

Review

Nuclear magnetic resonance spectroscopy of polymers at surfaces

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ABSTRACT

Nuclear magnetic resonance spectroscopy is used to probe the conformation and the dynamics of a macromolecular chain near a solid surface of the interface polymers grafted on silica. NMR of ¹³C, ¹H and ²H nuclei of grafted polymer chains permits to investigate the behaviour (conformation, mobility etc.) of polymers at the interface without introducing probe and to give access to the statistical organization of polymers at the interface. Utilisation of different techniques such as "Pseudo Solid Echo" sequences, "Magic Angle Spinning" with variable temperature, observation of the relaxation function of different nuclei (¹H, ²H, ¹³C) and "Cross Polarisation" (¹H-¹³C) allow to propose a methodology of approach. The example chosen for illustration is poly(ethylene) oxide grafted on silica. For grafted polymers, the dipolar interaction is an important factor in the relaxation process. This interaction, which depends on the local concentration of monomer-units, allows an original approach to polymer motion and conformation of polymers at the interface. Using NMR technique, we have shown the possibility of proposing some schematic representations of conformation of polymers at the interface and suggesting different models for the surface layer for the two extreme grafting levels. NMR appears to be a powerful, sensitive and versatile method for probing the structure and organisation of a polymer layer attached to a solid surface at the molecular level.

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1. INTRODUCTION

In the present study, nuclear magnetic resonance spectroscopy is used to probe the conformation and the dynamics of a macromolecular chain near a solid surface of the interface polymers grafted on silica.

One of the fundamental problems of grafted polymers on a solid surface is the determination of the disposition of monomer units near the surface and the concentration. ¹H, ²H, ¹³C NMR techniques are used to study the segmental motion and the organization of the grafted layer. The example chosen for illustration is poly(ethylene oxide) polymers grafted on silica.

Polymers grafted on the surface of a solid contribute to strong modifications in the properties of the media by their behaviour (conformation, mobility, etc.). Polymers are often used as coupling agents, modifying the naturally occuring interactions between the solid surface and the surrounding medium. Such effects are obtained through a judicious choice.

Polymer chains grafted onto solid surfaces are fundamental in many applications in colloid and surface science, as well as in biology [1-4]. These interfaces are objects of considerable interest for both practical and fundamental reasons [5-9]. Very little information is available on short grafted polymeric chains [10, 11]. The main practical applications of such systems include chromatography, colloid stabilisation, adhesion of biocompatible materials and the reinforcement of elastomers. Different techniques such as pseudo solid echo sequences, Magic Angle Spinning with variable temperature, observation of the relaxation function of different nuclei (¹H, ²H, ¹³C) and cross polarisation (¹H-¹³C) allow to propose some new approach methodologies.

The properties of a chain polymer should depend, essentially, on the polymer surface density (the grafting ratio) [12, 13], the length (molecular weight), the temperature, the surface [14] and the solvent. The solvent could, in appropriate situations, modify the configurations of the chains. The dependence of relaxation time on the grafting ratio and temperature is discussed qualitatively from a phenomenological point of view.

The grafting of a macromolecule on a solid surface must introduce a significant effect on its motion. It has already been shown that only the dipolar interaction between the nuclei is the cause of relaxation and that the motion of the monomer units is very anisotropic [15-18]. This interaction provides a new approach to polymer motion and conformation of polymers as well as the local monomer units concentration at the interface. The concentration of monomer units on the interface is evaluated. Different independent techniques namely « magnetic relaxation », « magic angle spinning (MAS) » and « pseudo-solid echo » show good agreement for the physical parameters describing the concentration of monomer-units on the surface. This behaviour has been studied as a function of grafting ratio and of molecular weight of the chains, and each time as a function of temperature.

2. Choice of model system: poly(ethylene oxide) grafted on silica

To describe the most general features of the phenomena, it is appropriate to choose a well designed model, like a neutral flexible chain, let us say poly(ethylene oxide) grafted on silica surface of high specific area, which exhibits all the major trends observed in such a system.

The nuclear magnetic resonance technique appears to be a well suited method for the study of the interfaces. In order to obtain easily interpretable signals, a better definition of materials at both the physical and the chemical scales is required. Poly(ethylene oxide) has some distinctive favourable properties which makes it convenient for the magnetic resonance studies. It can be used as a model system, since 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.

Poly(ethylene oxide) is commercially available in an extremely broad range of molecular weights. The most studied polymer was poly(ethylene oxide) (PEO) 2000 of molecular mass number 1980 (from Fluka). The oxygen in the backbone makes it very flexible. In NMR this polymer is very convenient because there is only one chemical shift both for ¹H as well as for ¹³C.

The molecular weight and polydispersity of the PEO was determined by gel permeation chromatography. The length of the chains always corresponds to a molecular weight of 2000 with a polydispersity of 1.04.

The silica are relatively well defined solids, commercially available, with well known specific surfaces, porosities and high degree of chemical purity.

The silica used was pyrogenic Aerosil A300 (from Degussa), prepared by a thermal process. This powder is essentially not porous and consists of large aggregates of small spheres, from 7 to 12 nm in diameter. Its specific area, measured by nitrogen gas adsorption is ca. $300 \text{ m}^2 \text{ g}^{-1}$. This material was selected because it has a high degree of chemical purity and it is not porous at a molecular scale. The number of silanols on a silica surface is about 5 per square nanometers for a fully dehydrated silica. They are assumed to be rather randomly distributed on Aerosil silica. Hence it seems a fair approximation to assume that the density of grafting points is constant.

The grafting reaction consists of an esterification of the silanol groups of silica by one of the terminal hydroxyl group of the poly(ethylene oxide) following the simplified scheme :

 $\equiv \text{Si-OH} + \text{HO-}(\text{CH}_2\text{-} \text{CH}_2\text{-}\text{O})_n\text{-}\text{H} \rightarrow \equiv \text{Si-O-}(\text{CH}_2\text{-} \text{CH}_2\text{-}\text{O})_n\text{H} + \text{H}_2\text{O}$

The grafting ratio τ , is expressed in weight %: it is the weight of the polymer irreversibly fixed on

PEO sample	τ _{mu} (number of monomer unit by unit surface)	τ (%) (grafting ratio expressed in weight%)
PEO 44	3.9	8.5
PEO 88	4.0	8.9
PEO 132	6.6	14.8
PEO 600	7.7	19.1
PEO 1000	15.4	15.4
PEO 2000	8.6	19.1

Table 1. Results obtained for various types of grafting ratios for PEO samples of different molecular weights grafted on silica.

Table 2. Various types of grafting ratios for PEO (M = 2000) grafted on silica at different temperatures.

Grafting temperature (°C)	τ _{mu} (number of monomer unit by unit surface)	τ (%) (grafting ratio expressed in weight%)
160	2.2	5.1
160	6.1	15.2
80	7.7	19
80	11	25
100	14.7	32.5
125	15.6	34.7
238	24	53.4

100 g of silica. When using pyrolysis procedure, τ is given by the following relationship:

$$\tau = \frac{\Delta m}{m_i - \Delta m} \cdot 100 \tag{1}$$

where m_i is the weight of the initial sample and Δm is the weight loss after pyrolysis. The numeral grafting ratio τ_{mu} is defined as the number of monomer units in the grafted polymer per unit surface area, as follows:

$$\tau_{mu} = \frac{6.10^{23}.\tau}{44.S} \tag{2}$$

where S is the specific surface area $(m^2.g^{-1})$.

The values of different definitions of grafting ratios are given in Tables 1 and 2.

3. Physico-chemical parameters and approach methodology

The objective of this work is to get information about the difficult problem of the description of the segmental motion and the organization of the grafted layer and to propose new approach methodologies. The simplest way is to investigate successively each of the basic physico-chemical parameters influencing the phenomena.

The physico-chemical parameters like the chain length or molecular weight denoted M that appears through the number of monomer units, the coverage or grafting ratio in macromolecules per surface unit denoted τ , the temperature and the effect of solvent on the static conformation are investigated and explained by the different interaction energies involved. Thereafter the dynamics with different times and length scales are characterised, with the introduction of the anisotropy brought by a solid wall occupying half a space.

