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Solvent and temperature effects on chain conformations in interfaces of polymers grafted on silica. Study by ^{1}H NMR

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Abstract

The ^{1}H NMR technique is used to study the behaviour of the poly(ethylene oxide) chains grafted chemically on silica in presence or not of solvent. A noticeable influence of the different physicochemical parameters on the conformation of the grafted macromolecules is evinced. The grafting ratio, the temperature, the solvent can all in well chosen situations modify the configurations of the chains. The macromolecules can lay flat on the surface, or be swollen and spread out. Depending on the conformations the dipolar interactions between monomer detected by NMR are different and inform on the behaviour of the chains. In particular a static contribution also called pseudo-solid effect is measured, which is an indication of the local concentration of segments in the vicinity of the surface.

Keywords: NMR; Grafted polymer; Interfaces

1. Introduction

In order to modify the interactions between a solid and the surrounding medium one of the way is to graft polymers at the interface. In turn these interactions depend on the conformations and mobilities of the chains. Such interfaces are used in many areas like colloid stabilisation, and chromatography [1], where this interfacial layer controls selectivity. Similar interfaces are also found in composites, for example in rubber reinforcement, where the manufacturing of materials with interesting physical and chemical properties, like tires, implies a good mixing between the filler and the matrix. In this case the polymer at the interface acts as a coupling agent [2].

The fundamental problem to be solved for grafted macromolecules is the configuration adopted by the polymer at the interface. Macromolecules have a very high flexibility and a great number of configurations at the interface is possible. This number increases with the number of segments. Now precisely the equilibrium conformations at the interface control the fundamental aspects of the phenomena [3].

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 [4].

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 [5]. The strong PEO/silica interactions cause the polymer to adopt a flat configuration by spreading on the solid surface [4]. From the dynamic point of view, one can imagine that the diffusion of the monomer units along the axis perpendicular to the surface is more perturbed than the diffusion of monomer parallel to the surface. Thus the grafting of a macromolecule on a solid surface must introduce a significant anisotropy in the segmental motion. On the other hand, it is known that a macromolecule has a complex motion even in solution [4,6]. Indeed only a few data concerning the chains dynamics are available in such heterogeneous systems. Some investigations by deuterium

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(^{2}H) NMR, which is sensitive to the anisotropy of molecular motion were performed [7].

In this paper, we describe the behaviour of PEO with an average molecular weight of 2000 grafted on silica and immersed generally in benzene. From the point of view of NMR, the spectrum of the polymer in solution is a simple line for this high value of molecular weight.

2. Experimental

2.1. Materials and grafting method

Silica: the silica used is pyrogenic Aerosil A300 (from Degussa), prepared by hydrogenation process. This material is not porous and consists of large aggregates of small spheres, from 7 to 12 nm in diameter. Its specific area, measured by gas adsorption is ca. 300 $m^2\ g^{-1}$. This material was selected because it has a high degree of chemical purity and it is not porous.

Polymer: the polymer was PEO 2000 of molecular weight 1880. The oxygen in the backbone makes it very flexible. In NMR it is very convenient because there exist only one chemical shift as well for ^{1}H than for the ^{13}C.

Grafting reaction: this silica is dried, agglomerated in acetone(RP) and brought at 150 °C in an oven. It is then dispersed in a PEO solution to achieve the desired impregnation ratio. The solvent is evaporated in a rotating evaporator under a pressure of 2.10^3 Pa. The powder is again dried and degassed in a vacuum of 0.1 Pa and then kept in nitrogen. For the grafting reaction the vessel was maintained in an oil bath at a temperature fixed at ± 3 °C. The reaction time varied for the chosen temperature between 4 h at 113 °C and 1 h 30 min at 234 °C. This last case corresponds to the highest coverage achieved.

Once the grafting performed the unbounded polymer was removed by a long extraction in a Soxhlet. The grafted silica was first dried in air to remove most of solvent and finally put in a dynamic vacuum of 0.1 Pa during 24 h in an oven kept at 60 °C to avoid the degradation of the polymer. The grafting ratio (Tables 1 and 2) evaluated by elemental analysis or by pyrolisis weight between 25 and 750 °C under oxygen.

Definition of grafting ratio: the grafting ratio τ, is expressed in wt%, is the weight of polymer irreversibly fixed on 100 g of silica. When using a pyrolysis procedure at 800 °C, τ is given by the following formula:

$$\tau_m = \frac{\Delta m}{m_i - \Delta m} 100$$

where m_i is the weight of the initial sample and Δm is the weight loss after pyrolisis. Two extreme cases of grafting ratios were studied, namely 5 and 53%.

Solvent: as a solvent, deuterated benzene or chloroform is used in order not to produce a proton NMR signal and in order to decrease the dipolar interaction between the nuclei of benzene or chloroform and the nuclei of polymer.

