular weight in Fig. 5. The first important result is that the correlation time τ_c decreases with molecular weight while τ_l remains constant.

The study of the influence of molecular weight shows that the segmental motion characterised by τ_c decreases when the molecular weight increases. The evolution about τ_l is constant.

This study allows us to point out the mobility of the monomer-unit. In fact, the existence of the residual linewidth of the resonance line when the sample is rotated is an important characteristic of the dynamics of internal motion of polymer grafted on silica. Such a characteristic is attributed to fast segmental motion. We can thus deduce the correlation time of the motion for different molecular weights. The correlation time of slow motion is deduced from a study of the linewidth versus frequency of rotation.

8. Influence of temperature

The experiment has been performed on PEO grafted on silica with molecular weight 2000. It was chosen because it quickly gave a good NMR signal. Fig. 6 shows the evolution of linewidth versus rate of rotation for different

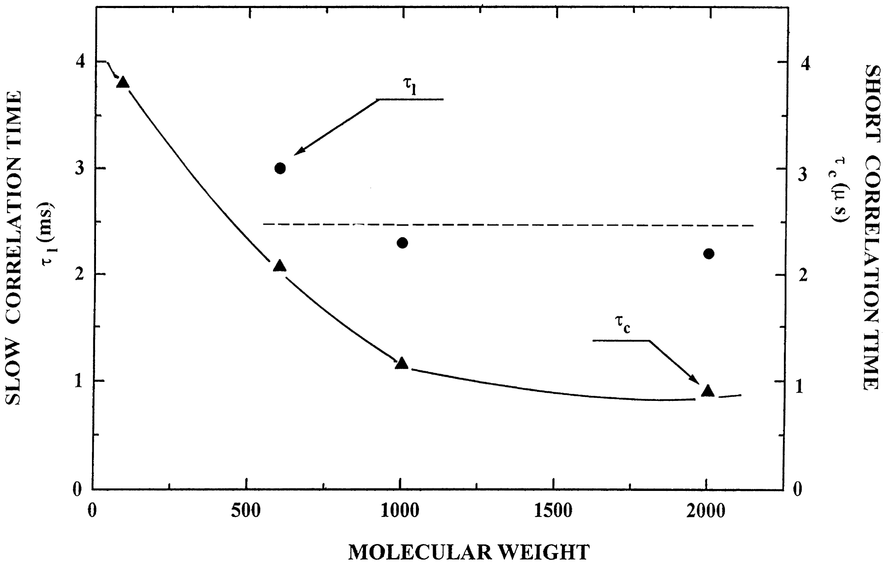

Fig. 5. Evolution of the correlation times τ_c and τ_l as a function of the molecular weight, for a grafted poly(ethylene oxide). Data obtained from ^{1}H NMR spectroscopic measurements at 300 MHz.

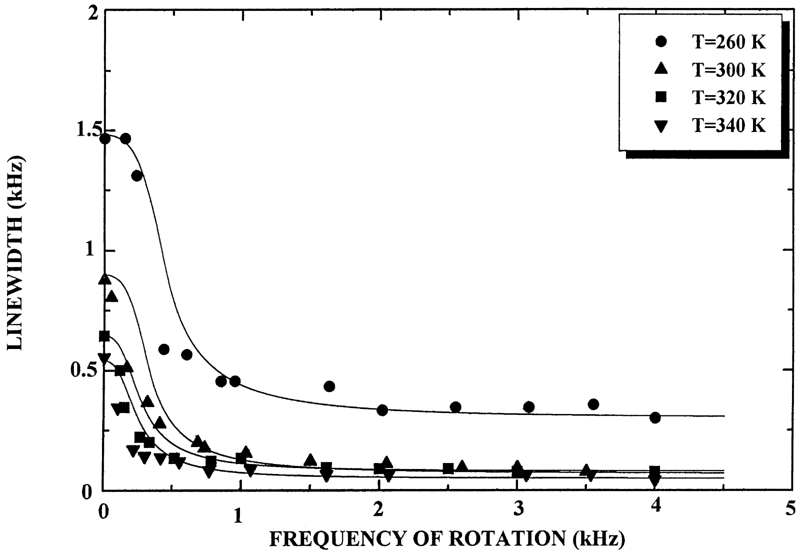

Fig. 6. Evolution of linewidth versus rotation frequency of samples at different temperatures for grafted poly(ethylene oxide). Molecular weight $M = 2000$. Data obtained from ^{1}H NMR spectroscopic measurements at 300 MHz.

temperatures in the range 260–360 K. The same evolution is observed in our experiences.

