Dynamics of adsorption of poly(ethylene oxide) on a silica surface modified by grafting

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Electron spin resonance spectroscopy of spin-labelled poly(ethylene oxide) terminally anchored on silica and in contact with solutions of poly(ethylene oxide) in different concentrations in benzene has been used to detect indirectly the adsorption process. The nitroxide free radical was 2,2,5,5-tetramethyl-3-pyrroline-1-oxyl-3-carboxylic acid. The ratios of the population of free end segments in solution to that of adsorbed segments on silica as a function of temperature have been evaluated. The conformations of the chains depend upon the concentration of polymer in solution, on their molecular weight and on the grafting ratio already achieved on the surface. The number of molecules that can be accommodated reaches a limiting value. The time involved in the reorganization of the surface layer has been evaluated to amount to several weeks.

(Keywords: poly(ethylene oxide); dynamics; adsorption; electron spin resonance spectroscopy; interfaces)

INTRODUCTION

Polymers at interfaces, physically adsorbed as well as chemically grafted, play an important role in colloid protection, adhesion, paintings, coatings and chromatography. A large body of knowledge is now available mostly on the static properties, for example the average conformations of the chains or the concentration profile. More recently the kinetics of the establishment of adsorption equilibrium and the relaxation of the surface layer has attracted much attention[1-4].

Indeed the first approaches dealt with saturated rather thin and fully relaxed layers[5-9]. For adsorbed polymers the concentration profile was predicted and experimentally demonstrated to be self-similar[10]. For a grafted brush[11-13] the analytical calculations predict a somewhat smoother than step-wise profile, in fact a parabolic one[14]. Here we consider a combination of both situations, which is of interest in the understanding of the mechanism of grafting[15,16]. It is known that a chemically modified surface[17] can also be a repulsive wall and a depletion layer then forms in the vicinity of the solid[18,19]. Therefore an interesting point is to investigate how a polymer chain in the surrounding solution moves inside a diffuse layer of the same polymer already terminally anchored on silica. Some experimental[20-22] and theoretical[23] models on similar but not identical situations have been proposed. Probably the specific feature here is that some of the chains have a fixed end at a definite point of the surface, which greatly restricts the mobility.

We have chosen a model problem: the adsorption of poly(ethylene oxide) in solution in benzene on a surface of silica covered with grafted chains of the same poly(ethylene oxide). The chemical nature of the macromolecule leads to its great flexibility, which is easily observed[24]. The experimental method is the spin-labelling of the free end of the grafted chains. The e.s.r. spectrum of the nitroxide label, which is very sensitive to motion[25,26], gives an indication of the conformation, flat or extended, of the grafted chain and indirectly of the whole process of adsorption[27].

EXPERIMENTAL

Materials

Silica. The silica used was pyrogenic silica[28] obtained in a flame by combustion of $SiCl_4$ (Degussa, Frankfurt am Main, Germany). Aerosil 300 has a specific surface area measured by nitrogen adsorption of about 310 $m^2 g^{-1}$. It is indeed formed of aggregates of small spheres, which are fractal, but at the characteristic length of the macromolecular chains, the radius of gyration, it is reasonably planar.

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Polymer. The polymer was poly(ethylene oxide) (PEO) 2000 of molecular weight 1880, i.e. with about 43 monomer units (Fluka Chemie AG, Buchs, Switzerland). The polydispersity of this PEO was 1.09. This polymer, which was grafted on silica, is the same as that used previously[29]. When additional PEO was physically adsorbed on the modified surfaces, PEO 2000 and PEO 6000 (Merck, Hohenbrunn bei München, Germany) of molecular weight 1900 and 6000 respectively were used.

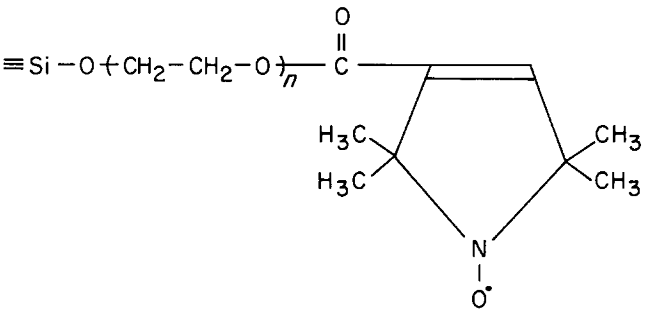
Grafting reaction

The grafting reaction was simply the direct esterification of a surface $\equiv$SiOH group, which is naturally abundantly present on silica, by one of the two hydroxyl ends of a macromolecule. The latter has about 1.6 OH groups at the free ends. The reaction was performed in the polymer melt under a nitrogen atmosphere at high temperature (200°C) for 1 h. Chains that have been attached to the surface through both ends are included in the estimation of the grafting ratio, and will also influence the conformations in the layer, but will not be detected directly by e.s.r. The probability of this event is expected to be small, according to the results obtained in the case of, for example, long chains of α,ω-diols.

The silica was thus first dehydrated[15,29], agglomerated with reagent pure acetone and heat dried at 150°C. Then, it was dispersed in a PEO solution to achieve the desired impregnation ratio of physically more or less strongly adsorbed polymer. The solvent was evaporated with a rotating evaporator at 2×10^{-3} Pa and stored in a container filled with nitrogen gas. For the grafting reaction itself the impregnated powder was held at the chosen temperature (the oil bath was controlled to within ±3°C). Once the grafting reaction was achieved, the ungrafted polymer was removed by extraction with acetone in a Soxhlet for 20 h. Finally the grafted silica was dried in air and then placed in a dynamic vacuum of 0.1 Pa for 24 h at 60°C. The grafting ratio determined by pyrolysis weight loss between 25 and 750°C under oxygen was found to be 0.045 molecules/nm^2, a situation where the inter-chain interaction should not be too strong. A second sample with a grafting ratio of 0.45 molecules/nm^2 was also prepared.