Table 1
Various types of grafting ratios for PEO ($M = 2000$) grafted on silica at different temperatures

Grafting temperature (°C)	τ(%)
160	5.1
238	53.4

Table 2
Various types of grafting ratios for PEO samples of different molecular weights grafted on silica

PEO sample	τ(%)
PEO 44	8.5
PEO 88	8.9
PEO 132	14.8
PEO 176	17.6
PEO 600	19.1
PEO 1000	15.4
PEO 2000	19.1

2.2. NMR technique

Experimental measurements were carried out on a Bruker Fourier transform NMR spectrometer operating at 300 MHz. The $\pi/2$ pulse width is less than 1.5 μs which corresponds to a B_1 rotating field of more than 60 Gauss. The dead time of the detection is less than 4 μs.

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

Experiments were carried out over the temperature range 240–360 K, with the latter being controlled by a variable temperature regulator.

This spectrometer was equipped with a 'double bearing' probe head allowing magic-angle spinning (at 54°44′) at rates going from 0 to 4 kHz. Rotation at room temperature is achieved by an air driven turbine in which the rotor itself is supported by gas bearing. Experiences at low temperature were achieved by using cold nitrogen gas as propulsor.

The experimental spectra were fitted with calculated Lorantzian lines, with the program Linefit from Bruker.

Samples:

- *Relaxation times experiment*: the sample were all prepared in Pyrex spheres of 5 mm diameter, which gave greater field homogeneity. First the grafted silica was dried by direct pumping. On the other hand, the solvent, deuterated benzene (C_6D_6), was degassed by repeated freeze-pump-thaw cycles and then added under vacuum to the grafted silica. At saturation, the mixture was sealed in a vacuum of about 1 Pa. A large excess of solvent has been put in contact of the grafted

silica, considering the radius of gyration of the polymer chains. Therefore seen from the surface layer the medium is homogeneous.

– *MAS experiment*: the powder samples (PEO grafted on silica) were placed in alumina cylindrical rotors of 5 mm diameter, volume about 0.3 cm^3 (about 0.15 g), spinning at the magic angle (54°44).

3. Results and discussion

3.1. Measurements of the linewidths and relaxation times

3.1.1. Room temperature studies

3.1.1.1. Influence of the solvent on samples with different grafting ratios. In order to investigate the influence of the solvent on the motions and conformations of the polymer chains on the grafted silica, measurements were carried out for PEO 2000 in presence of two kinds of solvents: deuterated benzene C_6D_6 and chloroform $CDCl_3$. The results obtained for two very different grafting ratios (Table 1), namely a low grafting ratio 5% and a high grafting ratio 53% are shown, respectively, in Figs. 1 and 2. In fact we wanted to stress first the main characteristics of the phenomena without going at once in a deeper analysis, which could be performed only as a second step. Consequently the results are presented qualitatively mostly.

In Fig. 1 the ^{1}H NMR spectra of PEO at low grafting ratio are given. Without solvent the line is very broad due to the steric hindrances to the motion caused by the silica surface on which the chains are strongly held. In presence of solvents motional narrowing occurs and the spectra become

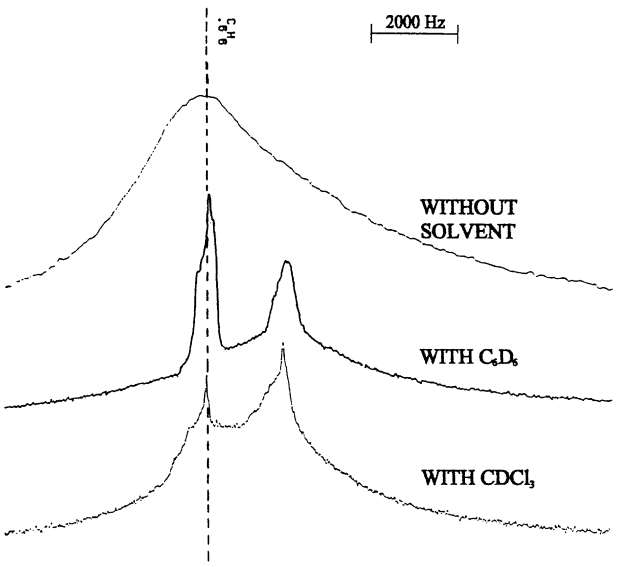

Fig. 1. ^{1}H NMR spectra of PEO 2000 grafted on silica with a low grafting ratio $\tau = 5\%$ at room temperature, (a) without solvent, (b) with solvent: deuterated benzene (C_6D_6), (c) with solvent: deuterated chloroform ($CDCl_3$).

