

Influence of chain length on conformations of poly(ethylene glycol) chains grafted on silica

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(Received 26 April 1982; revised 12 January 1983)

Electron spin resonance (e.s.r.) spectroscopy of labelled grafted poly(ethylene glycol) chains has been used to estimate the ratio of the population of end segments free in solution to that of ones adsorbed on the silica surface, as a function of temperature. In particular, the influence of chain length is investigated. The grafted molecules have the following molecular weights, 44, 88, 132, 176, 400, 600, 2000, and are in contact with benzene. Taking the random walk models as reference, two different behaviours are distinguished, one for the oligomers and one for the polymers. The measured values are consistent with an overall picture of 'brush bristles' for oligomers and of weakly overlapping partly collapsed coils for polymers.

Keywords Solid–fluid interface; polymers; spin labelling

INTRODUCTION

The conformations and mobility of polymers or short chains grafted on a solid surface are now under investigation both experimentally^{1–6} and theoretically^{7,8}. The practical applications (chromatography, etc.) as well as the fundamental interest of these materials justify these efforts⁹.

The method used here is the electronic paramagnetic resonance (e.p.r.) of grafted chains spin labelled at the free end with a nitroxide free radical. It gives information chiefly about the microscopic structure of the grafted layer. Indeed, the resonance lines are split into two groups: one, which is characteristic of adsorbed links with slow motion, has large linewidths, whereas the other, characteristic of mobile links in solution, has three narrow lines^{1,2}. The possibility of distinguishing and evaluating the respective populations as a function of the physical parameters allows the deduction of some requirements which the segment concentration profile should satisfy in order to account for the experimental results.

The principal physical parameters which in this case control the interaction between chain, solvent and solid surface are the temperature, the nature of the solvent, the grafting ratio¹⁰ and the chain length. The influence of this latter parameter is especially investigated in the present study which is devoted to ethylene glycol oligomers and polymers of low molecular weight.

EXPERIMENTAL

For the present study the samples were prepared more carefully than previously^{1,2}, since the earlier preparation

method is open to criticism mainly for the following reasons:

(1) The chosen grafting temperature (400°C) was too high and hence thermal degradation could occur.

(2) The polydispersity of the initial macromolecular materials was not well controlled.

(3) The porosity of the silica typical for liquid chromatography introduced supplementary difficulties affecting the mobility of the grafted chain.

Silica

In this study a non-porous pyrogenic silica, Aerosil 300 from Degussa, was selected. The particles, about 10 nm in diameter, develop a specific surface area, measured by nitrogen adsorption, equal to 310 m² g⁻¹. The surface content of silanol groups is equal to 3.3 group/nm². Before use, the silica was dehydrated by heating at 300°C under vacuum for 3 h.

Oligomers and polymers

The selected oligomers, mono-, di-, tri- and tetra-ethylene glycol, were supplied by Fluka as purissimum-grade products and were used without further purification. The low molecular weight poly(ethylene oxide) (PEO) was supplied by Merck (PEO 400 and PEO 600) and by Fluka (PEO 2000). Their polydispersities measured by us with g.p.c. are respectively equal to 1.12, 1.08 and 1.04. Only the PEO exhibits a low molecular polydispersity.

All these polymers were heat dried at 70°C, under vacuum for about 3 h.

These polymers were chosen because their high flexibility and fast local motion¹¹ give narrower lines on the e.p.r. spectra which are more conveniently tractable.

Table 1 Grafting ratios of ethylene oxides on Aerosil 300

Grafted compound	Grafting ratio	
	(wt%)	(molecules/nm ²)
Ethylene oxide	8.5	3.9
Diethylene oxide	8.9	2.0
Triethylene oxide	14.8	2.2
Tetraethylene oxide	17.6	1.9
PEO, molecular weight	400	12.7
	600	17.0
	2000	19.1