Utilisation of different techniques such as "Pseudo Solid Echo" sequences, "Magic Angle Spinning" with variable temperature, observation of the relaxation function of different nuclei (¹H, ²H, ¹³C) and "Cross Polarisation" (¹H-¹³C) allow to propose some new methodologies for approaching the problem.

4. Nuclear magnetic resonance spectroscopy

4.1. Basic principles and general view of the fundamentals of NMR

As in any spectroscopy [19], NMR consists in performing transitions between the energy levels of particles by submitting them to the action of an electromagnetic wave at the Planck frequency v_0 (in Hz) or ω_0 (in rad s-1).

The energy levels are the eigenvalues of a time independent Hamiltonian H₀. Transitions are induced by a time dependent Hamiltonian H₁ (t) representing a sinusoidal perturbation rf frequency v_0 , which is off-diagonal in the representation of the eigenstates of H₀.

4.1.1. The Zeeman interaction

The basic experiment in NMR is to expose a sample containing particles with nuclear spins I to an intense static magnetic field B_0 . Nuclei of angular momentum $\hbar \vec{I}$ are endowed with a magnetic moment $\vec{\mu}$:

$$\vec{\mu} = \gamma \hbar I \tag{3}$$

where γ is the gyromagnetic ratio and h is the Planck's constant in J.s.rad⁻¹. Each nuclear dipole $\vec{\mu}$ acquires a magnetic energy: $E = -\mu_Z B_0$ if the z-axis of the laboratory frame is taken along the direction of B₀, the longitudinal direction. This energy may assume a series of discrete values, in number 2I + 1, where I is the spin number of the observed nucleus. The energy levels E_m:

$$E_m = -\gamma \hbar B_0 m \tag{4}$$

correspond to different z projections (I_z) of the spin vector I and consequently, to different orientations of magnetic moment $\vec{\mu}$ with respect to the z-axis. They are the eigenvalues of the Zeeman Hamiltonian H_z^0 .

$$H_z^0 = -\gamma \hbar I_z \tag{5}$$

A case of fundamental importance in practice, which will be the only one considered in this work, is that of spin ½ nuclei, where I = ½ and m = ±1/2, with two energy levels $E_{\alpha,\beta} = \pm \frac{\gamma \hbar B_0}{2}$ for the two quantum states α (m = 1/2) and β (m = -1/2).

Transitions between α and β are performed at the resonance frequency:

$$\omega_0 = -\gamma B_0 \quad \text{or } \nu_0 = -\gamma B_0 / 2\pi \tag{6}$$

with a net absorption of energy from the RF wave as a result of slightly unequal Boltzmann populations N_{α} , N_{β} , of α and β states (Figure 1).

4.1.2. Thermal equilibrium: longitudinal relaxation

From the above treatment, it is clear that the RF wave is inducing transitions between α and β states with equal probabilities P in both senses. This would rapidly result into an equalization of Boltzmann populations N_{α} , N_{β} , and thus to an extinction of the NMR signal. This is a so called saturation phenomenon. In fact, relaxation processes ensure a fast return to the equilibrium of the longitudinal overall magnetisation $M_z(t)$

$$M_{z}(t) = \sum \mu_{z} \tag{7}$$

where the summation is over all nuclei in the sample, either in α or β state.

From a microscopic point of view, this means that the overall nuclear magnetisation M_z after being rotated by an angle γ (the flip angle) from its equilibrium position M_0 along B_0 , is spontaneously driven back to the position after the transmitter has been switched off, according to the phenomenological equation:

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} \tag{8}$$

 T_1 is the longitudinal relaxation time.

4.1.3. Free induction decay: transverse relaxation

The observation of the NMR signal involves only the transverse magnetisation. This means that a transverse relaxation time T₂ should be introduced the return of account for to transverse magnetisation to equilibrium. In thermal equilibrium, in the presence of the static field B_0 , all the nuclear dipoles have transverse components μ_{xy} , freely precessing at the Larmor frequency ω_0 , with a random phase angle ϕ . Their

macroscopic resultant M_{xy} is thus averaged to zero over an ensemble of nuclei. This shows that nuclear magnetization is purely longitudinal at equilibrium with a component $M_z = M_0$.

To observe a signal by pulsed NMR experiments, the RF field is switched on for a short time (a few tens of microseconds), thus driving the equilibrium magnetization into the transverse plane (Figure 2). The transverse magnetization obtained at the beginning of the receiving period,



Figure 1. Energy levels, Larmor free precession, Boltzmann populations of an assembly of spin $\frac{1}{2}$ nuclei. Straight or inverted arrows are conventionally used to represent z magnetization in α and β states.



Figure 2. Macroscopic longitudinal and transverse magnetizatios $M_z(t)$ and $M_{xy}(t)$ during the receiving period at successive times 0, $t_1, t_2, t_3, ..., (a)$ - the domain time signal(b) - the absorption spectrum(c).

 $M_{xy}(0) = M_0$, is then freely precessing about B_0 at the Larmor frequency, thus inducing an electrical signal of frequency ω_0 in a transverse coil. This signal, the so-called free induction decay (FID), decreases indeed to zero in the course of time as a result of transverse relaxation.

From a macroscopic point of view, this decay is characterised by a transverse relaxation time T_2 and a rate law of the same type as that written above for longitudinal relaxation:

$$\frac{dM_{xy}}{dt} = \frac{-M_{xy}}{T_2} \tag{9}$$

The time-domain signal (FID) is then Fourier transformed to retrieve the resonance frequency ω_0 . The frequency-domain signal is represented by a Lorentzian curve centred at the frequency ω_0 , with a linewidth at half height:

$$\Delta v_{\frac{1}{2}} = \frac{1}{\pi T_2}$$
 (in Hz) or $\Delta \omega_{\frac{1}{2}} = \frac{2}{T_2}$ (in rad.s⁻¹) (10)

4.2. NMR experiments

The pulse method is used to study NMR signals in all experiments. The mostly used pulse sequences are the following: ($\pi/2$, Free Induction Decay FID), which gives the transversal relaxation time T₂, and the ($\pi-\tau-\pi/2$, FID) sequence which gives the longitudinal or spin-lattice relaxation time T₁ and the sequence (spin locking) which gives spinlattice relaxation time in the rotating frame T₁ ρ . More elaborated sequences are the pseudo-solid echo measurements (described in the next section) based on the fact that the transverse magnetization does not relax similarly depending on whether the process is monitored by a fluctuating dipolar interaction or a static dipolar interaction.

Through a well designed manipulation either in the real space (magic angle spinning "mas" technique) or in the spin space (pulses sequences), the different interactions can be selectively averaged and the different components of an overall environment can be studied separately. A Fourier transform algorithm computes the spectrum in the usual frequency domain.

5. Nuclear magnetic relaxation and dynamics of polymers

In this section, we shall examine the information that may be obtained on molecular dynamics from Nuclear magnetic resonance relaxation times, namely spin lattice relaxation time T_1 , the spin-spin relaxation time T_2 and the spin-lock relaxation time $T_{1\rho}$ and other relaxation parameters. The analysis of relaxation times allows the decription of segmental motion and the organization of the grafted layer. A noticeable influence of the different physicochemical parameters on the conformation of the grafted macromolecules is evidenced.

5.1. Relaxation times as a source of dynamical information

5.1.1. Effect of molecular weight on the relaxation function

The results of the measurements of both spin-lattice relaxation time T_1 and spin-spin relaxation time T_2 (T_2 is related to the inverse linewidth Δv ($T_2 = \sqrt[]{\pi(\Delta v)_{1/2}}$)) of ¹H as a function of molecular weight, denoted M, are shown in Figures 3 [20]. Without solvent, the linewidth increases with the molecular weight. However, when the compound is immersed in deuterated benzene the linewidth does not depend on M. The spin-lattice relaxation time on the other hand does not depend at all on molecular weight either with or without solvent. The evolution of ¹³C linewidth is presented in Figure 3 (inset). It appears to be completely independent of the molecular weight.