Spin-labelling

One per cent of these grafted chains were then spin-labelled at their free end. The free radical 2,2,5,5-tetramethyl-3-pyrroline-1-oxyl-3-carboxylic acid was purchased from Eastman (Eastman Organic Chemical, Rochester, New York, USA). This label in its acid chloride form was attached to the grafted chains. For 700 mg of silica, 2 cm^3 of a solution of 10 mg of label in 7 cm^3 are necessary. The 2 cm^3 of solution are introduced in a container of 50 cm^3 connected to a vacuum pump. About 5 cm^3 of toluene and then 2 cm^3 of $SOCl_2$ are added by cryodistillation. After a contact time of half an hour these solvents are evaporated by distillation. Then 7 cm^3 of toluene are added to the yellow solid by cryodistillation. At the same time the silica is dehydrated in a vacuum and dispersed in 5 cm^3 of toluene and 1 cm^3 of pyridine, which are cryodistilled. Finally 0.7 cm^3 of the yellow solution of the label in its acid chloride form are extracted under a dry nitrogen atmosphere and added to the silica. The mixture is shaken for half an hour and the solvent is distilled again under vacuum. The silica is washed with acetone and extracted for one night in a Soxhlet with the same solvent. A typical chemical formula of a grafted labelled polymer chain on silica is:



Samples

All the samples were prepared in Pyrex tube of 4 mm diameter. As a solvent we have chosen benzene even if there are some safety problems connected with its use, because there are already some data available on it[29] and the necessary amount of liquid is very small. First the grafted silica was dehydrated by direct pumping for 2 days and the remaining solvents from the preceding reactions were removed. A solution containing benzene and different amounts of PEO 2000 or PEO 6000 was then added. The whole sample was degassed by repeated freeze–pump–thaw cycles and sealed in a vacuum of 1 Pa.

The grafting ratio of the powder used is, as previously mentioned, 0.045 molecules/nm^2, or expressed in another equivalent way there are two repeat units per square nanometre (2 r.u./nm^2). We have denoted by n_a the number of repeat units per square nanometre pertaining to the added PEO. Of course, all of these added chains are not necessarily adsorbed on the silica surface. The value of this parameter is adjusted for each sample by weighing the amount of grafted powder (13 mg) and adding 0.2 cm^3 of a solution of PEO in benzene at different concentrations. Thus for example 2, 4, 6, 10, 50, 125 and 500 mg of PEO 2000 were added to 1 cm^3 of benzene. The values of the different n_a parameters are therefore: for PEO 2000, $n_a = 0$, 2.8, 5.7, 8.6, 14.3, 70, 168, 700 r.u./nm^2; for PEO 6000, $n_a = 2.8$, 5.7, 7.1, 14.3 r.u./nm^2. The coverage by a monolayer of repeat units corresponds to 6 r.u./nm^2, if the length of a segment is taken to be 2.9 Å. The solutions range from dilute to semi-dilute to highly concentrated.

The experimental study of the samples was then performed at temperatures well below 60°C in the presence of the relatively good solvent, which tends to swell the chains, and these conditions are very unfavourable for the grafting reaction to take place. It is therefore expected that there are no further modifications of the covalent bond in this state; the nature of the chains, grafted or physically adsorbed, remains the same and only the conformations of the chains, flat or extended, varies.

Analysis of the e.s.r. spectra

The e.s.r. spectra were recorded on a Varian (Varian, Palo Alto, USA) E-4 spectrometer operating at X-band at 9.15 GHz. The temperature was regulated by a Varian E-257 temperature controller within ±1°C. Each time,

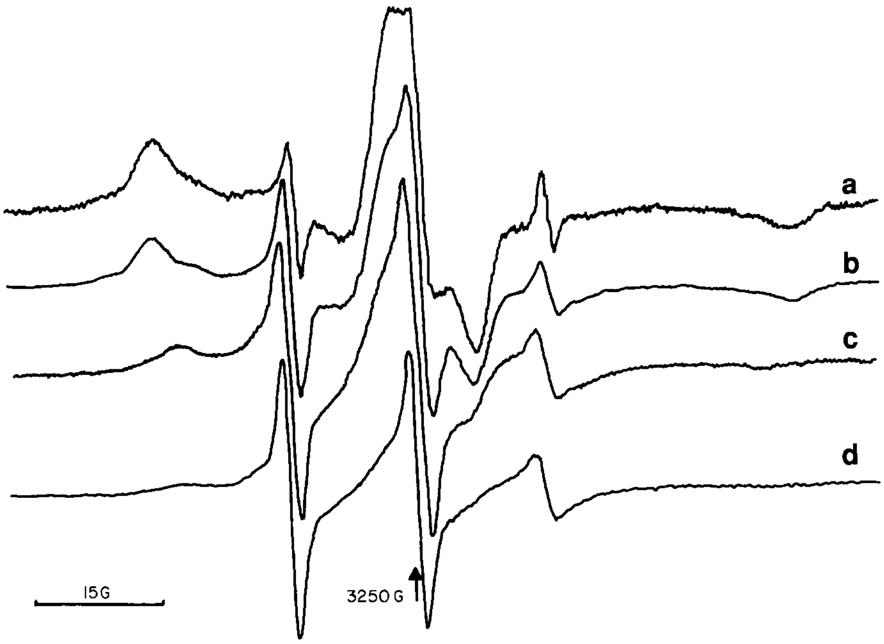


Figure 1 Typical e.s.r. spectra of spin-labelled poly(ethylene oxide) 2000 grafted on silica in contact with PEO 2000 in solution in benzene at different concentrations: (a) at 0°C, $n_a = 2.8$ r.u./nm^2; (b) at 0°C, $n_a = 5.7$ r.u./nm^2; (c) at -15°C, $n_a = 8.6$ r.u./nm^2; (d) at -15°C, $n_a = 14.3$ r.u./nm^2

10 min were allowed for thermal equilibration of the sample.

