

# Influence of the solvent on the conformations of poly(ethylene oxide) chains grafted on silica

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Electron spin resonance (e.s.r.) of labelled grafted poly(ethylene oxide) has been used to estimate (as a function of temperature) the ratio between the populations of free-end segments in solution to those adsorbed onto the silica surface. The influence of the solvents such as  $C_6H_6$ ,  $CHCl_3$ ,  $C_4H_8O_2$ ,  $C_6F_6$  and  $CCl_4$  has also been investigated. Better solvents produce greater swelling of the molecules, with more of the grafted layer extending into the solution. But solvent-surface and polymer-surface interactions must be taken into account to explain the results.

(Keywords: solid-fluid interface; polymer adsorption; spin-labelling; polyethylene oxide)

## INTRODUCTION

Polymers grafted onto solid surfaces are useful for processes such as colloid stabilization (or flocculation), chromatography, prostheses and the selective absorption of pollutants<sup>1</sup>. A large number of experimental<sup>1-8</sup> and theoretical<sup>9,10</sup> studies on the configuration of polymers at solid/liquid interfaces have been carried out.

In the study presented here the spin labelling technique was used to investigate the influence of the solvent on the configurations of poly(ethylene oxide) chains. These were grafted onto silica surfaces, with a nitroxide-free radical fixed at the free end. The e.p.r. signal consisted of two types of spectra: one with narrow lines characteristic of mobile labels in solution, and another with a large linewidth characteristic of labels immobilized on solid surfaces. The measurement of the ratio of fast:slow population of labels allows an evaluation of the concentration profile starting from the surface.

## EXPERIMENTAL

### Silica

A non-porous pyrogenic silica (Aerosil 300) from Degussa was used. Particles with a diameter of about 10 nm had a specific area (measured by nitrogen adsorption) of about 310 m<sup>2</sup>/g. The number of silanol groups on the surface is 3.3/nm<sup>2</sup>. Before utilisation the silica was dried at 300°C under vacuum for 3 h.

### Solvents

The following solvents were used: benzene  $C_6H_6$  (m.p. 6°C) chloroform  $CHCl_3$  (m.p. -63.5°C), dioxane

$C_4H_8O_2$  (m.p. 11.8°C), hexafluorobenzene  $C_6F_6$  (m.p. -13°C), carbon tetrachloride  $CCl_4$  (m.p. -23°C).

### Polymer

Poly(ethylene oxide) (PEO) (m.w. 2000 45 repetition units) was supplied by Merck. Its polydispersity measured by g.p.c. was 1.04. The polymer was dried at 70°C under vacuum for about 3 h.

### Grafting

The grafting reaction proceeded by the direct esterification of the silanol groups with the hydroxyl-end groups of the compounds. The reaction has already been described extensively<sup>8</sup>. The grafting ratio determined by pyrolysis weight loss at 700°C is 19.1% in weight or 0.19 molecules/nm<sup>2</sup>. This was checked by analysis of the products of the hydrolysis reaction<sup>8</sup>. The area occupied by a polymer segment being about 20 nm<sup>2</sup>, the number of molecules present on the solid surface in this same area is  $S=0.04$ .

### Spin-labelling

The grafting reaction of the free-radical nitroxide the 2,2,5,5 tetramethyl-3-pyrrolin-1-oxyl-3 carboxylic acid, is the same as previously described<sup>4,5,8</sup>.

### E.s.r. spectroscopy

The grafted silica was placed in contact with the different solvents, and each sample sealed under vacuum in e.s.r. tubes after repeated freeze-pump-thaw cycles. The e.s.r. spectra were recorded on a Varian E-4 spectrometer with a Varian E-257 temperature controller. 10 minutes

were allowed before each spectrum for thermal equilibrium. This method of analysis (of the spectra) has been described previously<sup>5,8</sup> and is shown on Figure 1. A fast motion spectrum of nitroxide spin labels consists of three well defined Lorentzian lines which can be explained by the Kivelson theory<sup>11</sup>. Such a spectrum is calculated on a Hewlett-Packard 9825 computer. It is then adjusted to the high and low field lines of the experimental composite spectrum, giving after integration, the fast fraction of labels. The slow fraction is obtained by subtraction of the fast motion spectrum from the experimental spectrum. The slow motion spectrum has a shape influenced by the anisotropic part of the spin and can be explained by the Freed theory<sup>12</sup>. At high temperatures only the fast motion spectrum remains detectable, (c.f. low temperatures where only the slow motion spectrum is detected). The typical composite shape has already been reported for physically adsorbed polymers<sup>13-16</sup> but the quantitative evaluation of the populations with different mobilities at different temperatures has been made less often.