The principal difference between ¹H NMR and ¹³C NMR is the sensitivity to the inter monomer units dipolar interaction. Such an interaction was observed only by the ¹H NMR. Consequently, this interaction increases with the molecular weight.

Even the slow mode of the segment motion which governs the spin-spin relaxation time of ¹³C [21, 22] does not change with molecular weight. When the sample is immersed in deuterated benzene, the molecular weight effect disappears because the local monomer units concentration decreases, i.e. the dynamic fluctuations of the segment-segment distance are higher and may average the inter monomer units dipolar interaction. In this case it is only a fluctuating effect which gives a relaxation mechanism superposed to the intra monomer-units spin-spin process.

5.1.2. Effect of the dipolar interaction for PEO

5.1.2.1. Transverse magnetic interaction

The relaxation function of the transverse nuclear magnetisation observed on grafted polymers results



Figure 3. Evolution of the linewidth (•) and the spin-lattice relaxation time (\blacktriangle) as a function of molecular weight, for a grafted poly(ethylene oxide). (\circ, Δ): with deuterated benzene. Data obtained from ¹H NMR spectroscopic measurements (300 MHz). (Inset) Corresponding results (linewidth) obtained from ¹³C NMR spectroscopic measurements (75 MHz).

from two contributions: (i) one is related to the dynamics of fluctuations of space variables describing monomer units positions, (ii) the other corresponds to the non zero average of the tensorial spin coupling. This non zero average is due to the constraints exerted on the chain segments by steric hindrances, due for example to the surface. The chains are not free to rotate completely with respect to each other.

More precisely, there exist two contributions due to the intermonomer unit and intramonomer unit interactions. The interaction can therefore be decomposed into two parts of the Hamiltonian (next section), which describes the dipolar interaction [15, 20, 23].

5.1.2.2. Hamiltonian of polymers grafted system

For polymer grafted on silica, dipolar interaction between adjacent nuclei is considered to be the only interaction responsible for nuclear relaxation processes. There exist two contributions due to inter monomer-units and intra monomer-unit interactions. The interaction can, therefore, be decomposed into two parts of the Hamiltonian [15, 20]:

$$H_D = H_D^{\text{int}\,ra} + H_D^{\text{int}\,er} \tag{11}$$

To investigate more thoroughly the influence of the second term, the Hamiltonian can be rewritten as follows [20]:

$$H_{D} = H_{D}^{1} + H_{D}^{2} \tag{12}$$

$$H_D^1 = H_D^{\text{int}ra} + H_D^{\text{int}er} - \overline{H}_D^{\text{int}er}$$
(13)

$$H_D^2 = H_D^{\text{inter}} \tag{14}$$

 H_D^1 is a fluctuating interaction giving rise to a narrowing of the line. The local motion of monomer units is relatively fast in comparison with the evolution to the equilibrium of the transverse magnetisation (<<T₂) and the average of H_D^1 is approximately zero (i.e. \overline{H}_D^1 #0).

 H_D^2 is a static interaction (i.e. $\overline{H}_D^2 \neq 0$) giving the residual interaction (nonzero average dipolar spin coupling). This interaction is due to the very slow anisotropic reorientation process of the monomer units relative to one another. The latter depends on the local density of monomer units. It is not averaged because the motion of the segments relative to each other is strongly hindered. The local motion of segments on the other hand is rapid enough to average the Hamiltonian \overline{H}_D^1 . The effects of both terms on the relaxation times T_1 and T_2 of the spin system are very different. The spin-lattice relaxation time T_1 depends only on H_D^1 whereas the spin-spin relaxation function T_2 depends on both H_D^1 and H_D^2 .

5.1.2.3. Existence of a residual dipolar interaction

Measurements of the spin-spin relaxation time T₂ for similar samples with different molecular weights of the same polymer show that there exists a pseudosolid effect. The dipolar interaction is not completely averaged by the motion of reorientation depending on the local concentration of monomer units. This observed pseudo solid effect results from the fact that the motion of reorientation of the monomer units versus each other is a very slow process. As a consequence, a residual dipolar interaction remains between nuclei of different monomer units, pertaining eventually to segments very far apart in the chemical sequence, which cannot be averaged to zero by the segmental motion. Another way of demonstrating this interaction is provided by magic angle spinning again for PEO (Figure 4) with an average molecular weight of 2000 grafted on silica [20]. In fact, a rapid rotation of the sample about an axis inclined at the 'angle magic' of 54°44 relative to the Zeeman field direction can remove the residual dipolar interaction [24, 25]. The rotation speed of the sample must be of the order of the static dipolar interaction to narrow the NMR spectra.

5.1.3. Effect of grafting ratio on the relaxation function

The presence of the nonzero average spincoupling in polymers grafted on silica reflects the nonisotropic motion of chain segments. Such segments are not free to rotate completely because of the constraints of the confinement near the surface due to the grafting. In the systems of polymers grafted on a solid surface, the parameter which seems to be the most sensitive to the variation of the grafting ratio is the number of monomer units per surface area. The choice of the number of monomer units per nm² seems to be the right parameter to account for the variation of both the grafting ratio and the molecular weight. The analysis of relaxation times allows the description of the grafted layer organization.

5.1.4. Influence of the grafting ratio on the relaxation times

From the relaxation theory, it is known that the linewidth is sensitive to the slow processes [21, 22] of motion of the monomer units (inter monomerunits contribution), and to the local concentration



Figure 4. Effect of narrowing central line and apparition side bands: (a) without rotation (b) with rotation.

of such monomer units. On the contrary, T_1 is only sensitive to the characteristic motion frequencies of the order of the Larmor frequency (the fast motion processes). It concerns essentially the local motions of the monomer-unit. Figure 5 shows the evolution of the linewidth and of the spin-lattice relaxation time T_1 as a function of the number of monomer units near the surface area. Since this relaxation time is shown to be dependent on the grafting ratios (even for low grafting ratios), this implies that the lateral constraints between chains exist, even for τ of the order of one monomer unit/nm². For low grafting ratios, the chains spread out on the surface occupying as much place as needed by their size, with a practically bidimensional conformation. The mobility of segments in these conditions is severely restricted. This fact explains that the linewidth is relatively important. The spin-lattice relaxation time T₁ increases when the mobility decreases. When the grafting ratio increases, the influence of this parameter on the relaxation functions ceases between 7 and 10 u.m./nm². It may be noted that the transition appears on the linewidth and on the T_1 for about 7 monomer units' nm⁻², which is approximately the value corresponding to one monolayer of segments on the surface. This value was already calculated [17, 26] and it corresponds to the limiting grafting ratio equal to

13% for our studied silica. The limiting grafting ratio corresponds to the maximum grafting ratio for no overlapping of the gaussian chains on the surface. When the grafting ratio increases, the bidimensional chains contract on the surface. The dimension of the chains reaches the Flory radius. Each chain occupies roughly a hemisphere with a radius comparable to the Flory radius R_F for a coil (the Flory radius $R_F = N^{1/2}$.a, where N is the number of repetition units and a is the length of segment). In this situation the entropy is at a maximum. This situation can explain the increase of mobility with the grafting ratio in the first part of the curves (Figure 5). Above this limiting grafting ratio, the behaviour is dominated by a homogeneous layer of polymer in a state reminiscent of the bulk.

5.1.5. Interpretation of NMR experiments in terms of organization of the grafted layers

Silica (Aerosil) is not microporous and it is considered to be planar at the molecular scale of the polymer. For a grafting ratio that is greater than 20% (about 7 u.m./nm²), which is approximtely the value corresponding to one monolayer of segments on the surface, the grafting ratio appears to have no effect on the macromolecular behaviour. In the case where the coils are separated, the motion arises on a plane parallel to the surface.



Figure 5. Evolution of the linewidth (\blacktriangle) and spin lattice relaxation time (\bullet) as a function of the number of monomer units per nm² for grafted poly(ethylene oxide). Data obtained from 1H NMR spectroscopy (300 MHz).