Our method of analysis of the e.s.r. spectra has been extensively described previously[29]. It is well known that the fast motion spectrum of nitroxide spin labels consists of three completely resolved Lorentzian lines, whereas in the slow tumbling region the spectrum has a very different shape influenced by the anisotropic part of the spin Hamiltonian[25,26]. As the temperature of the samples is raised, the slow motion spectrum disappears gradually and is replaced by three narrow lines. In the intermediate range the spectrum of grafted polymers appears as a superposition of the two shapes described above[27,29]. The signals arising from the two different environments, namely labels in contact with the surface and labels attached to tails protruding into the solution, are well defined and separated. The fast motion spectrum can be calculated theoretically on an Apple IIE computer (Apple Computer Inc., Cupertino, California, USA) and adjusted to the high- and low-field lines of the experimental spectrum. Therefore after integration the fraction of labels in solution can be evaluated exactly. The important parameter extracted from the spectra at different temperatures is put in the form of the ratio of the population of labels in solution over that of labels adsorbed on the surface.

RESULTS

Evidence for adsorption of polymers on a modified surface

The gyromagnetic tensor g and the hyperfine tensor A, which appear in the spin Hamiltonian[25,26], have been evaluated using as reference the spectra of the label at room temperature and at the temperature of liquid nitrogen in X-band and Q-band spectroscopy. The best fit was found for $g_{xx} = 2.0088$, $g_{yy} = 2.0058$, $g_{zz} = 2.0022$, $A_{xx} = 5.3$, $A_{yy} = 4.6$, $A_{zz} = 33.55$.

Typical e.s.r. spectra of labelled PEO grafted on silica in contact with different solutions of various concentrations are given in *Figure 1*. The composite spectra are even observed at different temperatures depending on the amount of physically adsorbed polymer. The higher the concentration of polymer in solution, the larger is the relative proportion of labels with fast motion, or the lower is the temperature at which the same shape is observed for the spectrum.

To put this qualitative observation on a more quantitative basis, the ratio of the population of labels desorbed in solution to that of labels adsorbed on the silica surface was evaluated and plotted as a function of the inverse of the absolute temperature in *Figure 2*. This ratio follows a Van't Hoff type of expression:

$$-\Delta G = kT \ln(P_{\mathrm{sol}}/P_{\mathrm{ads}})$$

or

$$\ln(P_{\mathrm{sol}}/P_{\mathrm{ads}}) = -\Delta H/kT + \Delta S/k$$

ΔH can be interpreted as the adsorption enthalpy of a monomer unit, whereas the entropic term ΔS is related to the loss of degrees of freedom between the state where the label is free to move in solution and the state where it is adsorbed. The experimental values of ΔH and ΔS, without taking into account the specific adsorption of the label, are given in *Table 1*. All the values are highly indicative that we are in a strong adsorption regime.

To compare such a measurement with a calculated model, it is probably appropriate to take a simple lattice scheme. Let us denote the layer parallel to the surface at a distance qa (where a is the length of a monomer unit and q is an integer) by the index q. It should then be possible to calculate the unnormalized probability of the nth link being in the q layer $P_q(n)$, which is related to the density profile calculated in most theories[13,14]. The experimentally measured desorbed and adsorbed popula-

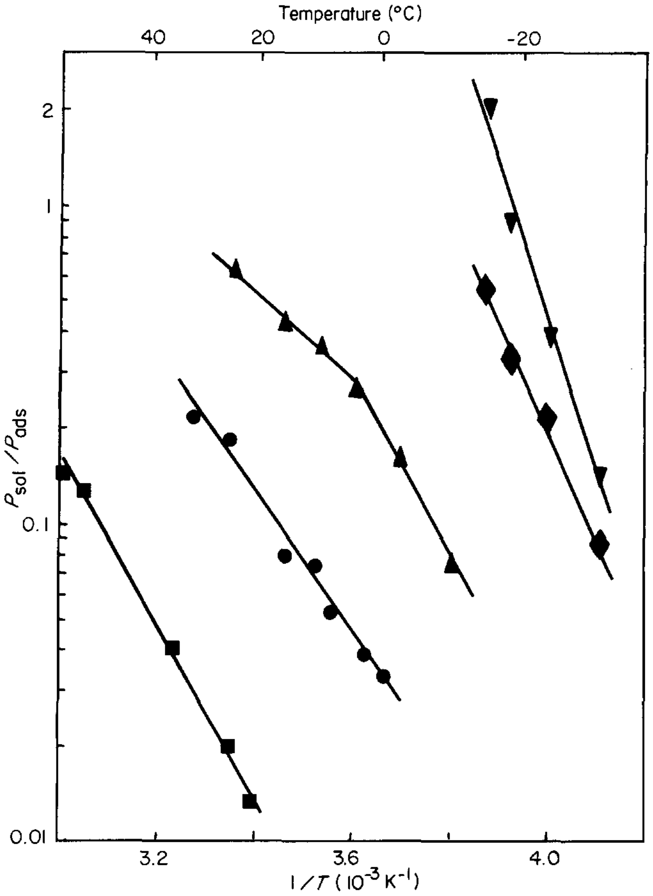


Figure 2 Evolution with temperature of the ratio of the two populations of labels (desorbed to adsorbed) for PEO 2000 grafted on silica in contact with PEO 2000 in solution in benzene observed after 4 months: (■) $n_a = 0$; (●) $n_a = 2.8$ r.u./nm^2; (▲) $n_a = 5.7$ r.u./nm^2; (◆) $n_a = 8.6$ r.u./nm^2; (▼) $n_a = 14.3$ r.u./nm^2

Table 1 Variation of the adsorption enthalpy ΔH and the entropic term ΔS per monomer unit, with the amount of added polymer n_a

n_a	0	2.8	5.7	8.6	14.3
ΔH (kJ mol^{-1})	51	42	45	60	94
$\Delta S/k$	16	15	20	27	42

tions of labels then correspond to:

$$P_{sol} = \sum_{q=1}^{N-1} P_q(N)$$

$$P_{ads} = P_0(N)$$

where N is the number of repeat units in the chain. For such a comparison to be realistic, it must be assumed that the motion of the label results only from the motion of a short segment and that the main hindrance is due to adsorption[24].