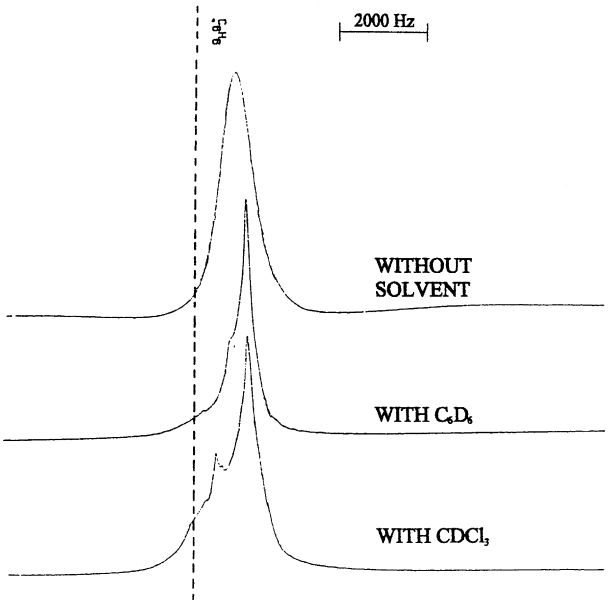

Fig. 2. ^{1}H NMR spectra of PEO 2000 grafted on silica with a high grafting ratio $\tau = 53\%$ at room temperature, (a) without solvent, (b) with solvent: deuterated benzene (C_6D_6), (c) with solvent: deuterated chloroform ($CDCl_3$).

structured with two main lines. The first corresponds to PEO chains, the second to impurities of the solvent. We can notice that the relative intensity of the peak assigned to impurities is very important. This is a consequence of the fact that at low grafting ratio the amount of polymer present is indeed very small and that a large number of accumulations is necessary to obtain a resolved spectrum, and the signal becomes comparable to that of impurities.

In Fig. 2 the ^{1}H NMR spectra of PEO at high grafting ratio are given. The lines are clearly more intense than previously. The trend is reminiscent to what was observed previously: without solvent the line is broader then with solvent. However, there appears also in addition to the now relatively small peak of impurities, a structure inside the peak of the PEO polymer itself. Indeed in Fig. 2 a structure is observed for the main peak: a shoulder appears on the left hand side. As shown previously [8], there are two phases that can be distinguished most clearly by applying the sequence $[\pi-\tau-\pi/2]$ + Fourier transform. A broad line relaxing faster and a narrow line relaxing slower can indeed be observed along the recovery spectra (see Fig. 3). The explanation is to distinguish inside the grafted layer two environments: loops and tails with a relatively fast motion and a narrow line and trains adsorbed on the surface with a hindered motion and a broader line.

3.1.1.2. Discussion. Without solvent and particularly at low grafting ratio the grafted layer is strongly held by hydrogen bonding to the highly attractive surface, and the chains adopt a rather flat conformation. The rate of motion could be relatively similar to what is observed in the bulk glassy state with an additional anisotropy [4,9]. When solvent is added

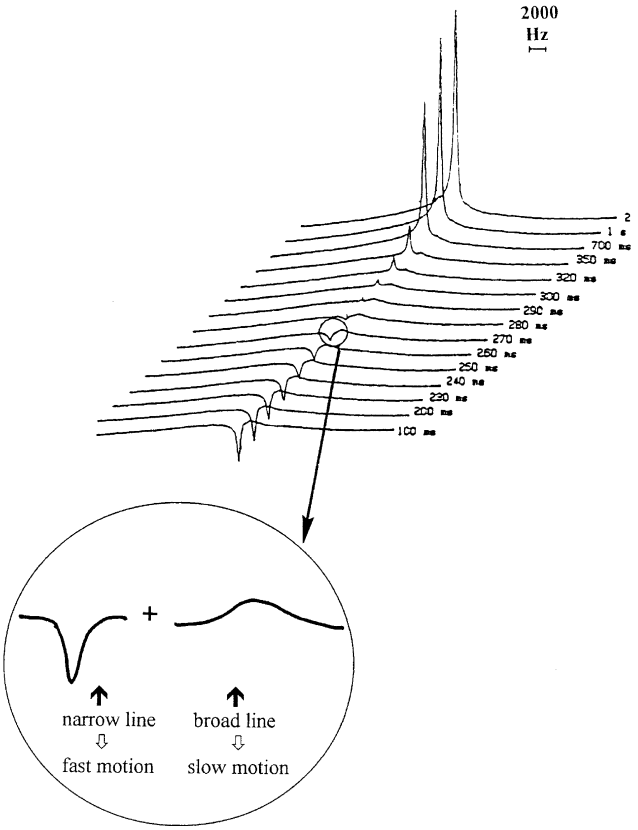

Fig. 3. ^{1}H NMR at 300 MHz observed with a pulse sequence $(\pi-\tau-\pi/2)_n$ + Fourier Transform. n is the number of accumulations. The sample is PEO 2000 grafted on silica with a high grafting ratio at room temperature.

in all cases a narrowing of the line is observed. The chains are more or less swollen by the solvents depending on their affinity for the polymer. They interact with each other, repel each other and protrude into solution increasing the signal of the mobile phase. Moreover, there is now a competition between polymer and solvent for surface sites, which remove some segments from the close vicinity with the silica. Particularly in the case of the high grafting ratio the presence of solvent permit clearly to distinguish now two phases, one rather mobile, which we associate with segments far from the surface, the other less mobile, associated with segments near the surface [8]. In the presence of solvents, or when the grafting ratio increases the chains spread out and adopt a more extended configuration. The average distance from the surface increases and due to the highly anisotropic medium the rates of motion are very different parallel and perpendicular to the surface [4]. The overall picture that thus emerges from the data can be illustrated by the schematic representations given in Figs. 4 and 5. These figures are also in agreement with the models of mushrooms and brushes proposed by de Gennes in different contexts [9,10]. An additional effect, which should be taken into account to explain the motional narrowing, is the rotation of the silica beads themselves, relatively more or less important depending of the frequency of the