Above the grafting ratio of 20% (about 7 u.m./nm²), the coils begin to overlap; a modification to the motion arises, where the motion is both simultaneously parallel and perpendicular to the surface. Two different forms of organization of the grafted layers can be distinguished: low grafting ratios (or low concentrations) and high grafting ratios (or high concentrations).

In the case of low grafting ratios (or low concentrations), we are in the situation where coils are considered as being separated or isolated from each other, since the surface is attractive to monomer units because of the interaction between the OH groups on the surface and the oxygen of the monomer units. The chains spread on the solid surface, and local motions could be hindered by the solid. On the other hand, the segments which are uniformly disposed on the surface are however, not relatively dispersed. The local concentration in the segments is relatively low and the motion is little influenced by a steric effect due to other segments. The segment density is probably not uniform on the surface. We can assume that the grafted layer is poorly organized, by analogy with various crystalline and amorphous structures.

In the case of high grafting ratios (high concentrations) the interfacial layer could be approximated by a step profile: the local density in the segments becomes uniform and no more variations are observed. From the schematic representation shown in Figure 6, we can obtain a picture of the organization of the grafted layers. At low grafting ratios, the surface is very attractive, and the chains adopt a flat conformation on the surface. When the grafting ratio increases, the chains spread out, starting to repel each other and adopt more extended configurations which are perpendicular to the surface. The grafted layer can be described here by a one-dimensional model.

5.2. Nuclear magnetic relaxation and investigation of local chain dynamics

In this section, we are interested in observing the modification of the dynamics of the polymeric chain induced by grafting. In fact, we will concentrate on those NMR parameters that are sensitive to high frequency motions, that is, the spin lattice relaxation time effect for unlike spins. For this purpose, the ¹H NMR spin lattice and the spin-spin relaxations were observed in a large temperature range, for poly(ethylene oxide) PEO with molecular weight 2000 grafted on silica with different grafting ratios. An important parameter for characterising the dynamics of the polymeric chain is the correlation time of the local segmental motions. This parameter was evaluated from spin lattice relaxation time versus temperature $(T_1(T))$ data. The analysis of the temperature dependence of T_1 permits a preliminary evaluation of the correlation time of the local dynamics of the polymeric chains and for different significant grafting ratios.

5.2.1. Spin lattice relaxation time study

The observation of the longitudinal magnetization in a large domain of temperature gives the possibility to evaluate the correlation time τ_C of the local fluctuations of the chain segments [27]. This evaluation becomes very simple when the minimum of the spin lattice relaxation time versus temperature $T_1(T)$ is observed.

The evolution of the spin-lattice relaxation time, for the polymer grafted on silica at different grafting ratios in the temperature range 220 K to 380 K are shown in Figure 7. This domain includes the temperature corresponding to the minimum of the relaxation time.

The expression of the spin lattice relaxation rate $1/T_1$ for identical spins is given by the relation [28]:



Figure 6. Schematic representations of the surface layer for: (a) low grafting ratio (b) high grafting ratio.

$$\frac{1}{T_1} = K \left[\frac{\tau_C}{1 + \omega^2 \tau_C^2} + \frac{4\tau_C}{1 + 4\omega^2 \tau_C^2} \right]$$
(15)

where K $({}^{K \propto} {}^{/}_{r^6})$ is a parameter depending on the distance between the interacting spins, ω is the resonance frequency of the protons, and τ_c is the correlation time of the spin motion.

Usually, the relaxation theory of Bloembergen, Purcell, Pound [29] for simple liquids is developed for the interpretation of the experimental data. One of the most used models for a quantitative estimation of the correlation time of molecular dynamics is based on the Kramer and Helfand theory [30, 31]. The mathematical expression for $\tau_{\rm C}$ is determined from a specific model for the chain dynamics. The temperature dependence of the correlation time is:

$$\tau_C = B \exp\left(\frac{E_a}{RT}\right) \tag{16}$$

where B is a parameter depending on the nature of the polymer, E_a is the activation energy required for conformational transition, and R is the universal constant of the gases. Using the parameters E_a and B obtained in this way, we generated the correlation time at any temperature over the transition temperature range using equation (16) as shown in Figure 8. These values of τ_c were calculated (Table 3). In the next section, the magic-angle spinning technique is equally used to study the macromolecule dynamics at the interface. It permits to determine correlation times for each grafting ratio. Such correlation time is compared to the time obtained by measurements of T₁.

6. Technique of « pseudo-solid » echo

The presence of a residual spin-spin interaction is easily disclosed experimentally by forming pseudo solid echo, which result from a combination of various pulse sequences. Such echoes look like solid echoes observed from nuclear spins embedded in any solid system. However, they spread over a long time interval because of the strength of the residual interaction.

A more sophisticated picture emerges when we observe the pseudo solid spin echo in NMR. The amplitude of the echo depends on the intensity of the static dipolar residual Hamiltonian.

The "pseudo solid" echo technique has been applied to a system of polymer grafted on silica. It is used to deduce the intensity of the non-averaged dipolar interaction. It gives an estimate of the local concentration of monomer-units. The "pseudo solid"



Figure 7. Temperature dependence of the spin-lattice relaxation time T_1 for PEO 2000 grafted on silica with molecular weight 2000 for different grafting ratios: (\bullet) 5%, (\bullet) 19%, (\bullet) 53%.



Figure 8. ¹H NMR. The values of τ_c generated with (8) for PEO 2000 grafted on silica with molecular weight 2000 at different grafting ratios: (•) 5%, (•) 19%, (•) 53%.

Table 3. Correlation times for PEO grafted on silica with molecular weight 2000 at different grafting ratios obtained at 300 K by MAS technique and T_1 measurements.

Grafting ratios	Correlation time $\tau_{C}(s)$ (by spin-lattice relaxation time T_{1})	Correlation time τ_c (s) (by mas technique)
5% (2 u.m./nm ²)		1.7 10-6
19% (24 u.m./nm ²)	6.4 10 ⁻⁹	1 10 ⁻⁶
53% (24 u.m./nm ²)	6 10 ⁻⁹	0.9 10-6

echo method has been observed particularly in concentrated polymer solutions [32, 33] and theoretically described in ref. 33. We use the notations of Cohen Addad [33, 34].

6.1. Basic principles

The pseudo solid echo measurements are elaborate sequences based on the fact that the transverse magnetization relax differently, depending on whether the process is monitored by a fluctuating dipolar interaction or a static dipolar interaction. In the frame OXYZ, rotating at the proton Larmor frequency, we characterise the radiofrequency pulse $\xi(\alpha)$, by the angle ξ and the axis α ($\alpha = X$ or Y) of the magnetisation rotation induced by the radio frequency field. We define the two pulse sequences as follows:

 $\sum_{i} = \left[\frac{1}{2}\pi(X), \tau, \frac{1}{2}\pi(Y)\right] \text{ and we measure the transverse} \\ \text{magnetisation along the OY axis: } M_{y}^{1}(t). \\ \text{The origin of time t is just after the first pulse. In the absence of any field inhomogeneity, the echo is expected to be observed and described by <math>M_{y}^{1}(t)$.

$$\sum_{2} = \left[\frac{1}{2}\pi(Y), \tau, \frac{1}{2}\pi(Y)\right] \text{ and we measure } M_{y}^{2}(t). \text{ On the other hand, we measure } M_{y}^{0}(t) \text{ after a } \frac{1}{2}\pi(X) \text{ pulse.}$$

We can define the parameter $E(t,\tau)$ which corresponds to the structure of signal function. Note that $E(t, \tau)$ traduces the "solid effect" since it is equal to zero if the residual dipolar energy is zero.

$$E(t,\tau) = \frac{\Delta^2}{\Omega^2} \left(\cosh(\Omega \cdot t) - \cosh(\Omega(t-2\tau)) \right) \quad (17)$$

where:

 Δ is a parameter corresponding to second moment and characteristic of residual interaction.

$$\Delta = \frac{9\gamma^4 \hbar^2}{4b^3} (1 - 3\cos^2\beta)$$

and

$$\Omega^2 = \theta^{-2} - \Delta^2$$

 θ is a parameter characteristic of spin dynamics. Its relative amplitude can be compared to that of Δ , the signal may or may not oscillate.