In the present case the situation is more complex because grafted and physically adsorbed polymers are simultaneously present, and there are not much data on the concentration profile expected in such occurrences.

From the observed data recorded in *Figure 2*, it is apparent that the ratio of labels in solution over adsorbed labels increases at a given temperature when the concentration of the surrounding solution increases. More and more chains are physically adsorbed when the concentration in solution is raised. These chains interact with and repel the grafted chains, and the latter adopt a more extended conformation. The phenomenon of adsorption of polymer on the modified silica surface is thus shown. It must be recalled that the monolayer coverage of monomer units corresponds to 6 r.u./nm^2 if the length of a segment is taken to be 2.9 Å and there are only 2 r.u./nm^2 that correspond to grafted chains. Therefore there is some room left on the silica surface.

Moreover the experimental points shown in *Figure 2* can be summarized with straight lines, which have been numerically extrapolated at different temperatures, assuming linear behaviour similar to that detected by the e.s.r. technique in a limited temperature range. Plots of (P_{sol}/P_{ads}) as a function of the concentration of polymers in the surrounding solution, or more precisely of the parameter n_a, which is the corresponding number of repeat units per square nanometre, are shown in *Figure 3* for different temperatures. This presentation is analogous to an 'adsorption isotherm' where the number of adsorbed molecules is detected indirectly through the change in the configurations of the chemically grafted chains. In fact n_a is the total number of added molecules

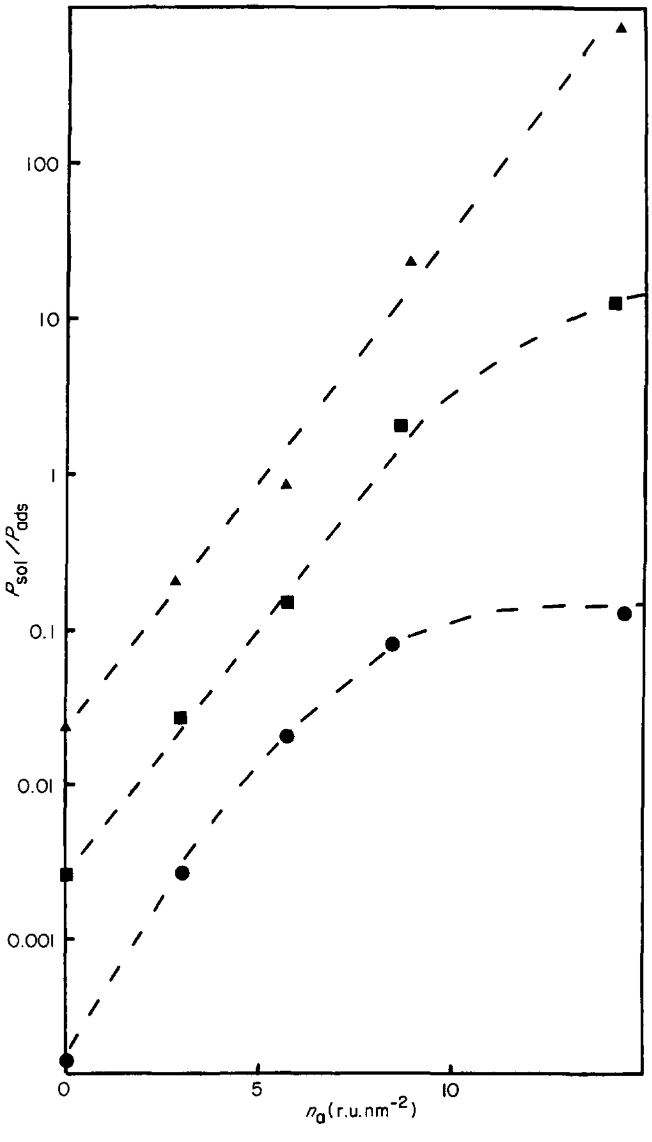


Figure 3 Extrapolated data from *Figure 2* indicating how, for a given concentration in the surrounding solution n_a, the configurations of the grafted chains evolve with temperature. The temperatures chosen are: (●) −30°C; (■) 0°C; (▲) +30°C

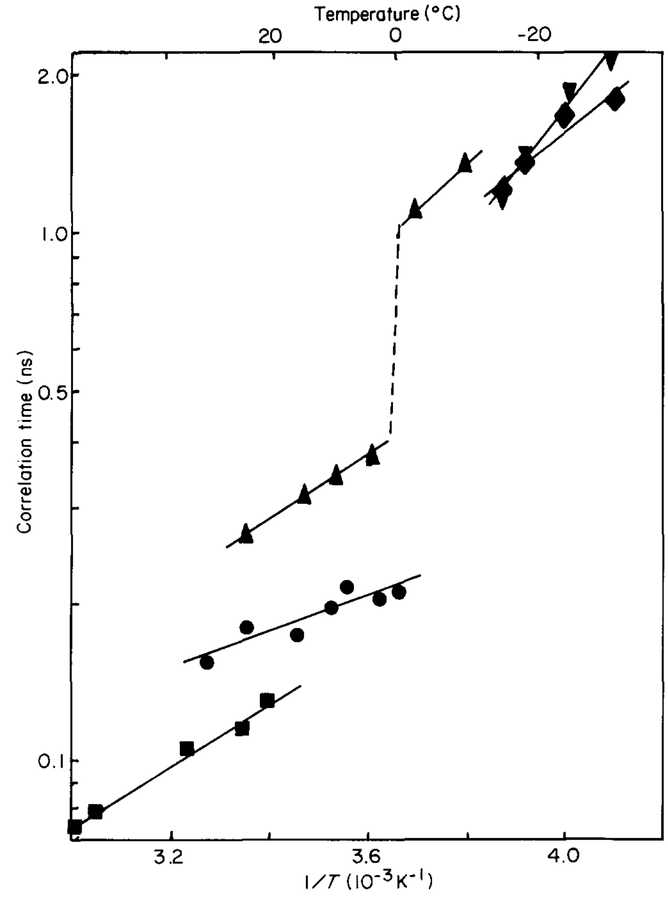


Figure 4 Evolution with temperature of the rotational correlation time of the desorbed population of labels for PEO 2000 grafted on silica in contact with PEO 2000 in solution in benzene observed after 4 months: (■) $n_a = 0$; (●) $n_a = 2.8$ r.u./nm^2; (▲) $n_a = 5.7$ r.u./nm^2; (◆) $n_a = 8.6$ r.u./nm^2; (▼) $n_a = 14.3$ r.u./nm^2

and it is of course unlikely that all these molecules are located at the interface. The whole adsorption process is therefore reflected in the signal of the spin label.

