

polymer papers

Nuclear magnetic resonance relaxation study of the organization of layers of poly(ethylene oxide) chains grafted on silica

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The proton nuclear magnetic resonance (n.m.r.) relaxation times of poly(ethylene oxide) grafted on silica were determined at 300 MHz. The dependence of the temperature and grafting ratio on the relaxation times is discussed qualitatively from a phenomenological point of view. Two models are proposed for the surface layer for the two extreme grafting ratio levels. At a low grafting ratio the chains lie very flat, whereas at a high grafting ratio, the layer is more organized. Data obtained for the proton relaxation time as a function of temperature show the existence of a transition for each grafting ratio used. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Modification of the characteristics of the polymer/solid interface depends essentially on the behaviour of the particular polymer chains (conformation, mobility, etc.). The main practical applications of such systems include chromatography¹, colloid stabilization², adhesion of biocompatible materials³ and the reinforcement of elastomers^{4,5}.

To modify the properties of such surfaces, we can use either the adsorption of a polymer in the presence of a solvent, or the grafting of chains without a solvent being present. The situation for grafted polymers on solid surfaces is similar to that of adsorbed polymers, except that in the former case the amount of polymer on the surface can be greatly increased, when compared to that of adsorbed polymer systems.

One of the fundamental investigations concerning a polymer grafted on to a solid surface is the determination of the disposition of the macromolecules on the surface and their corresponding mobilities. Therefore, the grafting ratio becomes a very significant parameter in the characterization of such systems.

A number of theoretical^{6–10} and experimental¹¹ approaches have been proposed to study the conformation and dynamics of the chains. In particular, ¹H and ¹³C n.m.r. spectroscopy is a powerful and frequently used technique for studying such systems. The spin-lattice relaxation time (T_1), spin-lattice relaxation time in the rotating frame ($T_{1\rho}$), and spin-spin relaxation time (T_2) (¹H and ¹³C linewidths) are sensitive to different kinds of motion. T_1 is sensitive to characteristic motion

frequencies of the order of the Larmor frequency¹², while $T_{1\rho}$ and T_2 are sensitive to the slower motion processes.

In this present paper, we report experimental results that have been obtained for the relaxation times of poly(ethylene oxide) (PEO), with a weight-average molecular weight of 2000, which has been grafted on silica (Aerosil) at different grafting ratios, both at room temperature and at various other temperatures.

PEO is a simple model system, in which all of the CH₂ groups are chemically identical (with the exception of the terminal groups), and the n.m.r. spectrum of the polymer has one simple line. The solid support is silica (Aerosil) with a high degree of chemical purity. The relevant parameters to be considered are the molecular weight (M), grafting ratio (τ) and temperature (T).

EXPERIMENTAL

Materials and grafting methods^{13,14}

The silica used is pyrogenic, Aerosil A300 (from Degussa), prepared by a 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 m²g⁻¹. The molecular weight and polydispersity of the PEO was determined by gel permeation chromatography.

For the grafting reaction, the following procedure was used in each case. The silica was dried, agglomerated with pure acetone and then dried at 150°C. The silica obtained in this way is dispersed in a solution of PEO in order to achieve the required impregnation ratio of physically adsorbed polymer. The solvent is then removed by using a rotary evaporator at 2 × 10³ Pa. The

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powder obtained is dried and then degassed under a vacuum of 0.1 Pa, and stored in a closed container under nitrogen. Finally, the grafting reaction is allowed to take place: the powder is raised to the chosen temperature (ca. 200°C) in an oil bath and the PEO becomes chemically fixed (the precision of the temperature of the oil bath was $\pm 3^\circ\text{C}$). The grafting reaction of the PEO takes place by a direct esterification of the surface silanol groups of the Aerosil by one of the two hydroxyl end groups of the polymer.

After completion of the grafting reaction, the ungrafted polymer is removed by prolonged extraction (20 h) with acetone in a Soxhlet extractor. The grafted silica is first simply dried in air to remove the bulk of the solvent, followed by drying in a vacuum oven at 0.1 Pa for 24 h (at a temperature of 60°C in order to avoid thermal degradation of the polymer).