 Ω^2 indicates the competition effect between the fluctuating part of the Hamiltonian (irreversible effect) and the static part (reversible part). For $\theta^{-1} > \Delta$, Ω is a real value whereas it is a complex value for the inverse situation.

The transverse magnetisation as detected corresponds to the free decay $M_y^0(t)$ plus an additional signal called "pseudo-solid echo". Its amplitude is strictly related to the presence of a nonzero average dipolar coupling.

To measure and follow the pseudo-solid effect, it may be interesting to define a parameter directly related to nonzero average dipolar coupling. Let us consider the normalised function $\eta(t, \tau)$. This function is easily drawn from the experiments:

$$\eta(t,\tau) = \frac{M_y^1(t) + M_y^2(t) - M_y^0(t)}{M_y^0(t)}$$
(18)

$$\eta(t,\tau) \cdot M_{y}^{0}(t) = \left\langle \Gamma(t)E(t,\tau)G(t) \right\rangle$$
(19)

where $\Gamma(t) = \frac{\hbar^2 \cdot \gamma^2 \cdot \omega_0}{2kT_e} \cdot \exp\left(-\frac{t}{T}\right)$ is a dissipative term and $G(t) = \int g(\delta) \cdot \cos \delta t \cdot d\delta$. $g(\delta)$ is the distribution function which characterises the space inhomogeneity of the steady magnetic field, and δ measures the frequency deviation from v_0 , the Larmor frequency. In the simplest case, we can write: $G(t) = \exp\left(-\frac{t}{T}\right)$. We can notice that for perfect homogeneous steady magnetic field: $M_x^2(t) = 0$.

Figure 9 presents the effect of different pulse sequences applied to a system of polymer grafted on silica and the obtaining of the signal $\eta(t,\tau)$ corresponding to several values of spacing pulse τ .

6.2. Application to systems of grafted polymers: investigation of residual dipolar interaction

6.2.1. Influence of the molecular weight

In order to investigate the influence of the molecular weight on the conformations and motions of polymers grafted on surfaces, the pseudo solid echo experiment was performed on two samples, one with a low molecular weight 44 g/mol and another with a high molecular weight 2000 g/mol. The results are presented in Figure 10. The function $\eta(t,\tau)$ corresponding to several values of τ recorded at room temperature are displayed. For the polymer of molecular weight 44 g/mol, the amplitudes of the echoes are very small and the residual interaction is practically inexistent. For the high molecular weight 2000 g/mol, the effect is very important indeed. In this case the existence of a residual interaction is confirmed. It is clear that the long chains favour the formation of more loops as explained before.

6.2.2. Influence of the grafting ratio

The pseudo solid echo experiment has been performed on PEO 2000 grafted on silica for three different grafting ratios. In Figure 11, the curves obtained for the same value of the time τ are shown. It is apparent that the residual dipolar interaction (given by the amplitude of the echoes) does indeed depend on the grafting ratio [21, 35].

In fact for a low grafting ratio, the amplitude of the echoes is very small. It becomes larger at higher grafting ratios. At a low grafting ratio the chains spread out on the silica and occupy a maximum of the available attractive surface. It is well possible that at low grafting ratios some part of the signal becomes lost as explained before. When the grafting ratio increases, the chains interact with each other, repel each other and tend to form more loops. The residual dipolar interaction which is related to the inter monomer interaction becomes accordingly more important with increasing grafting ratios, beginning at a somewhat negligible value at a very low coverage.



Figure 9. ¹H NMR. Experimental echo obtained at room temperature The function $\eta(t,\tau)$ corresponding to several values of pulse spacing τ ($\tau = .2, .4, .8$ and 1.2 ms).



Figure 10. Experimental echo obtained for samples with different molecular weights. The functions $\eta(t,\tau)$ corresponding to several values of τ at room temperature are given for a molecular weight of (A) 44 and (B) 2000.

6.2.3. Evolution of the pseudo solid effect with temperature

The pseudo solid echo experiment has been performed on PEO 2000 grafted on silica with a grafting ratio of 53% (24 u.m./nm²). The functions $\eta(t,\tau)$ corresponding to several values of τ have been recorded for different temperatures in the range 260-360 K. In order to determine Δ^2 , the parameter characteristic of the residual dipolar interaction, we follow the previously proposed method [32, 34]. Therefore, Δ^2 can be represented for different temperatures (Figure 12).

The reported evolution of the second moment shows that the intensity of the residual dipolar interaction is relatively small at low temperature. At high temperatures (300-360 K) it becomes more important. The transition between the two regimes occurs between 275-295 K as already observed by measurements of relaxation times. This outcome is the result of a balance between the two opposing effects.

At low temperatures, the chains are strongly held to the solid surface and even if they are relatively



Figure 11. Experimental echo obtained for samples with different grafting ratios and a molecular weight of 2000. The functions $\eta(t,\tau)$ corresponding to several values of τ at room temperature are given for a grafting ratio of (A) 5% and (B) 19% and (C) 53%.

closely packed on it their interaction does not appear enough in our experiments. They also have little motion in this state.

At higher temperatures, the chains begin to extend away from the surface and to have more motion. Many loops are formed and the monomers interact with each other, increasing further and further the residual dipolar interaction in this anisotropic environment. This process reaches its limit when the chains become largely swollen and with a higher flexibility and a fast motion, the interactions are averaged again.

7. Magic angle spinning technique: residual interaction study

The magic angle spinning technique is used in the first part of this section to measure the residual interaction side band second moment of the static part. In the second part "mas" technique is used to investigate local chain dynamics. It permits the determination of two correlation times for different grafting ratios: τ_1 characteristic of an environment with a slow motion and τ_c characteristic of the local segmental motion.

7.1. Residual dipolar interaction: measure and evolution

¹H NMR Nuclear magnetic relaxation permits some approach to a monomer unit scale of poly(ethylene) grafted on silica. The magic angle spinning technique confirms, by the narrowing of the central line and the apparition of side bands, the existence of residual dipolar interaction. Such interaction reveals the high monomer unit concentration at the surface. The study of the side bands permit calculation of the physical parameter: second moment, which gives in turn an indication of the evolution of the monomer unit's concentration on the surface. This behaviour has been studied as a function of molecular weight of the chains and grafting ratio. A fair agreement is obtained for the second moment and the linewidth, giving a consistent picture by two independent techniques: magnetic relaxation and magic angle spinning.

7.1.1. Residual dipolar coupling in grafted polymer as reflected by mechanical rotation

The spinning sample around an axis inclined at an angle θ with the static field has the effect to render the dipolar Hamiltonian dependant on time and can be divided into two parts:



Figure 12. Evolution of the second moment Δ^2 of the experimental echoes obtained for the sample of PEO 2000 with a grafting ratio of 53% at different temperatures.

$$H_{\rm D}(t) = \langle H_{\rm D} \rangle + H_{\rm D}(t) \tag{20}$$

- $\langle H_D \rangle$ is proportional to $(3.\cos^2\theta - 1)$. It disappears at $\theta = \theta_M = 54^{\circ}44$

- $H_{D}(t)$ depends periodically on time and is responsible for the apparition of side bands.

Different measurements are done on poly(ethylene) oxide grafted on silica at room temperature for different molecular weights and a different grafting ratio. An example of a sample rotation line narrowing and an apparition of side bands is given in Figure 13. In fact, a rapid rotation of the sample about an axis inclined at the 'angle magic' of 54°44 relative to the Zeeman field direction can remove the residual dipolar interaction [36]. The speed of rotation of the sample must be of the order of the static dipolar interaction to narrow the NMR spectra. Figure 13 shows the experimental curve and illustrates the evolution of central linewidth as a function of spinning rate Ω_R and the existence of side bands. It confirms the existence of a residual dipolar interaction. To acquire more quantitative results and information about the concentration of monomer units near the surface, we now develop the 'magic angle spinning'

technique to study the pseudo solid effect and deduce the intensity of residual dipolar interaction.