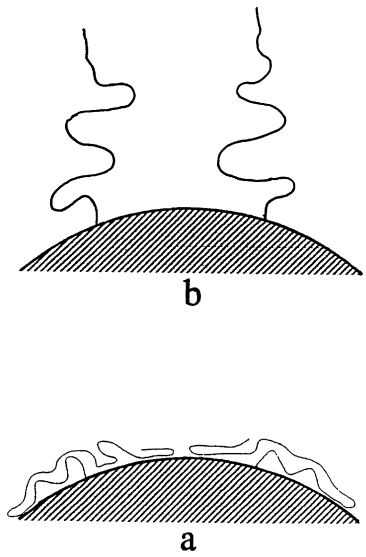

Fig. 4. Schematic representation of the surface layer for a low grafting ratio (a) without solvent; (b) with solvent.

measurements. This motion could simply be added to the segmental mobility of the chains. In the case of a high grafting ratio this effect should be smaller resulting from the massive presence of chains which cover the support surface.

3.1.1.3. Effect of the solvent on the motion of polymers with different lengths. The relaxation times T_1 and T_2 were recorded for different samples of PEO grafted on silica, at room temperature, and with the molecular weights of the chains varying in the range 44–2000 g. The values of the grafting ratios are listed in Table 2. The results for the spin–lattice relaxation time T_1, and for the linewidth as a function

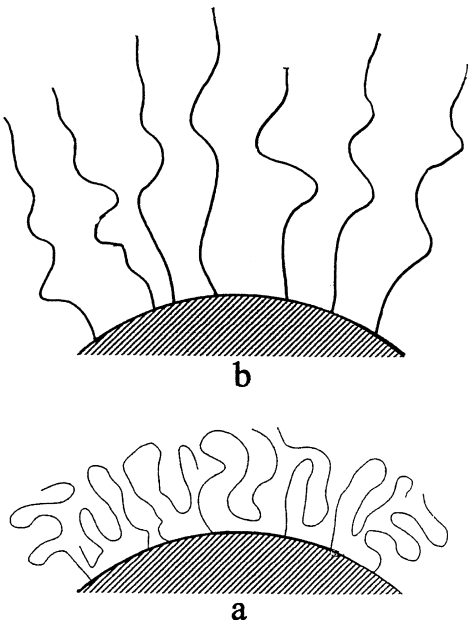

Fig. 5. Schematic representation of the surface layer for a high grafting ratio (a) without solvent; (b) with solvent.

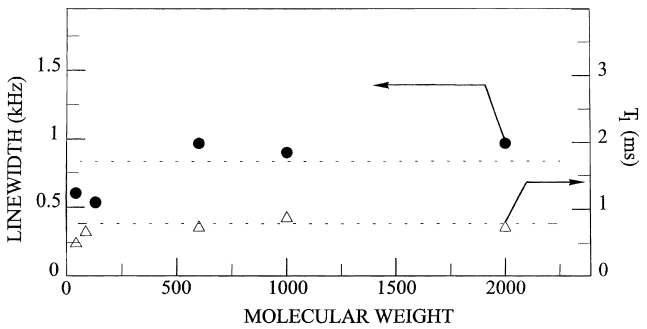

Fig. 6. Evolution of the linewidth (●) and the spin–lattice relaxation time (△) as a function of the molecular weight for different grafted poly(ethylene oxide). Data obtained from ^{1}H NMR spectroscopy at 300 MHz.

of molecular weight are shown in Fig. 6. The experimental spectra were fitted with calculated Lorantzian lines, with the program Linefit from Bruker.

Both parameters are completely independent of the molecular weight in the range studied. It is known from the theory of the relaxation that both relaxation times T_1 and T_2 are not sensitive completely to the same frequencies appearing in the spectral density. The spin–lattice relaxation time T_1 is only sensitive to motions whose characteristic frequencies are of the order of the Larmor frequency. On the other hand the linewidth (i.e. also the spin–spin relaxation time T_2) should also been sensitive to the processes associated with slow motion. A complete analysis would require a modification of the investigation frequency and also a comparison with the spin–spin relaxation time more sensitive to the slow motion of large portions of the chains. Our purpose was more limited here: it was only to observe if at a given molecular weight and with or without solvent there is indeed a detectable variation. Varying the chain length is a relatively natural way of probing the influence of short and long modes of molecular motion on the overall dynamical properties of the system as seen by the relaxation times. The spin–lattice relaxation time is mainly sensitive to the segmental motion associated with a short portion of the chains. In our system there is clearly no evolution at this length scale from one sample to the other. The fact that the same is true for the line width can be retraced to the presence of the solvent C_6D_6, which swells enough the layer to render the influence of the slow motion negligible.