The grafting ratios (Tables 1 and 2) are determined by measuring the weight loss after pyrolysis at temperatures between 25 and 750°C under a positive pressure of oxygen.

Definition of grafting ratio

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

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

where m_i is the initial weight of the sample and Δm the weight loss after pyrolysis.

The molecular grafting ratio, τ_M , is equal to the number of grafts per unit surface area, and is given by the following:

$$\tau_M = \frac{6 \times 10^{23}\tau}{SM} \quad (2)$$

where S is the specific surface area (m^2g^{-1}) and M the molecular weight of the graft. Finally, the numeral

grafting ratio, τ_{mu} , is defined as the number of monomer units in the grafted polymer per unit surface area, as follows:

$$\tau_{\text{mu}} = \frac{6 \times 10^{23}\tau}{44S}$$

In the case of a polymer grafted on to a solid, a detailed study of Aerosil shows that the parameter which seems to be the most sensitive to variations in the grafting ratio is the number of polymer units grafted per unit surface, defined as n . In fact, the latter varies both with temperature and molecular weight. Figure 1 illustrates the evolution of the grafting ratio n for PEO materials with different molecular weights as a function of time, on an Aerosil support. The grafting ratio increases with the molecular weight and grafting temperature (curves are measured at a temperature of 150°C). We observe that the effect saturates rapidly, with the saturation being independent of the molecular weight. This effect is also observed at other temperatures.

N.m.r. spectroscopy

Experimental measurements of T_1 (¹H) were carried out on a Bruker Fourier transform n.m.r. pulse spectrometer operating at 100 and 300 MHz by using the inversion-recovery pulse sequence ($\pi-\tau-\pi/2$); pulse repetition is 4 s. The pulse delay, $t_{\pi/2}$, is less than 1.5 ms, which corresponds to B_1 of 60 G ($6 \times 10^{-3}T$). The dead time of the detection system was less than 4 μs . $T_{1\rho}$ was measured by the use of a spin-locking (Fourier transform) pulse sequence.

Experiments were carried out over the temperature range from 200 to 380 K, with the latter being controlled and measured by a variable temperature regulator. The samples were all prepared in Pyrex spheres of 5 mm diameter, which gave greater field homogeneity; they were outgassed for 1 day and then sealed under a residual pressure of about 1 Pa.

RESULTS AND DISCUSSION

Room temperature studies

The ¹H and ¹³C n.m.r. spectra all exhibit a single line for different grafting ratios at room temperature. Results obtained for both T_1 and the linewidth as a function of the grafting ratio are shown in Figure 2. Values of the grafting ratios are listed in Table 2 for PEO with a molecular weight of 2000.

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

PEO sample	τ (%)	τ_M	τ_{mu}
PEO 44	8.5	3.9	3.9
PEO 88	8.9	2.0	4.0
PEO 132	14.8	2.2	6.6
PEO 176	17.6	1.9	7.6
PEO 600	19.1	0.57	7.7
PEO 1000	15.4	0.68	15.4
PEO 2000	19.1	0.19	8.6

Table 2 Results obtained for the various types of grafting ratios for PEO ($M = 2000$) grafted on silica at different temperatures

Grafting temperature ($^\circ\text{C}$)	τ (%)	τ_M	τ_{mu}
160	3.3 ± 1.2	0.03	1.3
160	5.1 ± 0.8	0.05	2.2
80	24.5 ± 0.5	0.246	11.0
100	32.5 ± 1.6	0.326	14.7
125	34.7 ± 0.6	0.348	15.6
160	39.6 ± 0.7	0.398	17.9
200	49.0 ± 1.4	0.492	22.1
238	53.4 ± 0.6	0.546	24.0