RESULTS

Figures 2 and 3 show some typical spectra with a composite lineshape of PEO 2000 (grafted onto silica) in the presence and absence of different solvents, C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>F<sub>6</sub>, CHCl<sub>3</sub>, C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, CCl<sub>4</sub> and without solvent. The temperatures of the samples for these comparable spectra were very different. This shows the drastic effect of the swelling of the chain, which depends on the solvent used. The plot of the logarithm of the ratio of fast:slow populations of labels  $P_f/P_s$  as a function of the inverse of the absolute temperature in the different solvents, CHCl<sub>3</sub>,

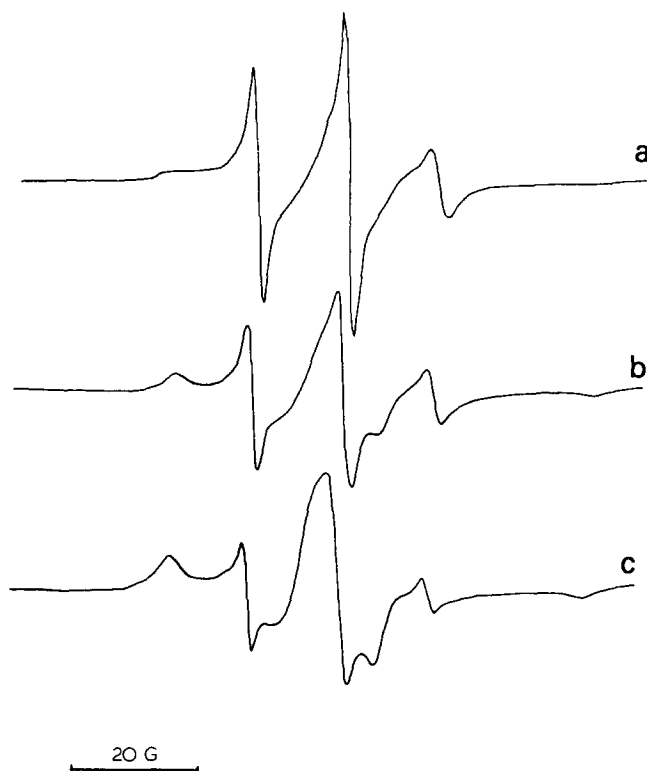


Figure 2 E.s.r. spectra PEO 2000 on Aerosil 300 in contact with different solvents: (A) control at 47°C; (B) with C<sub>6</sub>D<sub>6</sub> at -14°C; (C) with C<sub>6</sub>F<sub>6</sub> at -19°C