3.1.2. Influence of the temperature

In order to investigate the influence of the temperature on the motions and conformations of the polymer chains on the grafted silica, measurements were carried out for PEO 2000 in presence of deuterated benzene C_6D_6. The results obtained for two very different grafting ratios, namely a high grafting ratio 53% and a low grafting ratio 5% are shown, respectively, in Figs. 7 and 8.

In Fig. 7, at high grafting ratio and at low temperature the NMR spectrum presents a simple, relatively broad line. For polymers in a thin surface layer this temperature appears shifted in one or the other direction. In any case the slow motion expected in this region would give rise to such a broad line. When the temperature increases the progressive narrowing of the lines is apparent, the structure of the line begins to appear more and more clearly, the higher the temperature. The motion involves longer portions of the chains and each nucleus pertaining to a more extended loop experiences a faster rotation. Simultaneously the adsorption energy of the segments towards silica is balanced by a greater thermal agitation which tends to extend the conformations of the chains into solution.

In Fig. 8, at low grafting ratio the general trend is similar to what was described before. As the chains are particularly dispersed now, the cooperative effects due to interactions between segments are less important. The spectra are always structured and the peak due to impurities can always be clearly distinguished. The apparent relative intensities vary because at constant surface the line width changes with temperature a phenomenon more marked for a macromolecule like PEO than for a small solvent molecule.

3.1.2.1. Discussion. At low temperature the solvent is frozen. (The freezing temperature of pure benzene is 279 K). Several phenomena can be expected in this region.

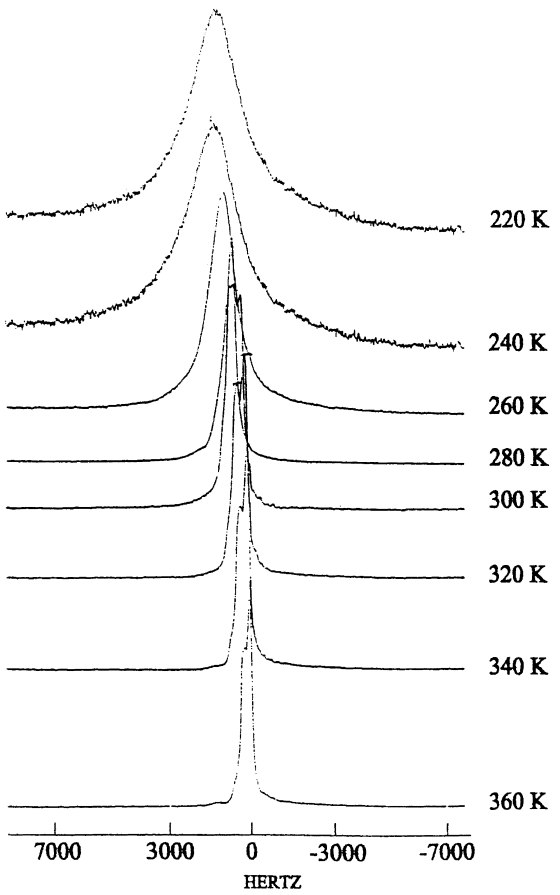

Fig. 7. ^{1}H NMR spectra of PEO 2000 grafted on silica with a high grafting ratio $\tau = 53\%$ at different temperatures. (Temperature range: 220–360 K).

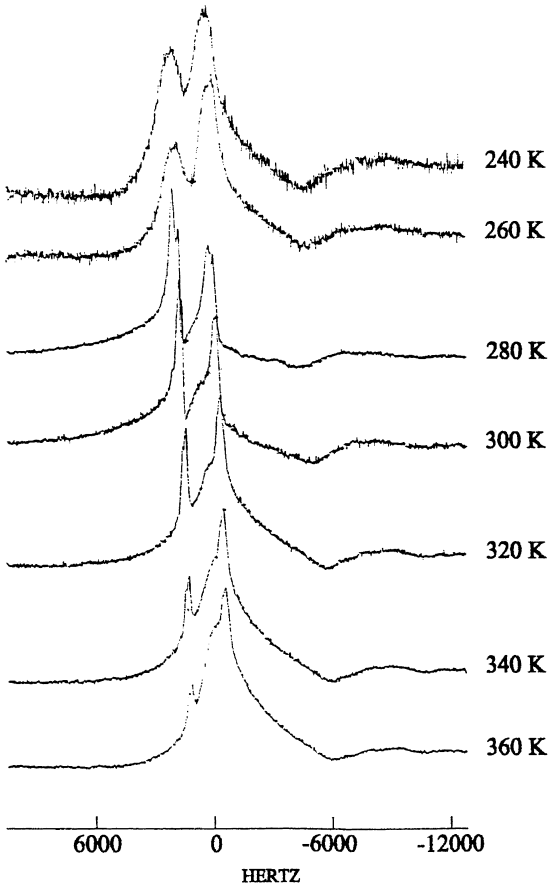

Fig. 8. ^{1}H NMR spectra of PEO 2000 grafted on silica with a low grafting ratio $\tau = 5\%$ at different temperatures. (Temperature range: 240–360 K).

