



Account / Revue

Study of the residual dipolar coupling by ^1H NMR MAS technique. Effect of the grafting ratio on interface polymer grafted on silica

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ABSTRACT

^1H NMR permits some approaches to a monomer unit scale of the macromolecular grafted on the solid. In the case of poly(ethylene) grafted on silica, the magic angle spinning technique confirms, by narrowing of the central line and apparition of side bands, the existence of the residual dipolar interaction, which reveals the high monomer unit concentration at the surface. The study of the side bands permits calculation of the physical parameter: the second moment, which gives in turn an indication of the evolution of the monomer unit concentration on the surface. This behavior 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.

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R É S U M É

La RMN du proton permet une approche à l'échelle de l'unité monomère des macromolécules greffées sur support solide. Dans le cas du polyoxyéthylène greffé sur silice, la technique de rotation à l'angle magique confirme par le rétrécissement de la raie centrale et l'apparition des bandes de rotation, l'existence de l'interaction dipolaire résiduelle qui révèle la forte concentration des unités monomères à l'interface. L'étude des bandes de rotation permet de calculer le paramètre physique : second moment qui donne une indication sur l'évolution de la concentration des unités monomères sur la surface. Ce comportement a été étudié en fonction de la masse moléculaire et du taux de greffage. Un accord a été obtenu pour le second moment et la largeur de raie par deux techniques indépendantes : relaxation magnétique et rotation à l'angle magique.

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1. Introduction

The modification of the characteristics of the polymer–solid interface depends essentially on the behavior of particular chains, such as conformation, mobility, etc. The properties of polymers at interfaces are of growing technological importance due to the extended use of

surfaces modified by polymer films and polymer grafting and also due to the fundamental interest of surface effects of both polymer conformation and chain dynamics [1–3].

The configuration and the properties of chain polymer should depend essentially on the polymer surface density [4,5], length (molecular weight), and the nature of the solid surface. Very limited information about short grafted polymeric chains is available [6,7].

Currently, all experimental approaches rely on the anisotropy of segmental motions in polymeric systems, by

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which tensorial NMR interactions (mostly ^2H quadrupolar and ^1H dipolar interactions) are incompletely averaged, leaving small residual quantities. For example, ^1H multiple-quantum experiments, which are readily applicable to unlabeled materials, represent a particularly promising class of techniques, which have been successfully applied to a quantitative measurement of the residual ^1H dipole-dipole coupling constants in various systems [7,8,9].

The knowledge of the dynamics of grafted polymers may also provide essential data for the understanding of global surface properties like wetting and adhesion. The study of molecular dynamics is very important for the understanding of how the motions of polymer chains are affected by different anchoring points on the solid surface. It has appeared that the grafting ratio becomes a very significant parameter in the characterization of such systems [10,11,12].

Poly(ethylene oxide) (PEO) is a simple polymer, that 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. The solid support is silica (Aerosil) with a high degree of chemical purity [10].

The relaxation function of the transverse nuclear magnetization observed on grafted polymers results from two contributions [13,14]:

- one is related to the dynamics of fluctuations of space variables describing monomer units positions;
- 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, caused by, for example, the surface. The chains are not free to rotate completely with respect to each other.

Indeed, it has been demonstrated that there exists a residual dipolar interaction which is not averaged in a time shorter than the spin-spin relaxation time [12,14,15]. It has also been observed and shown by the effect of sample rotation on the spectra. It is well known that NMR spectra of solids can be narrowed by fast rotation of samples [16]. The rotation of solid samples at very high speed can be used to progressively eliminate the dipolar coupling so as to finally observe fine structures analogous to those observed in high-resolution spectra of liquids.

It is thus possible to study dipolar interaction by rotation of the sample at the magic angle. When the fast rotation occurs at the “magic angle”, the dipolar Hamiltonian becomes a periodic function of time and generates satellite lines distant of $N \cdot \Omega_R$ ($N = 1, 2, 3, \dots$) on either side of the central spectrum [16,17], Ω_R being the rotation frequency of the sample. This line narrowing will be effective when the rate of rotation Ω_R becomes of the order of the static linewidth. These effects are in fact used here to give information about the concentration of monomer units on the surface. In the present paper, we report on experimental results that have been obtained by ^1H NMR of PEO with a weight-average molecular weight of 2000, which has been grafted on silica (Aerosil) at different grafting ratios.