The rotational correlation times of the desorbed fraction of labels as a function of temperature and of the concentration of polymer in solution or n_a are given in *Figure 4*. These correlation times increase as the temperature decreases and as n_a increases. In fact rotation is a thermally activated process and the motion depends very much on the local microviscosity of the medium. The viscosity increases when the temperature decreases and also when polymer is added to the solution of benzene, and this is indeed what is observed. Below the melting temperature of benzene, such an evolution is no longer detectable. A disordered matrix or interphase of benzene mixed with polymer certainly exists at low temperature and this situation justifies that the study was extended in this range.

Influence of molecular weight

In *Figure 5* is shown the evolution of the ratio of the population of labels desorbed in solution to that of labels adsorbed on the silica surface as a function of the inverse of the absolute temperature for physically adsorbed PEO 6000. When comparing these results with those of *Figure 2* it is apparent that the ratio (P_{sol}/P_{ads}) is higher when PEO 2000 is added than when PEO 6000 is added in concentrations such that the numbers of repeat units n_a are similar. It appears therefore that the low-molecular-weight chains lie closer to the surface than the large chains and can more easily displace the grafted chains. Moreover the high-molecular-weight chains reach, with n_a, a limiting value of (P_{sol}/P_{ads}) at a given temperature faster than the shortest chains. In fact this influence of molecular weight is not a simple one because the two systems under study are fundamentally different: in one case the surface layer is formed with the same PEO 2000 whereas in the other case two different chain lengths (PEO 2000 and PEO 6000) are simultaneously present. Certainly this leads to polydispersity effects, which are sometimes approximated by bimodal distributions.

Similarly, the results of *Figure 5* have been numerically extrapolated at different temperatures, assuming that the linear behaviour detected by the e.s.r. technique is valid in a broader range. Plots of P_{sol}/P_{ads} as a function of n_a for PEO 2000 and PEO 6000 are shown in *Figure 6*. In these indirect 'adsorption isotherms' only the end segment of the PEO 2000 chemically grafted on silica is detected and gives information on a more or less heterogeneous layer. It must be stressed that in such a measurement it is not the adsorbed amount of polymer that is evaluated, but only the free end of some of the chains.

Plateau value

In *Figure 7* the ratio of the population of labels desorbed in solution to that of labels adsorbed on silica

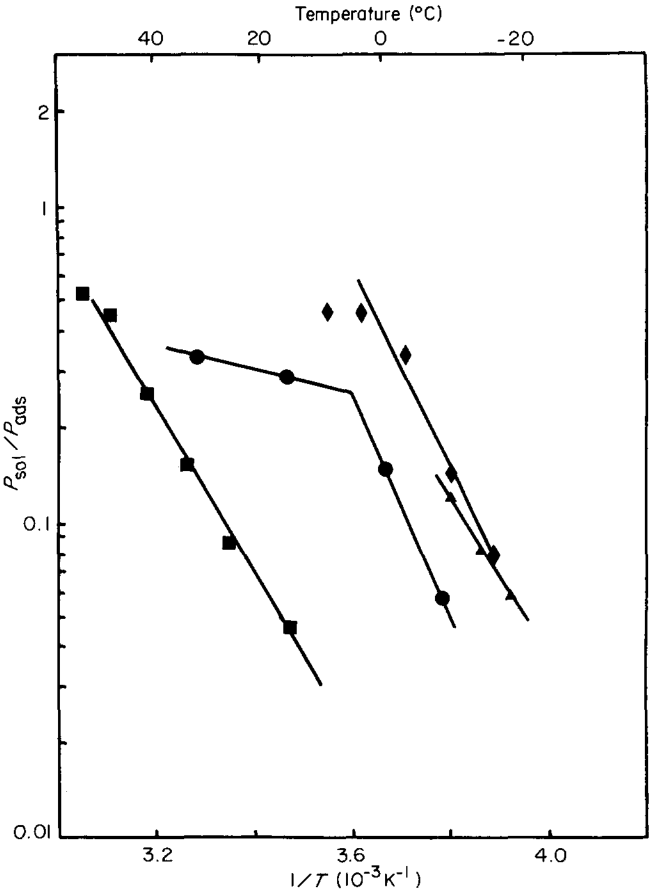


Figure 5 Evolution with temperature of the ratio of the two populations of labels (desorbed to adsorbed) for PEO 2000 grafted on silica in contact with PEO 6000 in solution in benzene observed after 4 months: (■) $n_a = 2.8$ r.u./nm^2; (●) $n_a = 5.7$ r.u./nm^2; (▲) $n_a = 7.1$ r.u./nm^2; (◆) $n_a = 14.3$ r.u./nm^2