Table 2 Characterization of grafted PEO 600 and PEO 2000

Measured quantity	PEO 600	PEO 2000	
Weight average molecular weight, \bar{M}_w	(a)	533	1910
	(b)	690	1860
Number average molecular weight, \bar{M}_n	(a)	480	1800
	(b)	640	1700
Polydispersity	(a)	1.11	1.06
	(b)	1.07	1.09
Grafting ratio	(g.p.c.) σ_G	18.4 wt%	23.7 wt%
	(pyrolysis) σ_p	21.8 wt%	33.9 wt%
	σ_G/σ_p	0.84	0.70

(a) Before grafting
(b) After grafting

Grafting method

The grafting reaction of PEO was achieved by direct esterification of the silanol groups by the hydroxyl end group of the oligomers and polymers. Practically, silica is dispersed in an excess of PEO. The dispersion is then carefully degassed and heated at 230°C, for 16 h, under pure nitrogen to prevent oxidation.

The reaction product was dispersed in acetone, filtered and the filtrate washed three times and finally solvent extracted for one day, always with the same solvent. The grafted silica was dried at 60°C under vacuum.

The grafting ratio was determined by pyrolysis weight loss at 700°C (Table 1) for the e.p.r. samples.

In general the silicic esters are known to be easily hydrolysed. Therefore all the e.p.r. spectra were taken with carefully dehydrated samples and solvents.

However, in order to check the values of the grafting ratios, some samples were prepared and the hydrolysis reaction was performed on them. Practically, grafted silica was dispersed at 200°C in water mixed with THF and maintained for 48 h at 60°C. After decanting of the silica the supernatant solvent was analysed by g.p.c. and the amount of desorbed polymer as well as its molecular characteristics (mass, polydispersity) measured. Some typical results are given in Table 2 for PEO 600 and PEO 2000. The molecular mass and polydispersity are slightly different after grafting. The grafting ratios are lower with g.p.c. than with pyrolysis but are still comparable. The comparison between the two techniques support the assumption that the values given (Table 1) are reliable enough.

The spin labelling

The labelling reaction was the same as previously^{1,2}. The nitroxide spin label (2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl-3 carboxylic acid) supplied by Kodak, in its acid chloride form, was allowed to react with the free hydroxyl end groups of the grafted PEO in the presence of pyridine. Very few chains were labelled. The labelled grafted silica was washed, extracted and dried under the same conditions as after the grafting reaction. The fixation of a free radical on an unmodified silanol group is unlikely to complicate the spectra. Indeed the e.s.r. spectrum of labels directly fixed and therefore completely immobilized would be very broad, of weak intensity and independent of temperature. It is undetectable compared with the interesting spectrum, particularly in the high-temperature region with high gains.

E.s.r. spectroscopy

The silica was dispersed in a solvent of PEO, namely benzene. In order to facilitate the comparison with the n.m.r. measurements^{4,5}, the same deuterated benzene C₆D₆ was used. The samples were sealed, under vacuum, in e.s.r. tubes after repeated freeze-pump-thaw cycles.

The e.s.r. measurements were performed on a Varian E-4 spectrometer. A Varian E-257 variable temperature controller was used to thermostat the sample. The spectra were recorded each time after waiting 10 min for thermal equilibrium.

Our method of analysis of the spectra has been described previously² and is shown in Figure 1.

The e.s.r. spectra of the grafted labelled PEO exhibit the typical shape already reported for both adsorbed¹²⁻¹⁴ and grafted¹⁻³ labelled polymers. This shape was interpreted as the superposition of two types of spectra: one,