2. Experimental

2.1. Materials and grafting method

2.1.1. Silica

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 on a molecular scale [18].

2.1.2. Polymer

The polymer was PEO (from Fluka). The oxygen in the backbone makes it very flexible. In NMR, this polymer is very convenient because there is only one existing chemical shift for ^1H as well for the ^{13}C . The molecular weight and polydispersity of the PEO were determined by gel permeation chromatography. Molecular weight varies from 44 (oligomer) to 2000 (molecular mass number 1980). The length of the chains is always that corresponding to a molecular weight of 2000 with a polydispersity of 1.04. The number of silanols on a silica surface is about 5 per nm^2 for a fully dehydrated silica. They are assumed to be rather randomly distributed on Aerosil silica.

The preparation of samples is described in detail in Ref. [19]. The grafting ratio was evaluated by elemental analysis or by pyrolysis weight between 25 and 750°C under oxygen.

2.1.3. Definition of grafting ratio

The grafting ratio, τ , is expressed in weight %: it is the weight of polymer irreversibly fixed on 100 g of silica. When using pyrolysis procedure, τ is given by the following relationship:

$$\tau = \frac{\Delta m}{m_i - \Delta m} \cdot 100 \quad (1)$$

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

$$\tau_{\text{mu}} = \frac{6 \cdot 10^{23} \cdot \tau}{44 \cdot S} \quad (2)$$

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

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

2.2. NMR technique

Experimental measurements were carried out on a Bruker Fourier transform NMR spectrometer ASX operating at 300 MHz. The $\pi/2$ pulse width was less than $1.5 \mu\text{s}$ which corresponds to a B_1 rotating field of more than 40 Gauss. The dead time for the detection was less than $4 \mu\text{s}$.

Experimental measurements of $T_1(^1\text{H})$ were carried out by using the inversion-recovery pulse sequence.

Table 1

Results obtained for various types of grafting ratios for poly(ethylene oxide) (PEO) samples of different molecular weights grafted on silica.

PEO sample	τ_{mu} (number of monomer unit by unit surface)	τ (%) (grafting ratio express 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 2

Various types of grafting ratios for poly(ethylene oxide) (PEO) (M = 2000) grafted on silica at different temperatures.

Grafting temperature (°C)	τ_{mu} (number of monomer unit by unit surface)	τ (%) (grafting ratio express in weight %)
160	2.2	5.1
160	6.1	15.2
80	7.7	19.0
80	11.0	25.0
100	14.7	32.5
125	15.6	34.7
238	24.0	53.4

This spectrometer was equipped with a “double bearing” probe head allowing magic-angle spinning (at 54°74) at rates going from 0 to 4 kHz. Rotation at room temperature was achieved by an air driven turbine in which the rotor itself was supported by a gas bearing.

The experimental spectra were fitted with calculated Lorentzian or Gaussian lines, with the program Linefit from Bruker. The spinning sidebands intensities were determined by fitting the MAS spectra.

The samples were prepared as follows: (i) *Relaxation times experiment*: the samples were all prepared in Pyrex spheres of 5 mm diameter, which gave greater field homogeneity. Before the experiment, the grafted silica was dried by direct pumping. (ii) *MAS experiment*: the powder samples (PEO grafted on silica) were placed in zirconium cylindrical rotors of 5 mm diameter, volume about 0.3 cm³ (about 0.15 g), spinning at the magic angle (54°74).

3. Result and discussion

3.1. Effect of molecular weight on the relaxation function

The results of the measurements of both linewidth and spin-lattice relaxation times T_1 as a function of molecular weight denoted M are shown in Fig. 1. Without solvent, the ¹H static linewidth increases with molecular weight, whereas, when the compound is immersed in deuterated benzene, the linewidth no longer depends on M. The spin-lattice relaxation time on the other side does not at all depend on molecular weight either with or without solvent. The evolution of ¹³C linewidth is presented in Fig. 1 (insert). It appears to be completely independent of the molecular weight.