7.1.2. Study of the side bands: evolution of the residual dipolar spin coupling

It is already known that the amplitude of the side bands increases with the intensity of the dipolar coupling. In particular it has been shown [22] that, if the sample rotates around an axis perpendicular to the magnetic field, the side band appears at frequencies $2N\Omega_R$. We have used the theoretical calculations elaborated in ref. [21, 22]. The intensity of the side band is proportional to $e^{-X}I_n(X)$, where $I_n(X)$ is a modified Bessel function. We can now deduce the argument X derived from mathematical tables from the experimental ratios I_1/I_0 of the side band intensities. Rotational side bands I1 and I2 are clearly evidenced in Figure 13 (inset). The expression of X is directly proportional to Ω_R^{-2} and M_2^0 (M_2^0 is the second moment, characteristic of the non averaged dipolar interaction deduced from the residual part of the dipolar Hamiltonian [22]). If we plot the argument X of I_1/I_0 as a function of $\Omega_{\rm R}^{-2}$, we note that a straight line is obtained. The slope of the argument X is proportional to M_2^0 , so we can measure the dipolar residual interaction.



Figure 13. Proton resonance spectra recorded during sample rotation. Spectra correspond to an increasing spinning rate Ω_R (from 0 to 3500 Hz). PEO 2000 grafted on silica. Room temperature. Inset shows line shape of proton resonance spectrum ($\Omega_R = 550$ Hz). Rotational side bands I₁ and I₂ are clearly shown. Data obtained from ¹H masNMR spectroscopic measurements (300 MHz).

Thus, we have a method to follow the evolution of the residual dipolar spin coupling as a function of the molecular weight and of the grafting ratio.

7.2. Evolution of the residual dipolar spin coupling as function of the molecular weight

The experiment has been performed on PEO grafted on silica at room temperature for different molecular weights (Table 1). From the ratio I_1/I_0 , the argument X is now indeed derived from mathematical tables and it is plotted as a function of Ω_R^{-2} , for different molecular weights. It is clearly seen from Figure 14 that the amplitudes of the side bands depend upon the spinning frequency Ω_R and that the amplitudes of the side bands are described in satisfactory agreement with the results predicted

by the theory [21]. From the spectra observed at resonance frequency equal to 300 MHz and with an effect of the sample rotation, the evolution of the dipolar residual interaction is obtained. Its dependence is plotted as a function of molecular weight in Figure 15. The intensity of the dipolar residual interaction characterised by $M^{\,0}_{\,2}$ increases with molecular weight. This is an important result because it is the same evolution that we obtained from the ¹H linewidth. It proves that with the use of two independent techniques, we are indeed probing the same phenomena. The second moment as well as the linewidth increase with the molecular weight because the residual dipolar interaction increases. It is also noteworthy to record that with a sample rotation experiment without solvent we find the same resolution as that with deuterated benzene without sample rotation [26].

7.3. Evolution of the residual dipolar spin coupling as a function of the grafting ratio

The presence of the nonzero average spincoupling in polymers grafted on silica reflects the nonisotropic motion of chain segments. These are not free to rotate completely because of the constraints of the confinement near the surface due to the grafting. In the system of polymer grafted on a solid surface, the parameter which seems to be the most sensitive to the variation of the grafting ratio is the number of monomer units per surface area, since this depends both on the grafting ratio τ and on the molecular weight M.

The experiment has been performed on PEO of molecular weight 2000 grafted on silica for a different number of monomer units per nm^2 (Table 2).

The same procedure as the previous one is applied to the side bands to determine the argument X. The latter is plotted as a function of Ω_R^{-2} , for a different grafting ratio (the number of monomer units per surface area) in Figure 16. The amplitudes of the side bands are described in satisfactory agreement with the results predicted by the theory. The Figure 17 shows the evolution of the residual dipolar interaction with the number of monomer units per surface area for PEO 2000 grafted on silica.

The intensity of the dipolar residual interaction characterised by M_2^0 increases with the grafting ratio.



Figure 14. Study of the ratio of the central to the first sideband intensities as a function of the square of the inverse of the spinning rate, for grafted poly(ethylene oxide) for different molecular weights. The amplitude I_1 of the first side band is compared with the amplitude I_0 of the central line. From ratio I_0/I_1 measured as a function of the spinning frequency Ω_R , the argument X is derived from mathematical table. The X is plotted as a function of Ω_R^{-2} for different molecular weights. (•) M = 2000; (•) M = 1000; (•) M = 600; (•) M = 88.



Figure 15. Evolution of the linewidth (\blacktriangle) and of the residual dipolar interaction characterized by the root second moment M_2^0 (•) as a function of different molecular weights, for a grafted poly(ethylene oxide).

This evolution occurs according to three stages. In fact, below transition at 7 monomer units/nm², when M_2^0 seems to be constant, the chains spread out on the surface occupying as much place as needed by

their size. It can be concluded that in this last grafting ratio range, the conformation of the macromolecules near or at the surface does not vary any more, neither does the local concentration of monomer units. After 7 m.u./nm², M_2^0 increases before it becomes constant at 7 to 14 m.u./nm² range. We can explain this situation by considering the influence of the first adsorbed layer of monomer units on the second one. In fact the second layer of monomer units in contact with the first is strongly immobilized and adopts the behaviour of monomer units adsorbed on a solid. Above 14 u.m./nm² where the thickness of the adsorbed layer becomes greater than the monolayer of monomer units, the concentration becomes very large and leads to the formation of loops. This engenders the increase of the residual dipolar interaction.



Figure 16. Study of the ratio of the central to the first sideband intensities as a function of the square of the inverse of the spinning rate, for grafted poly(ethylene oxide) for different number of monomer units per nm². The X is plotted as a function of Ω_R^{-2} for different number of monomer units per nm²: (\bullet) $\tau_{m.u.} = 24$; (\bullet) $\tau_{m.u.} = 15.4$; (\bullet) $\tau_{m.u.} = 11$; (\bullet) $\tau_{m.u.} = 8.6$; (\bullet) $\tau_{m.u.} = 7.7$; (\bullet) $\tau_{m.u.} = 4$; (\triangleright) $\tau_{m.u.} = 2.2$.



Figure 17. Evolution of the residual dipolar interaction characterized by the root second moment $(M_2^0)^{1/2}$ as a function of different number of monomer units per nm², for grafted poly(ethylene oxide).

The difference in the evolutions of the ¹H static linewidth and the second moment below transition at 7 m.u./nm² is of a dynamic nature. In fact, since this relaxation time is shown to be depending on the grafting ratios (number of m.u./nm²) this implies that the lateral constraints between chains exist, even for the order of 1 m.u./nm². The chains spread out on the surface occupying as much place as needed by their size, with a practically bidimensional conformation. The mobility of segments in these conditions is severely restricted. This fact explains that the linewidth is relatively important. The spinlattice relaxation time T₁ increases when the mobility decreases. Above the transition, the grafting ratio does not influence the relaxation functions.

8. Magic angle spinning technique: dynamic study

8.1. Determination of correlation times

8.1.1. Investigation of local chain dynamics

The molecular dynamics is a complex process, extended within a large temporal and spatial range, going from the fast motions of the monomeric units to the slow process of the reorientation of monomer units with each other.

This section focuses on the local chain dynamics in polymers. The magic angle spinning technique is used to investigate local chain dynamics. It permits to determine two correlation times for different grafting ratios: τ_1 characteristic of an environment with a slow motion and τ_c characteristic of the local segmental motion. This correlation time is compared to that obtained by measurements of T₁.

8.1.2. Rotation effect and limit linewidth study

The magic angle spinning technique was used to study the dynamics of the polymeric chain and to determine two correlation times (τ_1 and τ_c) for each grafting ratio. We assume that in our system, macroscopic and microscopic effects coexist and that the fluctuation of local dipolar field arises from two contributions [20, 37]:

- the reorientation motion of monomer-units relative to each other described by the $H_D^{\text{int er}}$ Hamiltonian (11) and characterised by the relatively longer correlation time τ_1 .
- the local motion of monomer-units, relatively fast, and described by the H^{int ra}_D Hamiltonian (11) and characterised by the short correlation time τ_c.