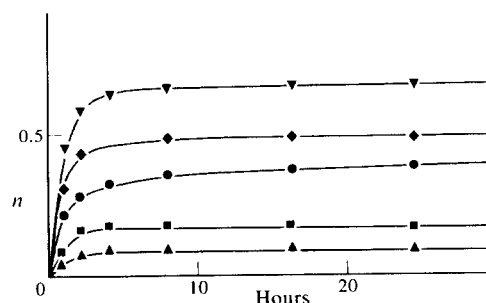


Figure 1 Evolution of the number of polymer units, n , per nm^2 as a function of the reaction time for PEO samples with different molecular weights: (∇) PEO600; (\blacklozenge) PEO1000; (\bullet) PEO2000; (\blacksquare) PEO4000; (\blacktriangle) PEO10000

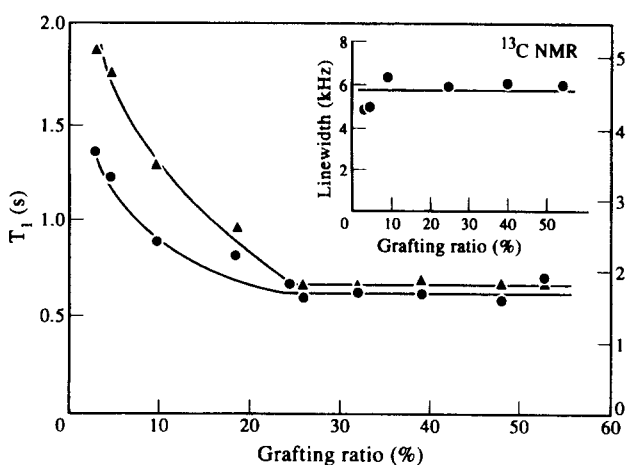


Figure 2 Evolution of the linewidth (●) and the spin-lattice relaxation time (▲) as a function of the grafting ratio for a grafted poly(ethylene oxide) with a molecular weight of 2000, with data obtained from ^1H n.m.r. spectroscopic measurements (300 MHz). Inset shows corresponding results obtained from ^{13}C n.m.r. spectroscopic measurements (75 MHz)

The proton linewidth decreases until a limiting value of the grafting ratio of about 20% is reached. The same dependence is observed for T_1 , which decreases and then eventually becomes independent of the grafting ratio over the same range. The dependence of the ^{13}C n.m.r. linewidth is also presented in Figure 2 (as an inset); this linewidth appears to be independent of the grafting ratio.

It is known that the ^1H n.m.r. linewidth is sensitive to the slow processes¹² of motion of the monomer units (inter-monomer units contribution), and to the local concentration of these monomer units, whereas the ^{13}C n.m.r. linewidth is sensitive to the mobility of the monomer units. The ^{13}C - ^1H n.m.r. interaction is essentially related to the intra-monomer units.

The proton n.m.r. linewidth shows a considerable increase at low levels of the grafting ratio until a value of ca. 20% is reached, which corresponds to the distance separating the two polymers, and is equal to the Flory radius $R_F = N^{1/2}a$, where N is the number of repetition units and a is the length of segment). Each chain occupies roughly an hemisphere with a radius comparable to the Flory radius R_F for a coil¹³.

For a grafting ratio greater than 20%, the grafting ratio appears to have no effect on the macromolecular behaviour.

This effect is not observed in the ^{13}C n.m.r. linewidth measurements. It does not depend on the grafting ratio. This shows that the segment mobility is not sensitive to the density of monomer units, with T_1 only being sensitive¹² to the characteristic motion frequencies of the order of the Larmor frequency (the fast motion processes). It concerns essentially the motions of the local monomer units. The motion is perturbed by the local environment around the monomer units mainly at low grafting ratios. Therefore, the local motions of the monomer units are less sensitive at low grafting ratios than at high levels.

As far as the dynamics of the motions are concerned, the chains are adsorbed on essentially flat surfaces (Aerosil is not microporous, and is considered to be planar at the molecular scale of the polymer). In the case where the coils are separated, the motion thus arises on a

plane parallel to the surface. Above a grafting ratio of 20%, the coils begin to overlap; a modification to the motion arises, in which the motion is both simultaneously parallel and perpendicular to the surface¹⁵.