Since the essential difference between ¹H and ¹³C NMR is the sensitivity to the inter monomer unit dipolar

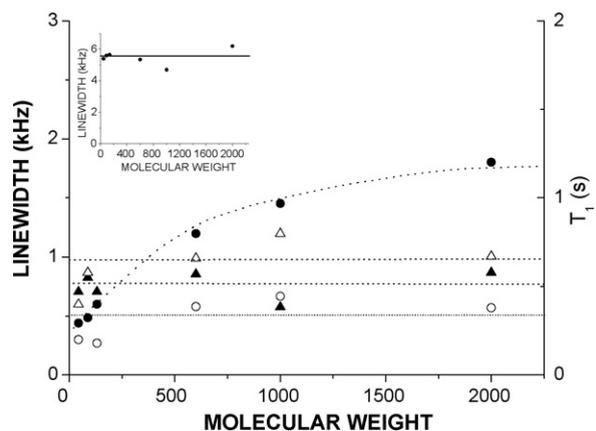


Fig. 1. Evolution of the linewidth (●) and the spin-lattice relaxation time (▲) as a function of the molecular weight, for a grafted poly(ethylene oxide). (○, △) with deuterated benzene. Data obtained from ¹H NMR spectroscopic measurements (300 MHz).

Insert shows corresponding results (linewidth) obtained from ¹³C NMR spectroscopic measurements (75 MHz).

interaction, which is only observed by ¹H NMR, it implies that this interaction increases with molecular weight.

Even the slow mode of the segment motion which governs the spin-spin relaxation time of ¹³C [20] does not change with molecular weight. When the samples are immersed in deuterated benzene, the molecular weight effect disappears because the local monomer unit concentration decreases, i.e., the dynamic fluctuations of the segment-segment distance are higher and may average the inter monomer unit 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.

More precisely the Hamiltonian, which describes the dipolar interaction, can be written as mentioned below [13,14]:

$$H_D = H_D^{\text{intra}} + H_D^{\text{inter}} \quad (3)$$

H_D^{intra} is the contribution of all the protons in a monomer unit. H_D^{inter} is the dipolar interaction between the nuclei of different monomer units.

Because of the very slow and anisotropic reorientation process of one monomer unit relative to the other, the dipolar interaction H_D^{inter} between the nuclei pertaining to different segments but close in space, is not completely averaged in a time characteristic of the evolution to the equilibrium of the transverse magnetization.

To more thoroughly investigate the influence of the second term, we rewrite the Hamiltonian as follows [21]:

$$H_D = H_D^1 + H_D^2 \quad (4)$$

$$H_D^1 = H_D^{\text{intra}} + H_D^{\text{inter}} - \bar{H}_D^{\text{inter}}$$

$$H_D^2 = \bar{H}_D^{\text{inter}} \quad (5)$$

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 to the evolution of the equilibrium of

the transverse magnetization ($\langle T_2 \rangle$) as the average of H_D^1 is approximately zero. (i.e., $H_D^1 \neq 0$).

H_D^2 is a static interaction (i.e., $H_D^2 \neq 0$) giving the residual interaction (non-zero average dipolar spin coupling). This interaction is due to the very slow anisotropic reorientation process of the monomer units relative to one another. This interaction 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 H_D^1 . The effects of these two 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 .

A rapid rotation of the sample about an axis inclined at the "angle magic" of $54^\circ 74'$ relative to the Zeeman field direction can remove the residual dipolar interaction [17]. The speed of rotation of the sample must be of the order of the static dipolar interaction to narrow the NMR spectra. Fig. 2 shows the experimental curve and illustrates the evolution of central linewidth as a function of spinning rate Ω_R . 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" (MAS) technique.

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

To show that the correlation time is slower than the spin-spin relaxation time (i.e., there exists a pseudo-solid effect), we use the magic angle spinning technique.

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

$$H_D(t) = \langle H_D \rangle + H'_D(t) \quad (6)$$

- $\langle H_D \rangle$ is proportional to $(3\cos^2\theta - 1)$. It disappears at $\theta = \theta_M = 54^\circ 74'$;
- $H'_D(t)$ depends periodically on time and is responsible for the apparition of side bands.

Different measurements are done on PEO grafted on silica at room temperature for different molecular weight and different grafting ratio. An example of sample rotation line narrowing and apparition of side bands is given in Fig. 2.