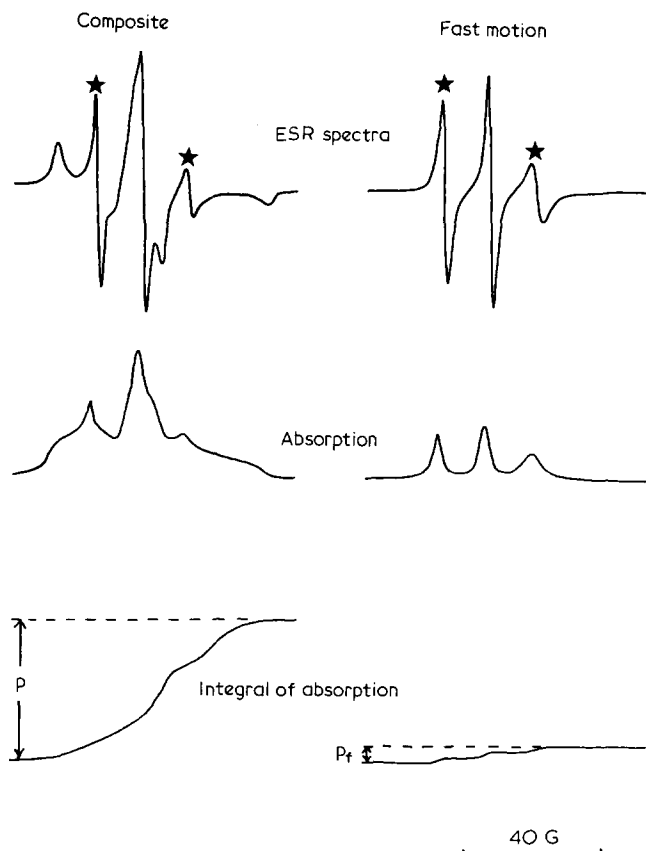


Figure 1 Method of analysis of the spectra: the theoretical spectrum is adjusted to the experimental composite spectrum and the integrals of the absorption give the fast and slow populations

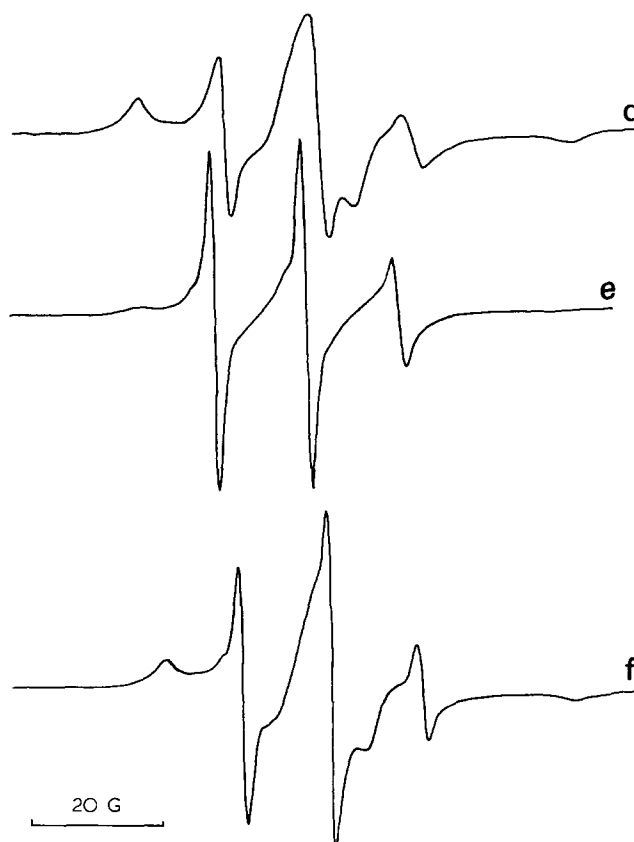


Figure 3 E.s.r. spectra of PEO 2000 on Aerosil 300 in contact with different solvents: (D) with CHCl<sub>3</sub> at -74°C; (E) with dioxane C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> at -24°C; (F) with CCl<sub>4</sub> at -30°C

dioxane  $C_4H_8O_2$ ,  $C_6D_6$ ,  $C_6F_6$  and without solvent is shown in Figure 4. The expression describing this behaviour is of the Van't Hoff type:

$$\ln(P_f/P_s) = -A/T + B$$

The composite spectra were detected in very different regions of temperature. The values of the parameters  $A$  and  $B$  are given in Table 1. The fact that there appears to be no drastic variation of the e.p.r. spectra at the melting point of the solvent, indicates that the matrix made up by the solvent, is not tightly bound in the vicinity of the grafted silica surface.