The matrix made up by the crystallised solvent is not so strongly bonded in the vicinity of the surface. Some segregation may occur and the solvent could be partially expelled from the polymer layer. The net effect is that the motions of the polymer chains are hindered from both sides as well by silica than by benzene. When raising the temperature these constraints are progressively relaxed and in the contrary the solvent becomes now able to swell the polymer and to enhance the motion of the segments. When the line width becomes small enough the structure becomes apparent, and it becomes possible to distinguish the two phases. The effect of raising the temperature seems at the end, to lead to a result, similar to that obtained at room temperature by magic angle spinning, as it is shown in Section 3.1.2.2

3.1.2.2. Evidence for a transition temperature. The temperature dependence of the linewidth was recorded for PEO 2000 with solvent (deuterated benzene) at two grafting ratios: a low grafting ratio (5%) and a high grafting ratio (53%). The results obtained are reported in Fig. 9. The qualitative behaviour is the same for both samples. There is a high and a low temperature region where the line width does not change significantly. Very naturally at high temperature the line width is smaller, associated with relatively faster motion, whereas at lower temperature the line is broader probably due to a slower motion. Between 270 and 300 K there is a relatively broad transition connecting the two regions. Such a variation has already been observed previously in the case of PEO without solvent [4]. The characteristics of the transition differ for both samples. The intensity of the jump of line width is more important for the higher grafting ratio, and this was not the case for dry PEO. Now the vitreous transition of bulk PEO is normally observed at 210 K. The broad transition shown here is reminiscent of this situation. However, the system is different here. There is a solid surface in the vicinity of the polymer and the surrounding medium is a solvent. The overall picture that emerges therefore is that of polymers strongly adsorbed on silica, forming a relatively dense layer with little solvent inside, which exhibit a variation of the dynamical parameters of the motion, similar to a vitreous transition but shifted towards the higher temperatures due to the hindrances to segmental tumbling brought by the solid. This transition is more marked at high grafting ratio, when there is enough polymer to build up a relatively homogeneous layer.

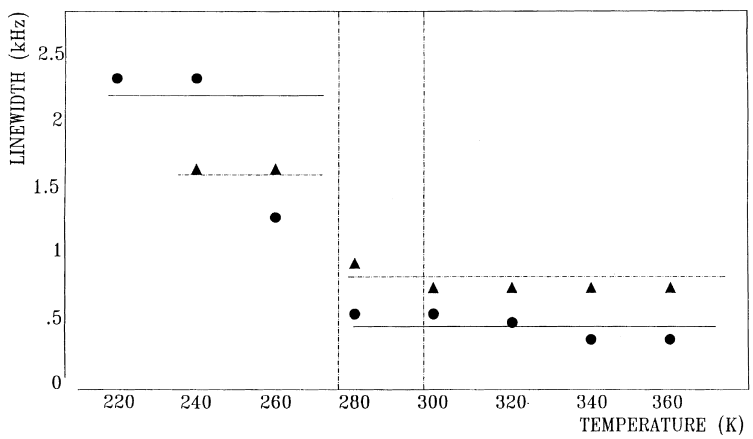

Fig. 9. Evolution of the linewidth as a function of temperature for poly(ethylene oxide) ($M = 2000$) at different grafting ratios: (▲) 5%, (●) 53%. Data obtained from ^{1}H NMR spectroscopy (300 MHz).

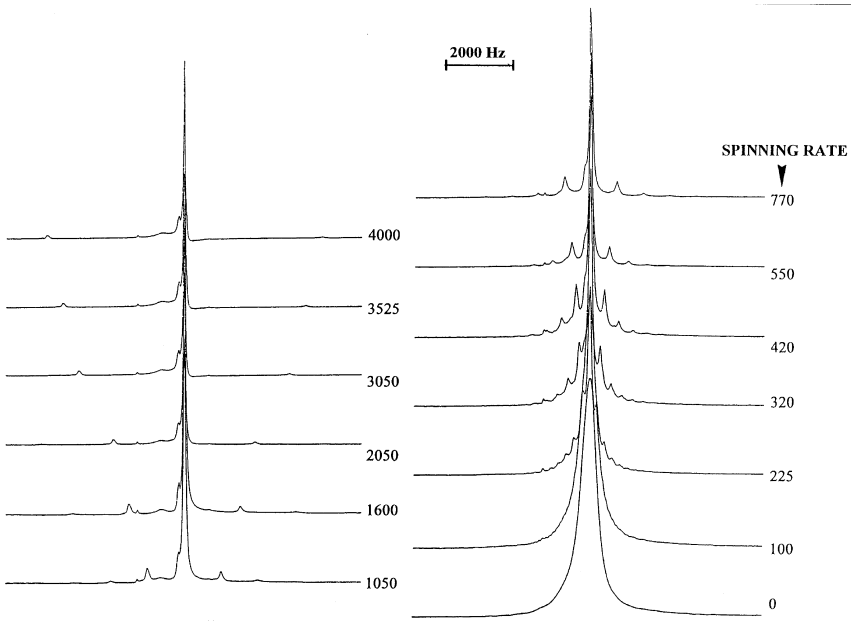

Fig. 10. ^{1}H MAS NMR spectra recorded during rotation of the sample. The spectra correspond to an increasing spinning rate Ω_R (from 0 to 3500 Hz). PEO 2000 is grafted on silica with a grafting ratio of 53%. The temperature is 340 K. The proton resonance frequency is 300 MHz.