In this situation, the rigid lattice second moment $(\delta \omega_0)^2$ [41, 49] results from two contributions:

$$\left(\delta\omega_0\right)^2 = \left(\delta\omega_c\right)^2 + \left(\delta\omega_l\right)^2 \tag{21}$$

Here, $(\delta \omega_c)^2$ corresponds to the intramolecular part averaged by random microscopic motion characterised by a correlation time τ_c and $(\delta \omega_l)^2$ corresponds to the intermolecular part removed by the more macroscopic motion characterised by a correlation time τ_l . We can assume: $\tau_c \ll \tau_l$

The resulting spectral density $J(\omega)$ is illustrated in Figure 18 (inset). The BPP model [29] has been used, which introduces for a simple isotropic and random motion of the lattice, a spectral density function with a normalised form

$$J(\omega) = \frac{\tau}{\pi (1 + \omega^2 \tau^2)}$$
 where τ is the rotational

correlation time of the supposedly thermally activated process. Such an approximation, which could seem crude, appears to be relatively suited here because it explains the effects of a rotational motion when there are simultaneous fast internal movements and a slow reorientation of the lattice and it allows an estimation of the linewidth in the static case and even in the case of a macroscopic spinning [21, 24, 29].

When the axis rotation is inclined at the magic angle, the linewidth, when the sample rotates at ω_r , can be written as [36, 38]:

$$(\delta\omega_r)^2 = \frac{2}{\pi} (\delta\omega_c)^2 \cdot \tau_c \cdot \delta\omega_r + \frac{(\delta\omega_l)^2}{\pi} \cdot \frac{2}{3} [\operatorname{arctg}(\omega_r + \delta\omega_r)\tau_l - \operatorname{arctg}(\omega_r - \delta\omega_r)\tau_l]$$

$$\cdot \frac{1}{3} [\operatorname{arctg}(2\omega_r + \delta\omega_r)\tau_l - \operatorname{arctg}(2\omega_r - \delta\omega_r)\tau_l]$$
(22)

We can notice that the evolution of the linewidth with the rotation frequency deduced from the expression (22) is in agreement with all our experiences.

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

$$\left(\delta\omega\right)_{li} = \frac{2}{\pi} \left(\delta\omega_c\right)^2 \tau_c \tag{23}$$

The residual linewidth must therefore give the correlation time of fast internal motion. From this expression, we can confirm that the faster the segmental motion, the smaller the linewidth. In order to study this motion, we adopt the Andrew approach [38] introduced above. A computing program has been elaborated using the previous expressions. The last relation (22) permits to plot a theoretical curve and to fit it by varying τ_c and τ_1 . τ_c is deduced from the expression (23). τ_c and τ_1 are determined in this way.

8.1.3. Influence of the grafting ratios: determination of the correlation times

Some experiments have been performed on PEO grafted on silica at room temperature [20, 39]. In Figure 18 the evolution of the linewidth versus the rate of rotation at different grafting ratios are shown. The NMR line narrowing effect by high speed rotation is observed in the same samples with different grafting ratios. In fact, when the rotation frequency increases, one observes a line narrowing for $\omega_r \approx 1/\tau_1$. After this transition, the linewidth will be limited to $(\delta \omega)_{li}$ independent of the rotation rate, because of the very large value of $1/\tau_c$. This behaviour is characteristic of the coexistence of two motions, fast and slow, described respectively by $H_D^{int ra}$ and $H_D^{int er}$ and characterised by the respective correlation times τ_c and τ_l . The resulting spectral density is illustrated in Figure 18 (inset). The study of the NMR linewidth as a function of ω_r is therefore interesting for evaluating the correlation time τ_c in PEO/silica systems. τ_c and τ_l are determined.

In Figure 19, the evolution of the correlation times as a function of the number of monomer units per nm² has been reported. The first important result is that the correlation time τ_1 decreases with grafting ratios and τ_c remains constant. The sub

chain mobility, characterised by τ_l , decreases when the grafting ratio increases. The value of τ_c decreases when the grafting ratio increases and becomes constant after about 7 monomer units per nm². This study allows to point out the complex behaviour of the monomer units mobility. In fact, the existence of a residual linewidth in the resonance line when the sample rotates is an important characteristic of the dynamics and of the internal motion of polymers grafted on silica.

Experimentally, it appears that the motion at the scale of the monomer unit does not depend on the coverage of the surface, and could simply be related to the rotation around the backbone of the macromolecule. The slow motion related to the static interaction is more sensitive to the coverage: the higher the coverage, the shorter the correlation time. Probably the average conformation of the chains extends far from the surface, the chains interact with each other, repel each other and are then more free to move in a more diluted medium.

8.1.4. Comparison of the correlation times

Correlation times characteristic of the fast segmental motion are determined by two different techniques: (i) spin-lattice relaxation time T_1 (ii) mas technique. The comparison of the values obtained (Table 3) at 300 K shows a great difference. We observe a ratio from approximately 100 [40]. This variation can be explained as follows.

The spin lattice relaxation which limits the lifetime of spin in a given state can lead to a linewidth of about $1/T_1$. In the polymer grafted system, the local motion of the monomer units which is relatively fast represents a significant mechanism of relaxation. According to BPP [29] model the components of the order of the Larmor frequency ω_0 (and 2 ω_0) of the local motion could produce transitions between the states of nuclear spins, supporting the transfer of energy between the spins and the lattice.

The macroscopic rotation of the sample does not have a significant effect on this type of mechanism of relaxation. In fact, the macroscopic frequency of the rotation reached is much weaker than ω_0 . The spin lattice relaxation time T₁ and the linewidth which results from it are not modified by the rotation of the sample. Thus, one could notice that the linewidth generated by a spin lattice relaxation



Figure 18. Evolution of linewidth versus rotation frequency of sample. Different number of monomer units per nm² at room temperature for grafted poly(ethylene oxide). (\checkmark) 2.2 um/nm², (\bigcirc) 7.7 um/nm², (\bigcirc) 11 um/nm², (\checkmark) 14.7 um/nm², (\checkmark) 24 um/nm². Inset : Effects of sample rotation on linewidth when two molecular motions τ_c and τ_l are present in a sample.



Figure 19. Evolution of the correlation times τ_c (\blacktriangle) and τ_1 (\bullet) as a function of number of monomer units per nm² for a grafted poly(ethylene oxide).

mechanism is generally negligible compared to the limiting linewidth.

9. High resolution: mas/cross polarisation

9.1. ¹³C high resolution NMR

Poly(ethylene oxide) is the most widely studied material in use as a solid polymer electrolyte. There have been numerous investigations in conditions that favor crystalline formations [41-43]. PEO is well known to be semi-crystalline at higher polymer lengths [44]. We have tried to know if PEO 2000 is semi-crystalline or completely amorphous. To assess this point, specific NMR measurements including Cross Polarisation and Magic Angle Spinning (CP-MAS) between ¹H and ¹³C have been performed.

The use of cross-polarisation has been suggested due to different reasons. Firstly, in association with magic angle spinning (CP/MAS) the expected resolution should be very good [44, 45]. The protons of the PEO chains constitute an abundant spin reservoir. Their spin-lattice relaxation time in rotating frame $T_{1\rho}$ is of the order of a few milliseconds [17, 21], sufficiently long to transfer completely the polarisation of the ¹H spins to the ¹³C spins. Indeed the proton magnetisation of the ¹³C. Depending on their mobility, the ¹³C nuclei are in more or less important

dipolar interaction with the ¹H (abundant spins). This property is used to selectively enhance the signals of certain ¹³C, thus allowing a qualitative or quantitative analysis. These measurements have also been performed in order to gain a better understanding on the motion and the dynamical properties of the grafted molecules.