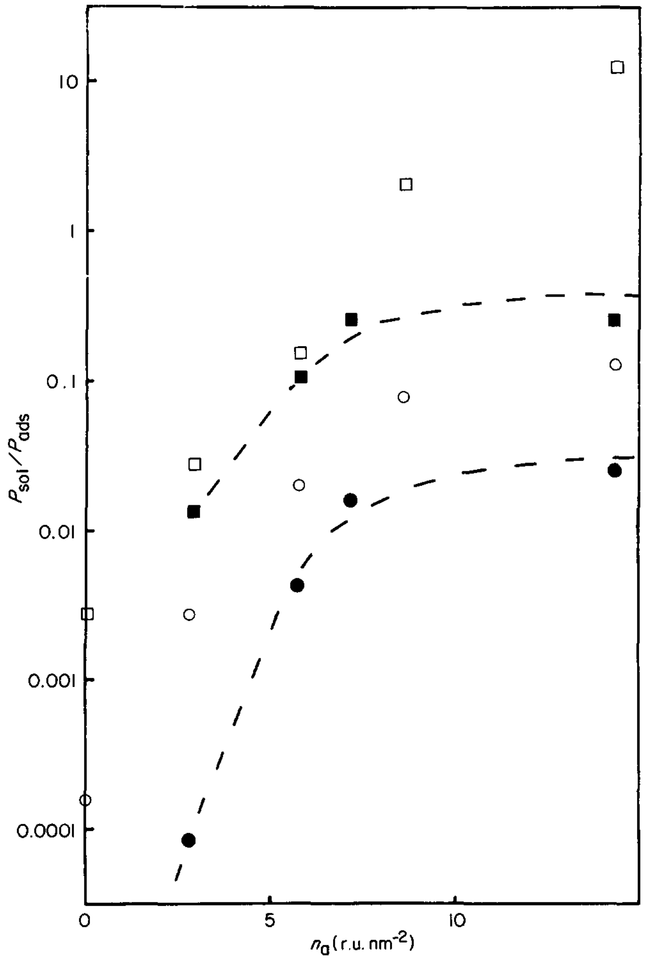


Figure 6 Extrapolated data from *Figures 2* and *5* indicating how, for a given concentration in the surrounding solution n_a, the configurations of the grafted chains evolve with temperature: (○) PEO 2000 at −30°C; (●) PEO 6000 at −30°C; (□) PEO 2000 at 0°C; (■) PEO 6000 at 0°C

is plotted as a function of the inverse of the absolute temperature for very different values of n_a and for adsorbed PEO 2000. The ratio (P_{sol}/P_{ads}) reaches a limiting value above n_a = 14 r.u./nm^2. It seems that the surface is completely covered with polymers at this point and that the layer is no longer affected by additional polymer in solution.

The same limit is observed for the rotational correlation times of the label in solution, as shown in *Figure 8*. These times vary with temperature as expected, but no more with n_a.

Influence of the grafting ratio

When PEO 2000 is grafted on silica at very high coverage, namely 0.45 molecules/nm^2 or 20 r.u./nm^2, the modified surface reacts differently to polymers added in solution. In *Figure 9* the ratio of the population of labels desorbed in solution to that of labels adsorbed on silica is plotted as a function of the inverse of the absolute temperature for different values of n_a. The plateau value is reached at once and the grafted layer no longer evolves to accommodate supplementary chains.

Relaxation of the layer

In *Figure 10* the ratio of the population of labels desorbed in solution to that of labels adsorbed from the silica surface as a function of the inverse of the absolute temperature taken at different times from 2 weeks to 4 months is shown. It is apparent from this plot that a very slow process occurs within the grafted layer. As the sample was stored at relatively low temperature (room temperature and below) and in a solvent, benzene, the grafting reaction or also the degrafting reaction should probably not be preponderant. It is therefore postulated that there exists a kinetically very slow adsorption of additional polymers on a partially covered powder. The grafted chains are displaced by degrees and there are adsorption sites left for physically adsorbed chains. As some of the chains are covalently bound to silica the reorganization or relaxation process is much longer than would be observed if the chains were free to move at least parallel to the surface.

DISCUSSION

Expected phenomena

A physically adsorbed layer of polymer on a solid surface cannot usually be entirely removed by a pure solvent[6–8]. However, it has been shown that the chains are not irreversibly bound to the substrate. They can be exchanged with a chemically identical polymer, particularly of higher molecular weight, present in solution[1–3]. The times involved in such a process of entry and exit near a diffuse layer, the 'breathing modes' and the relaxation, cover a very broad range[23], and it is

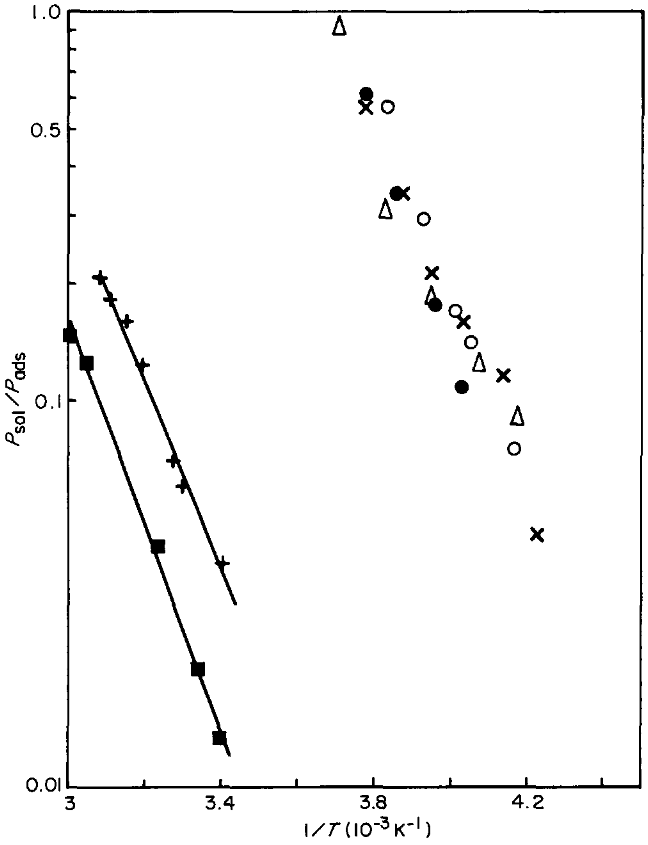


Figure 7 Evolution with temperature of the ratio of the two populations of labels (desorbed to adsorbed) for PEO 2000 grafted on silica in contact with PEO 2000 in solution in benzene observed after 5 weeks: (■) n_a = 0; (+) n_a = 2.8 r.u./nm^2; (●) n_a = 14.3 r.u./nm^2; (Δ) n_a = 70 r.u./nm^2; (×) n_a = 168 r.u./nm^2; (○) n_a = 700 r.u./nm^2