From these results, two different forms of organization of the grafted layers can be distinguished, which can be described as follows.

Low grafting ratios (or low concentrations). In this case, 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 interactions between the OH^+ groups on the surface and the negative charges 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 not uniformly disposed on the surface, are nevertheless not relatively dispersed; the local concentration in the segments is relatively low and the motion is little influenced by steric effects due to other segments. This second effect is predominant in the evolution of T_1 and T_2 , which become longer at lower grafting ratios.

The density of segments is probably not uniform on the surface. We can assume that the grafted layer is poorly organized, by analogy with various crystalline and amorphous structures¹⁶.

High grafting ratios (or high concentrations). In this case the interfacial layer could be approximated by a step profile⁶: the local density in the segments becomes uniform and no more variations are observed.

From the schematic representation shown in Figure 3, 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, start 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. These two different types of behaviour for the grafted layers have been further confirmed by the results obtained from electron proton resonance spectroscopic measurements^{17,18}.

Influence of temperature

In order to compare the motions and the conformations of the polymer chains grafted on silica at different

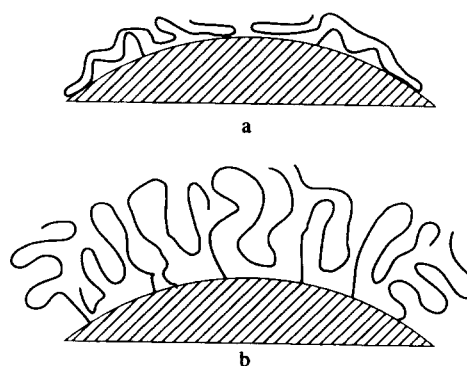


Figure 3 Schematic representations of the surface layer for: (a) low grafting ratios; (b) high grafting ratios

grafting ratios, measurements of the temperature dependence of the relaxation time was carried out for PEO 2000, at three different grafting ratios, namely a low grafting ratio (5%), an intermediate grafting ratio (19%), and a high grafting ratio (53%). The results obtained for the temperature dependence of the linewidth and T_1 for these three grafting ratios are presented, respectively, in Figures 4 and 5.

We observe the same evolution for all of the three grafting ratios, namely both T_1 and the linewidth decrease with increasing temperature. At high temperatures (300–380 K), however, these parameters show no temperature dependence. In addition, we observe a transition situated between 270 and 300 K, which mainly affects the fast processes of motion.

This temperature transition depends on the grafting ratio, and also on T_1 and the linewidth. We can observe that the intensity of the transition jump decreases as the grafting ratio increases. The limiting value of the ^1H n.m.r. linewidth after the transition decreases as the grafting ratio increases, whereas T_1 is independent of the ratio. Finally, for the intermediate grafting ratio (19%), this transition shows an abrupt decrease in the linewidth as a function of temperature.

This transition becomes more important when the grafting ratio is low (5%), while it is very broad for the intermediate grafting ratio (19%). In this latter case, the transition concerns both fast and slow motions (plus very slow motion) as can be observed in Figure 6 where $T_{1\rho}$ displays a jump at the transition temperature.

As far as we are aware, this is the first time that a transition affecting an adsorbed polymer phase has been clearly observed from such measurements.

These results show that the transition has a strong dependence on the grafting ratio. In fact, the spin lattice relaxation time is also very sensitive to the transition.

This transition is observed for all grafting ratios, while the jump is more important for low grafting ratios than for high ratios. It is situated in the 240–340 K range.

The transition is not a vitreous transition of poly(ethylene oxide) because the latter (for free PEO macromolecules) is situated at 210 K. 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.

For temperature lower than the transition temperature, the grafted chains adopt the behaviour already observed at room temperature for levels of low grafting ratio. Above the transition temperature, the behaviour is similar to that observed at room temperature for chains with a high grafting ratio.