9.2. Organisation of grafted layers approach

The effect of the contact time variation on the shape of lines is shown in Figure 20. Indeed it is dependent on this time. At short contact times, a superposition of two types of lines is observed: the ¹³C CP/MAS solid state NMR spectrum of PEO grafted has superimposed broad and narrow components. The narrow component has been assigned to amorphous region and the broad component to the cristalline PEO fraction. A broad line and a narrow one are superposed. Probably these two lines are originating from segments with two different mobilities mentioned before. The narrow line comes possibly from segments having a faster motion because they belong to loops and tails. The broad one corresponds to the signal of segments in trains with restricted motion. At long contact times it seems reasonable to assume that the broader line is associated with the shortest spin-lattice relaxation time in the rotating frame. There seems to be a locally stable organisation of the segments in close contact with the solid which



Figure 20. ¹³C NMR at a frequency of 75 MHz with CP/MAS method of a sample of PEO 2000 grafted silica. Separate spectra of the crystalline and amorphous resonance.

could be similar to a crystalline phase [44, 46]. The most mobile mode to the loops and tails where the motion is more free could be similar to a "amorphous" phase. It must however be noted that the two signals are difficult to separate, the chemical shift between both being so small.

Figure 21 shows the ¹³C CP/MAS amplitude of the main peak of PEO grafted on the silica spectrum for two polymer lengths 44 and 2000 as a function of the contact time. Similar results have been obtained on PEO 2000 and PEO 44 grafted on silica.

The evolution of the amplitude as a function of the contact time can be fitted by [47]:

$$M = M_0 [1 - \exp(-t_c / T_{C-H})] \cdot \exp(-t_c / T_{1\rho H})$$
(24)

where t_C is the contact time, T_{CH} is the polarisation time, $T_{1\rho H}$ is the spin-lattice time in the rotating frame and M_0 is the magnetisation at equilibrium actually proportional to the number of carbon nuclei. It is apparent that at short contact times, the curve is mainly controlled by the cross polarisation time T_{CH} , whereas at longer contact times, the magnetisation decreases exponentially like that of the ¹H spins with a time constant $T_{1\rho H}$.

Since the same evolution of the magnetisation is observed in our experiences (the increase of the magnetisation at short contact times and the decrease at higher contact times) it is possible to define the similarity "average" parameters T_{CH} , $T_{1\rho H}$ and M_0 .

10. ²H NMR: study of the anisotropy

The ²H NMR approach consists in studying how the nuclear (quadrupolar) interactions acting along the C-D bonds are time averaged by the molecular motions [48, 49]. In general, in solution the ²H NMR spectrum is a single narrow line since the quadrupolar interactions are time averaged to zero by the rapid isotropic molecular motions [39]. On the contrary when the motion is anisotropic, the nuclear interactions are only partially averaged.

10.1. Effect of the grafting ratio

The polymer was perdeuterated. Two extreme grafting ratios have been studied. The measurements at room temperature have been performed on deuterated PEO 2000 for the two grafting ratios (15% (5 u.m./nm²) and 53% (24 u.m./nm²)). In Figure 22 experimental ²H NMR spectra are presented.

The broadening of these spectra is due to the fact that certain movements become slower or if it reveals the presence of residual quadrupolar







Figure 22. ²H NMR spectra of perdeuterated poly(ethylene oxide) PPEO grafted on silica (averaged molecular weight 2000) for the samples. These samples differ only in the grafting ratio (τ): A : 15%, B : 53%. Data obtained from ²H NMR spectroscopic measurements (76 MHz) at room temperature.

interactions connected with movements that while remaining fast are in fact anisotropic [39]. The broadening of the lines of the grafted polymers is due to the fact that the quadrupolar interaction is not averaged to zero by the motion of the chain segments and that the overall dynamic is anisotropic (a given segment does not explore all the directions of space during the characteristic time υ_{0}^{-1}).

10.2. Influence of temperature

It is interesting to investigate more deeply the degree of this anisotropy, and particularly to show if possible the existence of a residual interaction as it has been done by the proton NMR measurements [20, 23]. Therefore measurements have been performed at different temperatures [39]. In the case of the low grafting ratio (Figure 23) the whole set of spectra obtained for the low grafting ratio has been reported. The overall shape of the line is rather Gaussian and structured, but

as the temperature increases this shape becomes less apparent and simultaneously the linewidth decreases. Consequently, the anisotropic character of the motion if it exists, disappears progressively as the temperature increases. However in the case of the high grafting ratio (Figure 23), the spectra similarly present a definite gaussian and structured shape, and as the temperature increases, this shape is progressively lost, the lines become narrower and the top of the peaks finer indicating that the motion tends progressively towards a more isotropic character. The simulation of the spectrum (Figure 23) obtained for the high grafting ratio at 260 K shows that it is composite and formed by the superposition of two gaussian lines of respective linewidths: 1400 Hz and 8900 Hz. This structure of the line or coexistence of two types of motions can be interpreted in the frame of the usual picture for grafted polymers: a fast motion part due to the loops and tails protruding away from the surface which are relatively free to move, and a slow motion part due to trains adsorbed on the solid with a strongly hindered tumbling.

of transition: It was Existence already demonstrated by measurements of relaxation times that there exists a transition situated between 280 K and 300 K. The transition is not a vitreous transition. It is of a dynamic nature, and corresponds to a modification of the motion of the monomer units, which is influenced by the grafting ratio. This transition concerns both fast and slow motion. It is observed for all grafting ratios. This transition is more important when the grafting ratio is low. In this respect, we can observe a jump only for the sample with a low grafting ratio. It is not possible to show the same anisotropy for results obtained at temperatures situated just in the transition.

In Figure 24 the linewidths of the peaks of the central line as a function of temperature have been reported. The behaviour for both samples, with a low and a high grafting ratio, of this parameter is rather similar. The linewidth decreases regularly as the temperature decreases. After transition, it becomes constant after 300 K for high grafting ratio. This comparable evolution can be retraced to slightly different stages of a similar mechanism. For the low grafting ratio, the anisotropic part of the motion, which is important



Figure 23. ²H NMR spectra of perdeuterated poly(ethylene oxide) PPEO 2000 grafted on silica with a low grafting ratio $\tau = 15\%$ (A) and high grafting ratio $\tau = 53\%$ (B) at different temperatures.



Figure 24. Evolution of the linewidth as a function of temperature for perdeuterated poly(ethylene oxide) of PPEO 2000 grafted on silica at different grafting ratios: (\bullet) 53%, (\bullet) 15%. Data obtained from ²H NMR spectroscopy (76 MHz).

particularly at low temperature, becomes weaker. For the high grafting ratio the segmental motion becomes faster, freer and more isotropic starting from the beginning at a higher value. The results are coherent with ¹H NMR relaxation time measurements as a function of temperature. The anisotropy is important only at low temperatures, and it is consistent to consider a rather isotropic motion at high temperature for the ¹H measurements.

11. CONCLUSION

The NMR technique appears to be a powerful, sensitive and versatile method for probing, at a molecular level, the structure and organisation of a polymer layer attached to a solid surface.

The behaviour of poly(ethylene oxide) grafted on silica has been studied by NMR relaxation. The NMR technique therefore appears to be a valuable tool for studying the polymers at solid interfaces either for their static conformations or for their dynamics, and precisely with the most suitable nucleus to be observed, ¹H, ¹³C, ²H. It is, indeed, able to give microscopic information about the polymer conformations.

The studies showed that NMR relaxation methods are highly sensitive to mobility of poly(ethylene oxide) chains at a silica surface. Since molecular mobility is closely coupled with the molecular weight, the grafting ratio, the solvent and the temperature, NMR relaxation methods can provide valuable information on the structure and organisation of a polymer layer. The analysis of relaxation times allows the description of segmental motion and the organisation of the grafted layer under different conditions.

Finally, the choice of the number of monomer units/nm² seems to be a right parameter to account for the variation of the grafting ratio and molecular weight.

We have presented an approach to the determination of residual dipolar interaction employing two independent techniques namely "pseudo solid echo" and "mas", taking into account the molecular weight and the temperature as pertinent parameters. A coherent agreement is obtained from the physical parameter which describes the monomer unit concentration on the surface by latest independent techniques.

The NMR spectroscopy appears as a well suited method to obtain rather local at-a-microscopiclevel information on the polymers lying on the surface. It permits to propose different models for the surface layer.

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