Table 2 shows the experimental results concerning the measurement of correlation times for PEO grafted on silica with molecular weight 2000 for different temperature T.

We have reported the evolution of correlation time as a function of temperature in Fig. 7.

The first important result is that we observe the same evolution for τ_c and τ_l as functions of molecular weight. Result are consistent with spin–lattice relaxation time measurements [21]. We observe a transition between 280 and 300 K as already observed by measurements of T_1 [21]. We observe the same evolution for both correlation times. They remain constant with temperature after the transition.

9. Conclusions

The behaviour of poly(ethylene oxide) grafted on silica has been studied by NMR relaxation. The present work shows that the technique of sample rotation is very important to study this interface. This technique is efficient when the linewidth is already partially narrowed by fast segmental motion.

Experiments about the narrowing line of polymer grafted of silica give the following results.

On the sample where dipolar linewidth is partially narrowed in the presence of molecular motion, it is possible to obtain a supplementary narrowing by macroscopic rotation.

The frequency of rotation necessary must be comparable to partially narrowed static linewidth.

With increasing frequency of rotation and for all molecular weights and for different temperatures, the resonance line takes, after a fast decrease, a value independent of rotation frequency, even when such a frequency exceeds the static linewidth. This limiting linewidth was found to be independent of molecular weight and temperature.

Two correlation times (i) τ_c, characteristic of the fast motion and (ii) τ_l, characteristic of the slow motion are determined. They are determined for all molecular weights.

A good agreement is obtained with linewidth measurements. For measurements at different temperatures for the same molecular weight (2000) sample, the results are consistent with spin–lattice relaxation time measurements.

Table 2
Correlation times and parameters for PEO grafted on silica with molecular weight 2000 for different temperatures

Parameter	Temperature (K)			
	260	300	320	340
Second moment ($\delta\omega_0$) (kHz)^2	202 000	104 000	67 000	65 000
Static linewidth ($\delta\omega_s$) (Hz)	1472	887	637	527
Limiting linewidth $(\delta\omega)_{li}$ (Hz)	346	100	90	70
Slow correlation time τ_l (ms)	3.2	4	4	4.2
Fast correlation time τ_c (μs)	3	1	1.3	1.3

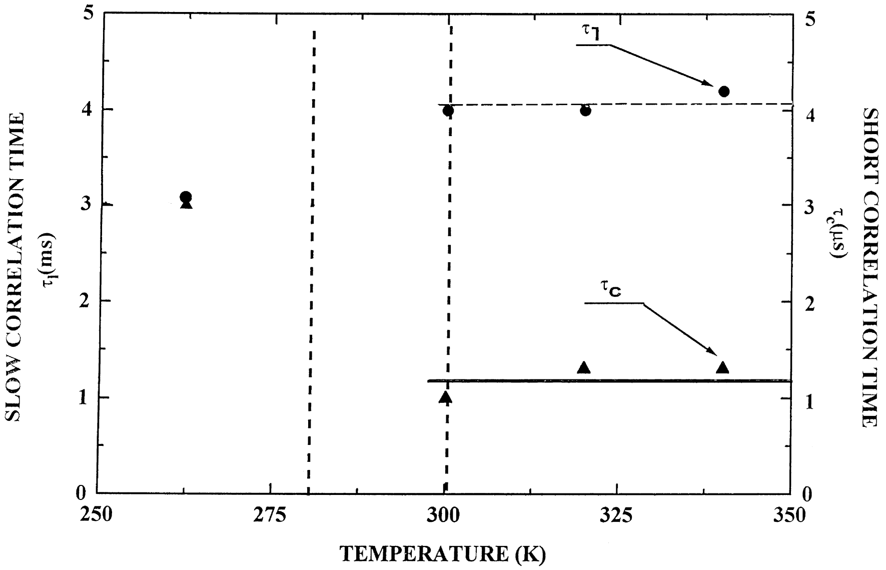

Fig. 7. Evolution of the correlation times τ_c and τ_l time as a function of the temperature for grafted poly(ethylene oxide). Molecular weight $M = 2000$. Data obtained from ^{1}H NMR spectroscopic measurements at 300 MHz.

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