3.2. Pseudo-solid effect

3.2.1. Existence of a residual dipolar interaction

It has already been established by measurements of the spin–spin relaxation time T_2 for similar samples with different molecular weight of the same polymer that there exists a pseudo-solid effect [6,11,13]. 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 there remains a residual dipolar interaction between nuclei of different monomer units, pertaining eventually to segments very far apart in the chemical sequence, that cannot be averaged to zero by the segmental motion. Another way of demonstrating this interaction is provided by magic angle spinning again for PEO with an average molecular weight of 2000 grafted on silica [12]. It was also demonstrated that this pseudo-solid effect increases with the grafting ratio [12,14]. The macromolecules should be flattened on the surface for low grafting

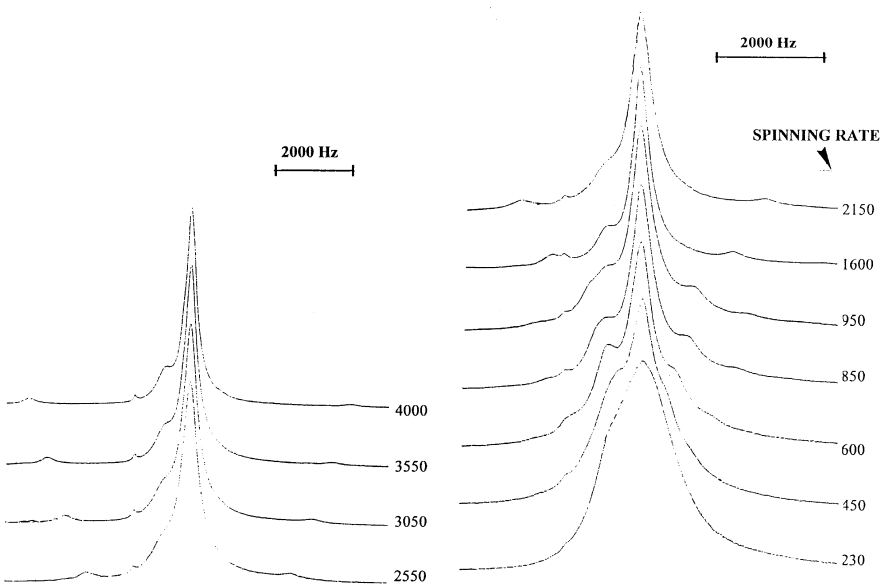

Fig. 11. ^{1}H MAS NMR spectra recorded during rotation of the sample. The spectra correspond to an increasing spinning rate Ω_R (from 0 to 3500 Hz). PEO 2000 is grafted on silica with a grafting ratio of 53%. The temperature is 260 K. The proton resonance frequency is 300 MHz.

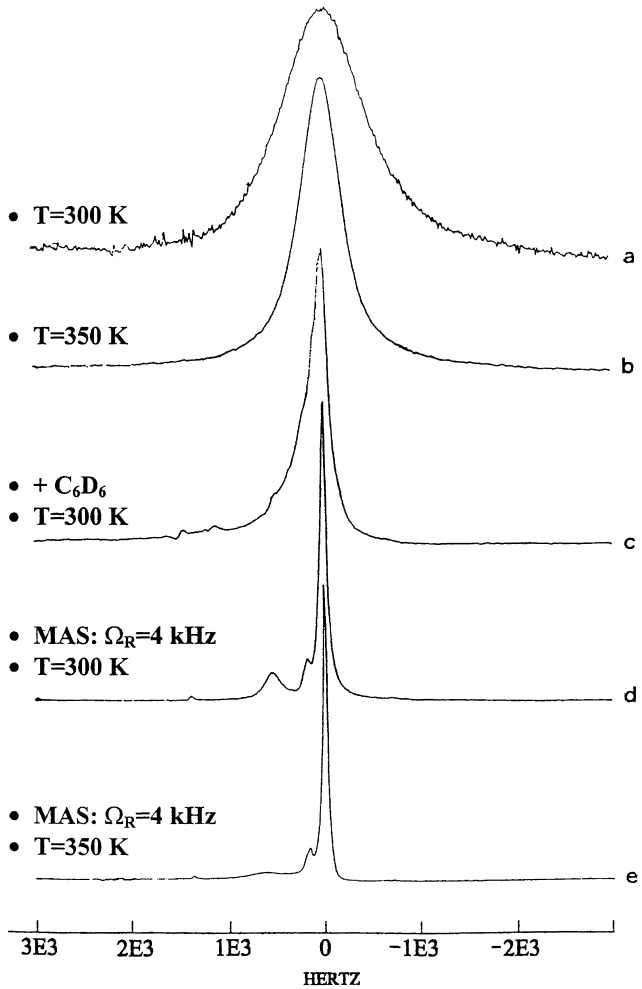

Fig. 12. ^{1}H NMR spectra of PEO 2000 grafted on silica: (a) Proton resonance spectrum recorded at a temperature of 300 K; (b) Proton resonance spectrum recorded at a temperature of 350 K; (c) Proton resonance spectrum recorded at a temperature of 300 K when the sample is in contact with benzene (C_6D_6); (d) Proton resonance spectrum recorded during rotation of the sample ($\Omega_R = 4$ kHz) and at a temperature of 300 K; (e) Proton resonance spectrum recorded during rotation of the sample ($\Omega_R = 4$ kHz) and at a temperature of 350 K.