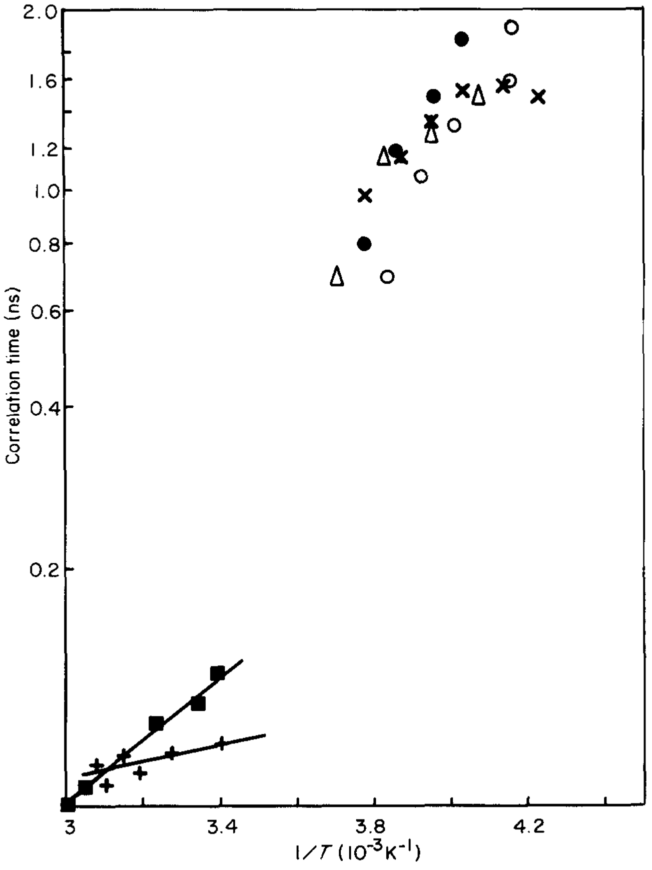


Figure 8 Evolution with temperature of the rotational correlation time of the desorbed population of labels for PEO 2000 grafted on silica in contact with PEO 2000 in solution in benzene after 5 weeks: (■) $n_a = 0$; (+) $n_a = 2.8$ r.u./nm^2; (●) $n_a = 14.3$ r.u./nm^2; (Δ) $n_a = 70$ r.u./nm^2; (×) $n_a = 168$ r.u./nm^2; (○) $n_a = 700$ r.u./nm^2

important to understand the mechanisms underlying these phenomena. Indeed, the first approaches were usually set down in the frame of thermodynamic equilibrium. If the system studied is in fact in a metastable state with reorganizations occurring, it will not be surprising to observe differences between the results. The studies concerned with static properties need to be completed with experimental data on the dynamic aspects[21,22].

In dealing with chemically bonded, grafted, or anchored chains, the purpose was to investigate several parameters related to these problems. First of all, it is hoped that the grafting to the solid surface allows a discrimination between two dynamic scales, which are usually simultaneously present: the microscopic local motion of a small number of segments around the covalent bond in the chains, as detected, for example, by the magnetic resonance method; and the global rotation of the whole coil, which also contributes to the signal. The weight of each mechanism depends on the chain length. When a neutral flexible labelled chain moves inside a diffuse adsorption layer, its motion can be described as a form of reptation on a self-similar grid[23]. Here, as the chains detected have a completely fixed end, this process can be removed and the only remaining way to reorganize the conformations is through reorientation of single segments. On the other hand, the advantage of chemical bonding is to control from the outside the initial irreversible coverage of the surface and to create situations that are unlikely to happen in the adsorbed state. This could be interesting for protecting and coating surfaces, which very frequently have attractive interactions with the surrounding media. To modify the solid in such a way and to make up, for example, a repulsive wall, the mechanism of the grafting reaction[15,16] (which here was performed in the melt whereas the adsorption study was made in the presence of a solvent, benzene) must be better known. In particular, there seems to be a limiting grafting ratio experimentally accessible, and it would be interesting to determine if this is due to intrinsic steric hindrances of the chains at the interface or to kinetic factors like a diffusion-limited reaction. Finally, in addition to the fixed ends, there are some segments along the chains which are hydrogen bonded to the surface, and the conformations of the chains in this state can be glass-like and different from that of polymers free in solution[30]. The displacement of a segment from a silanol site also depends on the bonding energy and this can bring in other peculiarities.

Observations

Here the adsorption has been detected *in situ* by modifications of the e.s.r. signal of molecules already grafted on the silica surface. The effect of adding polymer in solution results in a significant change in the spectra, which shifts the straight line characteristic of the evolution of the populations of desorbed over adsorbed labels with temperature. This indirect measurement through variations of the superficial layer gives evidence