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 $2N\Omega_R$ frequencies. We have used in this case the theoretical calculations elaborated in Refs. [22,23]. 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

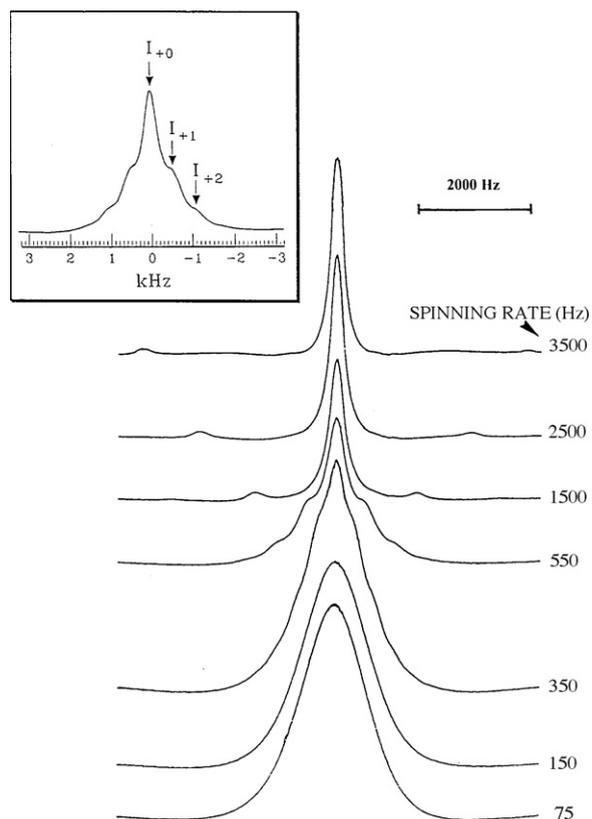


Fig. 2. Proton resonance spectra recorded during sample rotation. Spectra correspond to an increasing spinning rate Ω_R (from 0 to 3500 Hz). PEO2000 grafted on silica. Room temperature.

Insert shows line shape of proton resonance spectrum ($\Omega_R = 550$ Hz). Rotational side bands I_1 and I_2 are clearly evinced. Data obtained from ^1H MAS NMR spectroscopic measurements (300 MHz).

intensities. Rotational side bands I_1 and I_2 are clearly evinced in Fig. 2 (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 report the argument X of I_1/I_0 as a function of Ω_R^{-2} , we note that we obtain a straight line (Fig. 3). The slope of the argument X is proportional to M_2^0 , so we can measure the dipolar residual interaction. Thus, we have obtained a method to follow the evolution of the residual dipolar spin coupling as a function of the molecular weight and of the grafting ratio.

3.3. Study of the side bands: Evolution of the residual dipolar spin coupling

3.3.1. Evolution of the residual dipolar spin coupling as a function of the polymer length

The experiment was 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 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 Fig. 3 that side band amplitudes

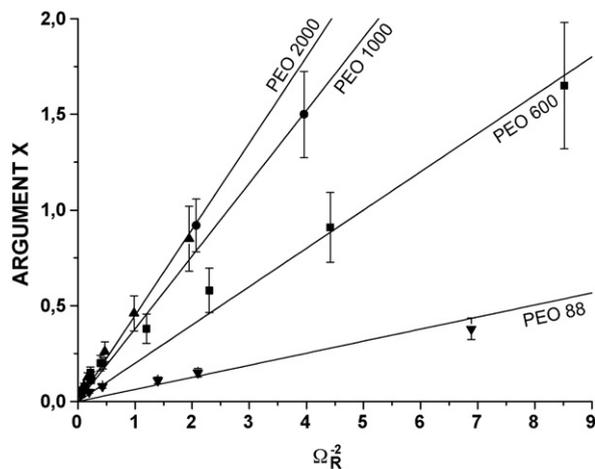


Fig. 3. Study of the ratio of the central to the first sideband intensities as a function of the square of the inverse of the spinning rate, for grafted poly(ethylene oxide) for different molecular weight. The amplitude I_1 of the first side band is compared with the amplitude I_0 of the central line. From ratio I_0/I_1 measured as 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 weight:

(●) $M = 2000$; (▲) $M = 1000$; (■) $M = 600$; (▼) $M = 88$.