## DISCUSSION

### Influence of the label

The influence of the specific adsorption of the label at the end segment has been discussed extensively from a theoretical point of view<sup>17</sup>. If  $U$  is the adsorption energy of the label, the ratio of the concentrations of label in solution to that in surface is  $\exp(-U/kT)$ . It is expected that if  $E$  is the adsorption energy of a monomer unit, the

value for unlabelled chains is given from the value for labelled chains by the expression:

$$\begin{aligned} \ln(P_f/P_s(E, N))_{\text{unlabelled}} \\ = \ln(P_f/P_s(E, N, U))_{\text{labelled}} + (U - E)/kT \end{aligned}$$

As can be seen from this formula the analytical form of the experimental law is not modified.

### Provisions of the theory

The theories describing the conformation of chain molecules fixed by one end at a solid surface, generally give a concentration profile which is perpendicular to the surface. We have chosen a random walk model on a cubic lattice. Like Rubin<sup>18</sup> we have characterized the layer parallel to the solid surface at a distance  $qa$  ( $a$  is the length of a monomer unit modified by the index  $q$ ). The problem is then unidimensional in the direction perpendicular to the surface. The calculations give the concentration profile in the form of  $P_q(n)$ , the probability for the  $n$ -th link being in the  $q$  layer. This can then be related to the measured values by:

$$P_f \sim \sum_{q=1}^N P_q(N)$$

$$P_s \sim P_0(N)$$

where  $N$  is the number of links of the chain. The fact that the polymer is grafted by one end, is included in the initial conditions, so that  $P_0(1) = 1$  and  $P_q(1) = 0$  for  $q \neq 0$ . To make this expression realistic, we have assumed that the main hindrance to the motion is due to the close contact with the solid's surface: and that the monomers at greater distances are not affected<sup>19</sup>.

There are many theories<sup>10,20-22</sup> giving values for interacting chains, where the effect of the solvent is taken into account using Flory's parameter  $\chi$ <sup>23</sup>. We have restricted ourselves to the mean field theories and in particular to the work of John and Richmond<sup>21</sup>. For isolated chains, the concentration profile is an exponential decay:

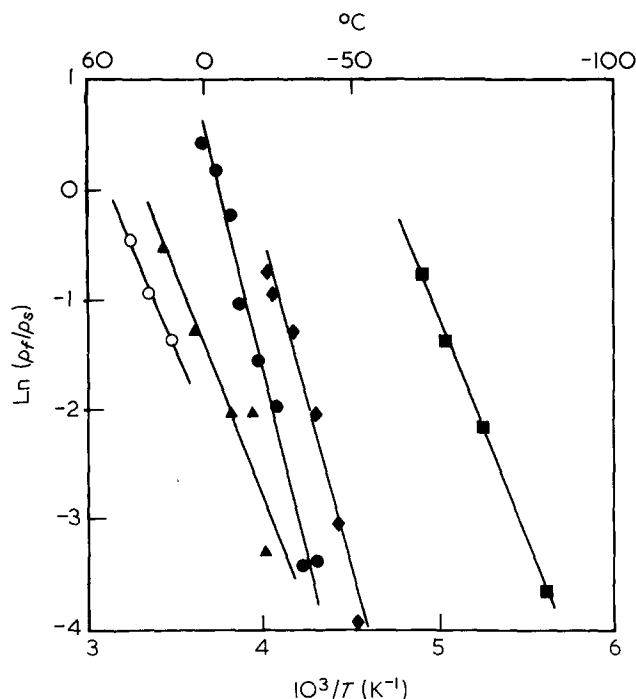
$$P_q(n) \sim \exp(-qE/kT)$$

where  $T$  is the absolute temperature. For interacting chains it is predicted that the concentration profile is still decaying exponentially at great distances from the surface. But the profile is more complicated near the surface (depending on the value of a factor  $NS(1 - 2\chi)$ ), where  $S$  is the grafting ratio in molecules/nm<sup>2</sup> and  $NS$  is the segment density. These predictions are consistent with the experimentally observed law for the ratio of fast to slow populations: the term  $A$  can be interpreted as an adsorption energy and the term  $B$  as an entropic term dependent on the factor  $NS(1 - 2\chi)$ <sup>23</sup>.