Concerning the intermediate grafting ratio of 19% (where each chain occupies roughly a hemisphere with a radius comparable to the Flory radius, R_F , for a coil), the n.m.r. linewidth measurements show that the transition is very broad. We can observe two types of behaviour, which depend both on the temperature and the grafting ratio:

1. at low temperatures (of the temperature range studied here), where the behaviour is identical to that adopted by samples with a low grafting ratio (5%) below the transition temperature;
2. at high temperatures, where the behaviour is identical to that adopted by samples with a high grafting ratio (53%) above the transition temperature.

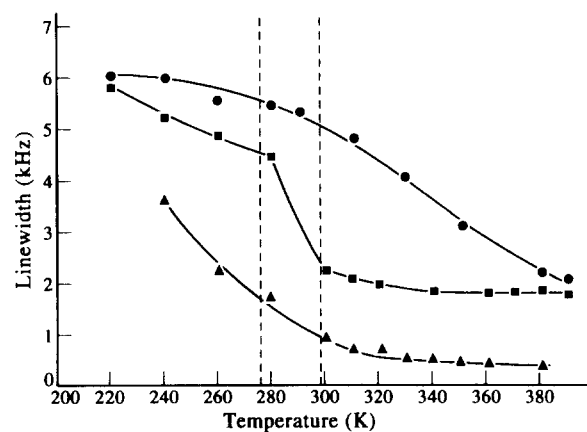


Figure 4 Evolution of the linewidth as a function of temperature for grafted poly(ethylene oxide) ($M = 2000$) at different grafting ratios: (●) 5%; (■) 19%; (▲) 53%. Data obtained from ^1H n.m.r. spectroscopy (300 MHz)

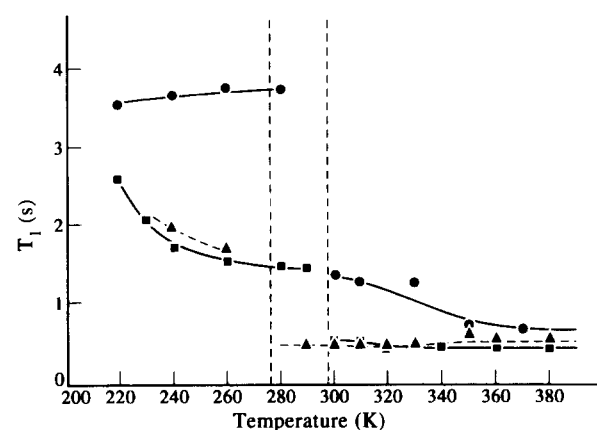


Figure 5 Evolution of the spin-lattice relaxation time as a function of temperature for grafted poly(ethylene oxide) ($M = 2000$) at different grafting ratios: (●) 5%; (■) 19%; (▲) 53%. Data obtained from ^1H n.m.r. spectroscopy (300 MHz)

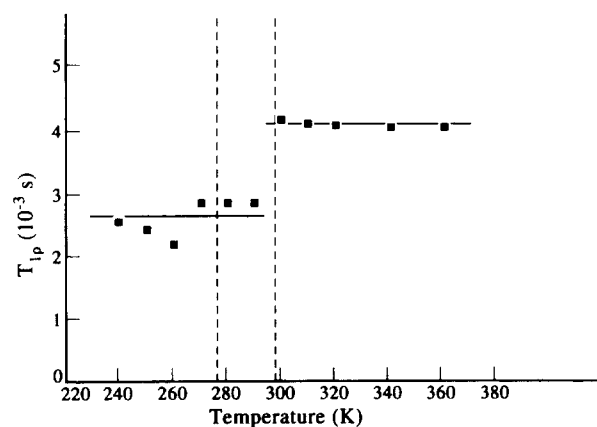


Figure 6 Evolution of the spin-lattice relaxation time in the rotating frame, $T_{1\rho}$, as a function of the temperature for grafted poly(ethylene oxide) ($M = 2000$) at a grafting ratio of 19%. Data obtained from ^1H n.m.r. spectroscopy (300 MHz)