dependence upon the spinning frequency Ω_R and the amplitudes of the side bands are described in satisfactory agreement with the results predicted by the theory [23]. From spectra observed at a 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 Fig. 4. The intensity of the dipolar residual interaction characterized by M_2^0 increases with molecular weight. This is an important result because it is the same evolution as the one we had obtained from the ^1H linewidth. It proves that by two independent techniques, we could probe the same phenomena. The second moment as well as the linewidth increase with the molecular weight because the

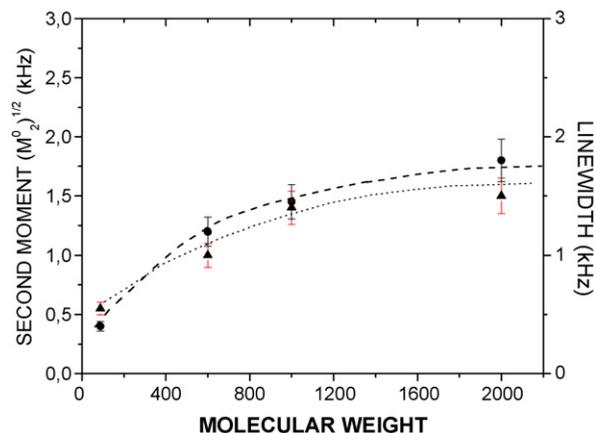


Fig. 4. Evolution of the linewidth (●) and of the residual dipolar interaction characterized by the root second moment M_2^0 (▲) as a function of different molecular weight, for a grafted poly(ethylene oxide). Data obtained from ^1H NMR spectroscopic measurements (300 MHz).

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 [19].

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

The presence of the non-zero average spin coupling in polymers grafted on silica reflects the non-isotropic motion of chain segments. These are not completely free to rotate 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 the molecular weight M .

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

Existence of transition: It was already demonstrated by measurements of relaxation times [12] that there exists a transition situated at about 7 u.m./nm^2 . In Fig. 5, we report the evolution of the ^1H static linewidth and of the spin-lattice relaxation time T_1 as a function of the number of monomer units near surface area.

The spin-lattice relaxation time T_1 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./nm^2 . Let us note that the transition appears on the linewidth and on T_1 for about 7 m.u./nm^2 , which is approximately the value corresponding to one monolayer of segments on the surface. This value 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 bidimensionnal chains are contracting 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

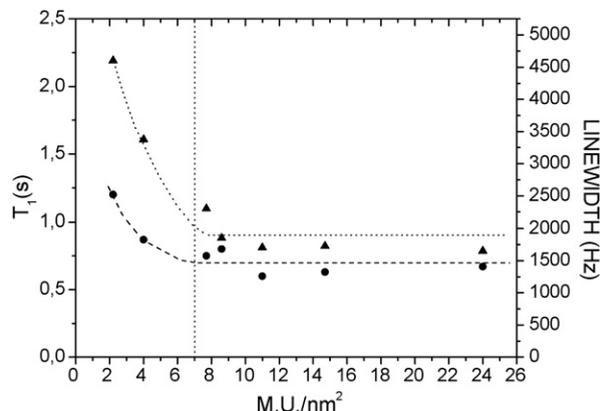


Fig. 5. Evolution of the linewidth (▲) and spin lattice relaxation time (●) as a function of the number of monomer units per nm^2 for grafted poly(ethylene oxide). Data obtained from ^1H NMR spectroscopy (300 MHz).