This prediction holds when the adsorption is strong i.e. when  $\ln(P_f/P_s) \leq -1.5$  and  $E \geq kT$ . As can be seen, in a good solvent ( $\chi < 0.5$ ) the fast population increases and the chain extends in solution  $\ln(P_f/P_s)$  increases. However, in a bad solvent ( $\chi > 0.5$ ) when the grafting ratio  $S$  increases, the chains collapse onto the adsorbing surface ( $\ln(P_f/P_s)$  decreases).

### Expected phenomena

The measured quantity  $P_f/P_s$  is characteristic of the conformation of the chain. The higher this ratio, at a given



**Figure 4** Evolution with temperature of the ratio of the two populations of spin labels (fast and slow) for PEO 2000 in different solvents: (■)  $CHCl_3$ ; (◆) dioxane  $C_4H_8O_2$ ; (●)  $C_6D_6$ ; (▲)  $C_6F_6$ ; (○) control

**Table 1** Experimental values of the parameters  $A$  and  $B$  which characterize the evolution of the two populations (as a function of the solvent)

Samples	A		B
	kJ	eV	
PEO 2000 grafted on Aerosil in			
Dioxane $C_4H_8O_2$	51	0.58	26.5
Benzene $C_6H_6$	50	0.57	24.6
Control (no solvent)	33	0.37	13.5
Hexafluorobenzene $C_6F_6$	32	0.36	13.8
Chloroform $CHCl_3$	32	0.36	19.5

temperature, the more the chains extend into the solution. We expect that the polymer conformation is the result of a competition between surface attraction and chain repulsion. In a good solvent the chains are swollen and the fast population tends to increase. But if the affinity of the solvent for the solid surface is poor, the first effect can be hidden by a stronger adsorption of the polymer on the surface, which increases the slow population.

Howard and McConnel<sup>25</sup> have estimated by B.E.T. analysis of vapour adsorption on Aerosil silica, that the heat of adsorption for  $C_6H_8O_2$  is 2.4 kcal mole<sup>-1</sup>, for  $C_6H_6$  1.4 kcal mole<sup>-1</sup> and for  $CHCl_3$  1.0 kcal mole<sup>-1</sup>. It can be argued that the affinity of a liquid for a solid surface is correlated with the heat of adsorption determined from the vapour isotherm. Making this assumption, we therefore have a qualitative, expected order, for some of the surface attractions.

The same authors<sup>25</sup> have shown that the solubility order as judged by intrinsic viscosity is

chloroform > benzene ~ dioxane

or by gel swelling is

chloroform > benzene > dioxane

On the other hand the  $C_6F_6$  is expected to be a worse solvent than  $C_6H_6$ . Likewise Graham *et al.*<sup>26</sup> give the order

chloroform > benzene > carbon tetrachloride

The result of the surface attraction and chain repulsion, can be measured experimentally by comparing at a given temperature the values of the ratios of fast to slow populations of labels. Because  $CHCl_3$  has a weaker surface affinity than  $C_6H_6$  and being a better solvent, it is expected that at a given temperature  $P_f/P_s$  should be higher. It is not possible to predict between  $C_6H_6$  and  $C_4H_8O_2$ , and the other solvents, which effect will predominate.

More precisely when comparing the experimental law with the theoretical model, it appears that the experimentally measured parameter  $A$  is an effective adsorption energy, which includes several contributions: it results from the adsorption of a polymer segment from the solution to a surface site and the displacement of solvent molecules. Consequently, it is mainly controlled by the solid/solvent and solid/polymers interactions. In our case,  $A$  should therefore be sensitive to the solid/solvent interaction.

The polymer/solvent interaction is characterized numerically by the Flory parameter  $\chi$ . If, in a first approximation, we neglect the variation of  $\chi$  with temperature, from the theoretical law it appears that it is mainly the experimentally measured entropic parameter  $B$ , which should be sensitive to the swelling of the polymer.