We can explain this situation by considering the influence of the first adsorbed layer of monomer units on the second one. In fact, at low temperatures the second layer of monomer units in contact with the first one is strongly immobilized and adopts the behaviour of monomer units adsorbed on a solid surface. At high

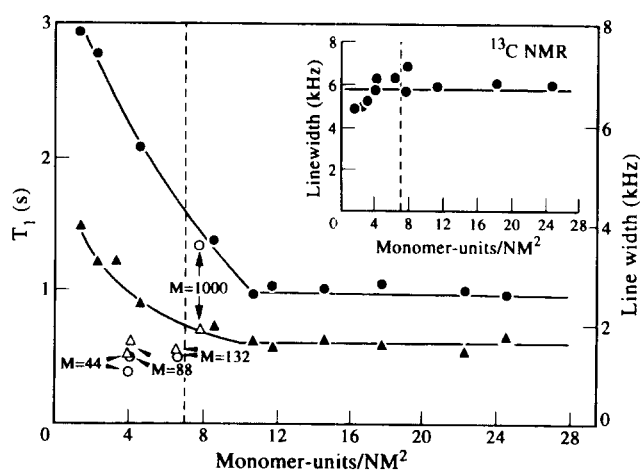


Figure 7 Evolution of the linewidth (●) and spin-lattice relaxation time (▲) as a function of the number of monomer units per nm^2 for a grafted poly(ethylene oxide) ($M = 2000$, with data obtained from ^1H n.m.r. spectroscopic measurements (300 MHz). Inset shows corresponding results for the evolution of the linewidth obtained from ^{13}C n.m.r. spectroscopic measurements (75 MHz)

temperatures, however, the monomer units are adsorbed less on the surface and are more free to move. Therefore, the chains are swollen.

In the system of polymer grafted on a solid surface, the parameter which seems to be the more sensitive to the variation of the grafting ratio is the number of monomer units per surface area, since this depends both on grafting ratio and molecular weight.

In *Figure 7*, we report the evolution of the linewidth and of T_1 as a function of the number of monomer units per surface area (see *Tables 1* and *2*). Let us note that the transition appears on the linewidth of 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 calculated¹¹, and it corresponds to the limit grafting ratio (τ_1) equal to 13% for our studied silica. The limit grafting ratio corresponds to the maximum grafting ratio for no overlapping of the chains on the surface.

For the low concentration of monomer units on the surface, we must distinguish the case of oligomer and polymer. For the oligomer, the motion of the segments does not depend on the concentration and is very free (narrow line), whereas for the polymer it is restricted when the concentration decreases. We can deduce from this observation that when grafted polymers are separated on the surface, the segments move freely and try to occupy all of the surface. It is certainly due to the fact that the surface of silica is very attractive for the monomer units, so, as it does not exist for lateral constraints, the motion of the segments is really parallel to the surface.

Otherwise, even for a low grafted ratio, the chains can be observed to interact with each other since the linewidth continues to depend on the grafting ratio. We cannot assume that the chains are isolated relatively to each other.

Since the surface is very attractive, the chain spreads out on the silica and occupies a maximum of surface

area. At the same time, it is stretching itself. Consequently, its motion becomes very slow.

When the grafting ratio increases, the mobility becomes larger. Above 7 monomer units nm^{-2} , where the thickness of the adsorbed layer becomes greater than a monolayer of monomer units, the concentration becomes very large and leads to the formation of loops. This engenders the residual dipolar interaction already pointed out by echo solid and MAS techniques^{12,18}.

CONCLUSION

The behaviour of grafted chains of poly(ethylene oxide) grafted on silica has been studied by n.m.r. relaxation. The analysis of relaxation time allows one to describe the organization of the grafted layer. At low grafting ratio, the chains lie very flat, whereas, at high grafting ratio, the layer is more organized. The measurements show that the transition depends considerably on the grafting ratio. This transition is of a dynamical nature. It is due to the modification of motion of monomer units. The transition is observed for every grafting ratio. Finally, the choice of the number of monomer units nm^{-2} seems to be the right parameter to account for the variation of grafting ratio and molecular weight.

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