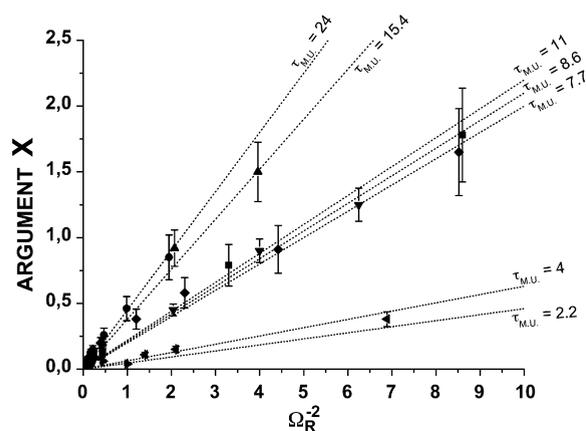


Fig. 6. Study of the ratio of the central to the first sideband intensities as a function of the square of the inverse of the spinning rate, for grafted poly(ethylene oxide) for different number of monomer units per nm^2 . The X is plotted as a function of Ω_R^{-2} for different number of monomer units per nm^2 : (●) $\tau_{\text{m.u.}} = 24$; (▲) $\tau_{\text{m.u.}} = 15.4$; (■) $\tau_{\text{m.u.}} = 11$; (▼) $\tau_{\text{m.u.}} = 8.6$; (◆) $\tau_{\text{m.u.}} = 7.7$; (◄) $\tau_{\text{m.u.}} = 4$; (►) $\tau_{\text{m.u.}} = 2$.

for a coil (the Flory radius $R_F = N^{1/2} \cdot a$, 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 the mobility with the grafting ratio in the first part of the curves (Fig. 5). Above this limiting grafting ratio, the behavior is dominated by a homogeneous layer of polymer in a state reminiscent of the bulk.

The same procedure as previously described is applied to the side bands to determine argument X . Argument X is plotted as a function of Ω_R^{-2} , for different grafting ratio (the number of monomer units per surface area) in Fig. 6. The amplitudes of the side bands are described in satisfactory agreement with the results predicted by the theory. Fig. 7 shows the evolution of the residual dipolar interaction with number of monomer units per surface area for PEO2000 grafted on silica.

The intensity of the dipolar residual interaction characterized by M_2^0 increases with grafting ratio. This evolution is done according to three stages. In fact, below transition at 7 m.u./nm^2 , when M_2^0 seems to be constant, the chains spread out on the surface occupying as much space 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 do not vary any more neither does the local concentration of monomer units. After 7 m.u./nm^2 , M_2^0 increases before it becomes constant in 7 to 14 m.u./nm^2 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 behavior of monomer units adsorbed on a solid. Above 14 m.u./nm^2 , 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 an increase in the residual dipolar interaction.

The difference in the evolutions of the ^1H static linewidth and the second moment below transition at 7 m.u./nm^2 is of a dynamic nature. In fact, since this

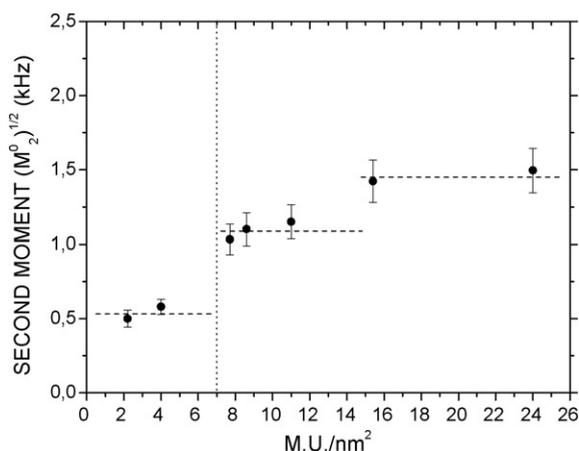


Fig. 7. Evolution of the linewidth (●) and of the residual dipolar interaction characterized by the root second moment M_2^0 (▲) as a function of number of monomer units per nm^2 , for a grafted poly(ethylene oxide).

Data obtained from ^1H NMR spectroscopic measurements (300 MHz).

relaxation time is shown to depend on the grafting ratios (number of m.u./nm^2) this implies that the lateral constraints between chains exists, even for the order of 1 m.u./nm^2 . 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 T_1 increases when the mobility decreases. Above the transition, the grafting ratio does not influence the relaxation functions.

4. Conclusion

The ^1H and ^{13}C NMR permits some approach at a monomer unit scale of the macromolecules grafted on the solid. In the case of poly(ethylene) grafted on silica, the magic angle spinning technique confirms through the narrowing of the central line and apparition of side bands the existence of residual dipolar interaction, which reveals the high monomer units concentration at the surface.

Moreover, the study of the side bands allows us to calculate second moment, which gives in turn an indication of the evolution of the concentration as a function of the length of 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.

The choice of the number of monomer units per nm^2 seems to be the right parameter to account for the variation with the grafting ratio. The analysis of second moment allows the description of the organization of the adsorbed layer.

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