#### Samples

At this point it must be recalled that the samples used were made of polymer chains of about 45 links terminally anchored on a solid surface. The samples are dried under vacuum and then placed in contact with the solvent. The chains as a whole can therefore never be desorbed. Only some segments along the chains can move from a surface

site to the solution. The distribution of segments as a function of the distance from the surface reaches its equilibrium profile, through this mechanism. In order to prevent metastable profiles, the samples were all initially cooled at low temperature and then slow heated (waiting 10 minutes at each point for thermal equilibrium). The values of the ratios  $P_f/P_s$  appear reasonably well reproducible.

#### Observations

At a given temperature the observed values of  $P_f/P_s$  increase for the different solvents in the following order: control (no solvent) <  $C_6F_6$  <  $C_6H_6$  <  $C_4H_8O_2$  <  $CHCl_3$ . As expected the ratio is much higher for  $CHCl_3$  than for  $C_6H_6$  or  $C_4H_8O_2$ . The comparison of  $C_6H_6$  with  $C_4H_8O_2$  suggests that in this case the surface solvent interactions outweigh the polymer solvent interactions. In  $C_6F_6$ , (a poor solvent) the chains are less extended in solution than in a good solvent of similar structure, such as  $C_6H_6$ .

The experimentally determined values of  $A$  (Table 1) follow the qualitative order of the solvent solid interactions given above. These interactions appear similar for  $CHCl_3$ ,  $C_6F_6$  and the control indicating a poor affinity of these solvents for the surface.  $C_4H_8O_2$  appears to have the highest affinity for the surface.

The situation is more complicated, for the pre-exponential factor  $B$ , which appears in the variation of  $P_f/P_s$  and no clear conclusion can be drawn from the order of the measured values. (Probably the precision of  $B$  is not so good as that of  $A$ ). But observation suggests also that the model does not yet satisfactorily explain the observed phenomena. A possible explanation could be, that the model, does not take into account the existence of long dangling tails observed by other authors<sup>1</sup>.

Comparing our results on grafted molecules with the physical adsorption study of Howard and McConnel<sup>25</sup> it could be interesting to extend the method to more polar solvents. But it must be recalled that such solvents are not convenient for e.s.r. measurement.

#### Comparison with n.m.r. measurements

Several techniques allow investigation of the environment surrounding the monomer units, these include e.s.r., i.r. and n.m.r. techniques. These are able to distinguish monomers inside the adsorbed layer which are close to those which are in loops and tails. However, i.r. spectroscopy is able to observe the adsorbed polymer segments<sup>27</sup>, which are at a distance smaller than a monomer length from the surface. Segments with different mobilities are distinguished by e.s.r. (randomly labelled chains) and pulsed n.m.r. The number of adsorbed links can appear higher with e.s.r. and n.m.r. compared with i.r. spectroscopy. (Short loops at a distance less than 3 to 4 monomer lengths from the surface<sup>3,27</sup> are considered to be 'trains').

For poly(vinyl pyrrolidone) adsorbed on silica, Barnett *et al.*<sup>2</sup> using pulsed n.m.r. have found highly adsorbed fractions of the segments. They have described a pulse sequence which allows the determination of the fast and slow populations without curve-fitting. Our results are in broad agreement with those of Barnett *et al.*<sup>2</sup>. They also studied terminally anchored PEO on lattices and showed that the concentration profile has a maximum at a certain distance from the surface, which is in agreement with

theory<sup>10</sup>. However in this case, the grafting ratio was very high and the chains did interact much more than in our studies. In spite of labelling the free end of the polymer we were not able to show evidence for long dangling tails, as observed by neutron scattering and photon correlation spectroscopy<sup>1,2,3</sup> and predicted theoretically<sup>22</sup>.

## CONCLUSION

The effect of different solvents on the conformation of poly(ethylene oxide) chains grafted on silica has been investigated at a molecular level using the spin labelling technique. In order to explain all the results, it appears that it is necessary to take into account the whole system and particularly the solvent-surface and polymer-surface interactions. In fact the affinity order of the solvents for the surface seems to control the adsorption energies measured by our technique. It is not so easy however to characterize the effect of the swelling of the chains in the solvent through a simple experimental parameter. The results on the ratio of fast : slow populations indicate only that the swelling of the molecules is more important when the segment interaction increases for similar solvents.

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