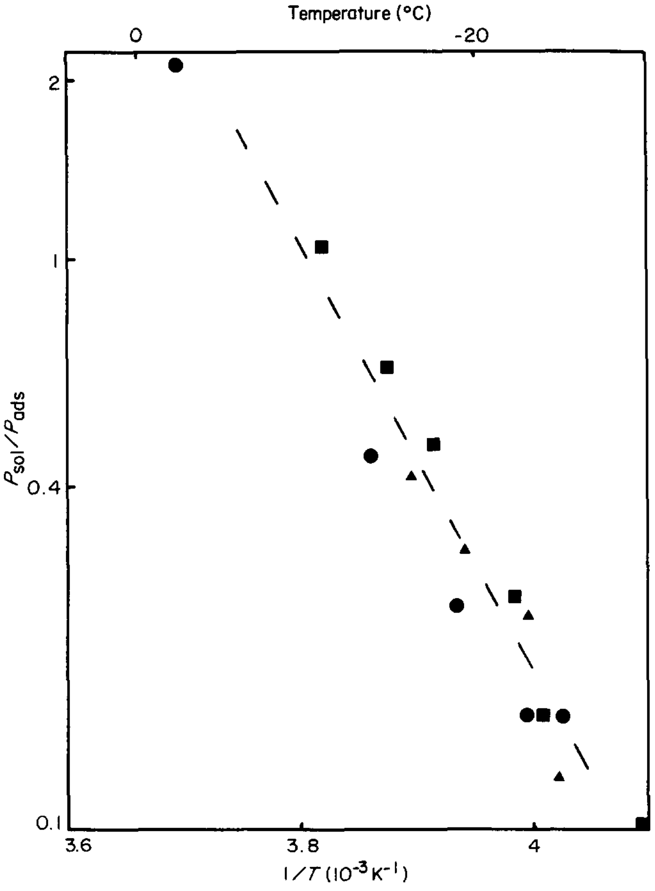


Figure 9 Evolution with temperature of the ratio of the two populations of labels (desorbed to adsorbed) for PEO 2000 grafted on silica in contact with PEO 2000 in solution in benzene observed after 4 months (the grafting ratio is 0.45 molecules/nm^2): (■) $n_a = 0$; (●) $n_a = 2.8$ r.u./nm^2; (▲) $n_a = 5.7$ r.u./nm^2

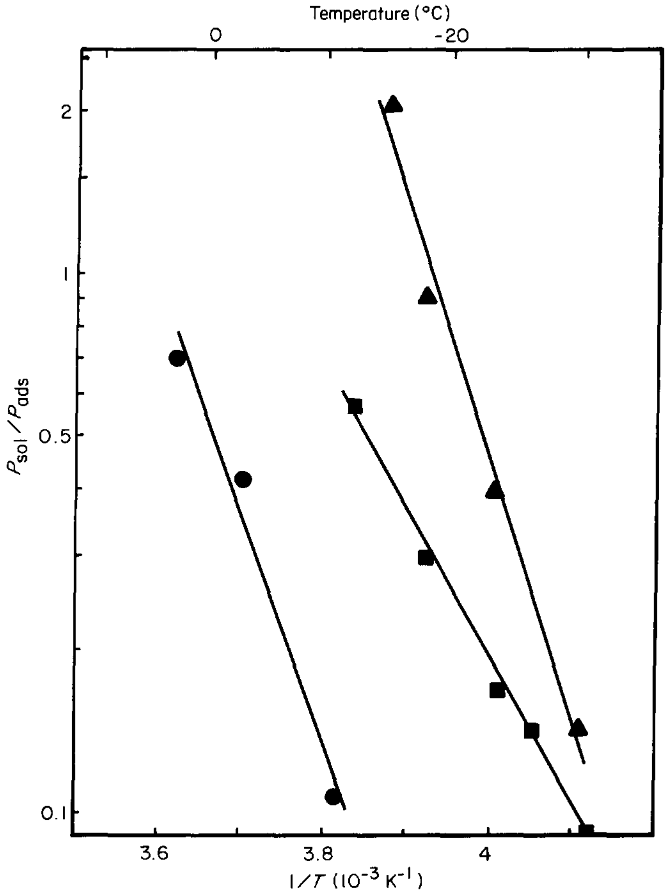


Figure 10 Evolution with temperature of the ratio of the two populations of labels (desorbed to adsorbed) for PEO 2000 grafted on silica in contact with PEO 2000 in solution in benzene, at $n_a = 14.3$ r.u./nm^2. The observation is made after: (●) 2 weeks; (■) 5 weeks; (▲) 4 months

of adsorption on a modified surface. It would seem tempting to extrapolate from these data and investigate the adsorption isotherm at different temperatures. However, it is apparent that the label itself gives an indication that is temperature-dependent. Indeed variations of temperature eventually induce variations in the number of adsorbed molecules, but also variations in the conformations of the chains and the average thickness of the layer, and these different contributions cannot be separated at the present time.

Concerning the influence of the molecular weight, a careful analysis of the results is also needed. It is known that the small molecules are adsorbed faster than the large ones owing to diffusion: the small molecules are adsorbed first and are then displaced by the large ones to attain thermodynamic equilibrium[31,32]. This leads to adsorption isotherms that are very sensitive to the polydispersity of the sample used[14]. In our case the large molecules of PEO 6000 simply cannot completely displace the small chains of PEO 2000, which are chemically bonded to the silica. Probably, in such a situation, the short chains are compressed on the surface.

Howard and McConnell[32] have studied the adsorption of PEO of molecular weight ranging between 390 and 190 000 on activated carbon black and also on Aerosil silica. They found that, for a molecular weight of 390, equilibrium is reached after 2 h, whereas 24 h are necessary for the polymer of molecular weight 10 000. This difference is attributed to the smaller diffusion coefficient of the large molecules. Pefferkorn, Varoqui *et al.*[1–3] on the other hand observe a displacement of adsorbed chains on very smooth surfaces with a characteristic time sometimes reaching more than 10 h. Cohen-Stuart *et al.*[4] have measured the hydrodynamic thickness of a freshly deposited adsorption layer and found it to decrease over a time of the order of minutes. Here the times involved are much longer, probably due to secondary processes of redistribution of the macromolecules and of the individual segments in the adsorbed system. The fact that the labelled chains are chemically bonded to the solid by one end certainly slows down the overall reorganization. Indeed most models[23] for the diffusion and mobility of the chains at an interface are based on the assumption that the coil can move freely inside and outside the layer. As this process is forbidden here, another mechanism, namely segmental motion, will prevail.

CONCLUSIONS

The adsorption of a polymer on a solid surface already modified by grafting has been observed indirectly through the evolution of the conformations of the chains at the interface as detected by e.s.r. of spin-labels. The macromolecules present are displaced by segments entering from the solution, interact with each other, are repelled and adopt progressively a more extended configuration. This effect depends upon the molecular weight of the added chains and on the grafting ratio achieved on the surface. The adsorption process reaches a limiting value when the number of added chains is equivalent to a quantity of 14 repeat units/nm^2. The kinetics of establishment of the final coverage has been detected: the relaxation times range from 2 weeks to 4 months. The long durations involved have been retraced to the chemical grafting of some chains, which slows down the diffusion of the coil as a whole, and allows only segmental motion.

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