ratios and the probability to have monomer units interacting with each other decreases. Whereas, for high grafting ratios more loop configurations are formed leading to a strong pseudo dipolar interaction. Thus the pseudo-solid effect is used to deduce the intensity of the non-averaged dipolar interaction. It can indeed give an estimate of the local concentration of monomer units [12].

3.2.2. Experimental confirmation of this static effect

Previously the measurements of the line widths have been performed under different conditions. The grafting ratios, the solvents, the temperatures were varied. All these results converge to demonstrate that the line narrowing exists and that in addition to segmental motion there exists a static effect sensitive to the average molecular conformations of the chains. When the grafting ratio increases, when the temperature increases and when a solvent is added a narrowing of the lines is observed. Finally here we show that the rotating of the sample at the magic angle permit equally to obtain a narrowing of the spectra.

In Fig. 10 the proton magnetic resonance spectra recorded during sample rotation at high temperature are shown. In Fig. 11 the same procedure is used for broader lines at low temperature. In each case a marked narrowing is obtained leading eventually to the apparition of a structured spectrum. Now it is well known that NMR spectra of rigid solids can be narrowed by a fast rotation of the sample [15]. Indeed the rotation of solid samples has been widely used to eliminate static interactions and to observe fine structures analogous to those observed in high resolution spectra of liquids. If only segmental motion was present in our samples of grafted polymers, the magic angle spinning would not be able to average the fluctuating interactions resulting from the tumbling of the monomers. There must be present also an interaction called static, which is sensitive to the action of the magic angle spinning. These converging results lead to an overall picture consistent with the presence of an additional dipolar interaction due to the close vicinity of monomers far apart in the chemical sequence but close in space, and which is therefore a measure of the average local concentration of monomers in the grafted layer.

3.3. High resolution in PEO grafted on silica

3.3.1. Study of residual line width

To better characterise the nature of the interactions responsible for the residual line width in NMR spectra of PEO grafted on silica, different averaging methods were used. In Fig. 12 a summary of proton spectra acquired via conventional $\pi/2$ pulse under different conditions such as low and high temperature, in presence of solvent at room temperature and with magic angle spinning is shown. Fig. 12a shows a relatively broad proton spectrum recorded at room temperature. The line becomes narrower at higher temperature as it is illustrated in Fig. 12b. Fig. 12c illustrates a spectrum narrowing effect observed at room temperature on PEO 2000 under addition of a solvent, C_6D_6. The line width is divided by a factor 2.8. The spectrum narrowing effect must be related to the presence of a nonzero average dipolar spin coupling. Fig. 12d shows a spectrum obtained at room temperature and with magic angle spinning (spinning rate 3500 Hz). It indicates that the residual nuclear spin interactions (dipolar, chemical shift and indirect dipolar ('scalar')) are small and may be either dynamic or static in nature. The comparison of the line width in the two spectra (Fig. 12a and d) indicates that about 70% of the broadening in the conventional spectrum must be due to static dipolar interactions (assuming as usual that indirect dipolar interactions may be ignored). The spectrum in Fig. 12d shows the large degree of narrowing achieved by magic angle spinning, and Fig. 12e at higher temperature indicates that the majority of the broadening is of static dipolar nature.

These magic angle spinning spectra illustrates clearly the desirability of averaging dipolar interactions, and this action should not remove the scalar coupling information, which is frequently necessary to characterise the molecular structure of the grafted layer.

4. Conclusion

The PEO grafted on silica presents a specific behaviour, which can be retraced to the heterogeneity of the medium, and in presence of a solvent is in fact due to three bodies interactions, that of chains, solvent and surface. Our results permit to better understand the different kinds of contributions involved. On one hand there exists a narrowing of the lines due to the segmental motion, and it can be monitored by varying the temperature. But a similar effect can also be obtained by adding a convenient solvent. In this case the mobility increases because the viscosity of the solvent is much smaller than that of bulk polymer. Moreover, the chains are swollen, they spread out and adopt a more extended conformation, and the local concentration of monomers decreases. Finally the shape of the spectrum obtained at the end of these variations becomes similar to that obtained by rotation at the magic angle. This latter method permits in turn to better separate the static and the dynamic contributions to the line width. The NMR spectroscopy appears therefore as a valuable tool for the characterisation of the interfaces, and precisely with the most suitable nucleus to be observed, ^{1}H, it is able indeed to give microscopic information on the conformations of the polymer.

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