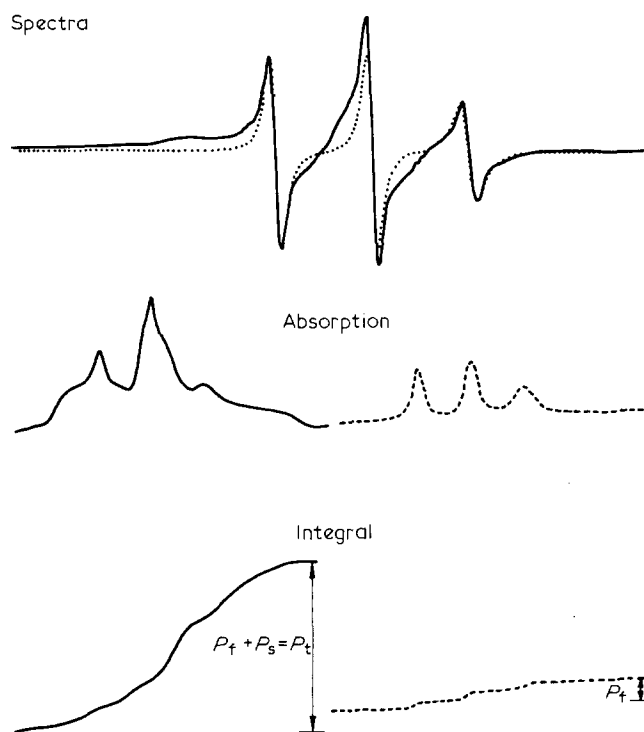


Figure 1 Method of analysis of the e.p.r. spectra. Full line, experimental spectrum; dotted line, theoretical fast motion spectrum

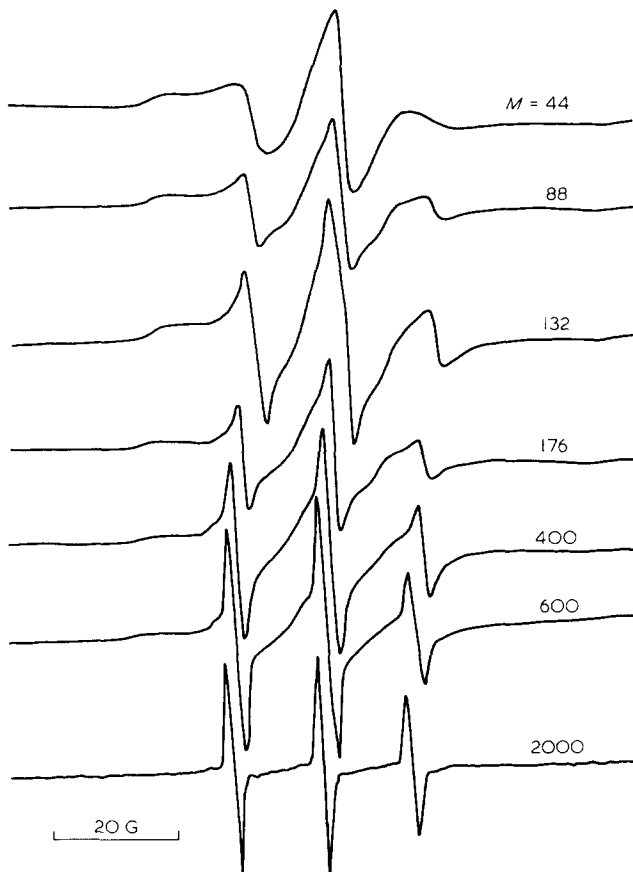


Figure 2 E.s.r. spectra of all the studied oligomers and polymers at 15°C

with a narrow linewidth showing three well defined lines, originating from the fast motion of the label, and is the only one existing above 50°C; the other, with a large linewidth and a shape influenced by the anisotropic part of the Hamiltonian, not wholly averaged in the slow tumbling region, can be attributed to the slow motion of the label, and remains the only one observable below -40°C. Thus in the most interesting region the simple two-state model was used. When this interpretation became doubtful, possibly because the motion of the label was anisotropic, the data obtained were no longer discussed.

The fast motion spectra are explained by the Kivelson theory¹⁵. In fact the only assumption used here is that the shape of each of the three lines is Lorentzian and that their areas are the same. This property is true even if the motion is anisotropic, provided it is fast enough¹⁶. The corresponding spectra were calculated on a Hewlett Packard 9825 computer and fitted to the experimental curves. The shape of the slow motion spectra is known and explained by the Freed theory¹⁷. Actually the spectra corresponding to the slow motion were deduced by subtracting the previous ones from the experimental curves.

As our purpose was to study the main features of the phenomena, we do not claim extreme precision (see Figure 4 below).

RESULTS

The existence of an equilibrium between slow and fast motion of monomer units of the grafted polymer has also

been observed by Facchini *et al.*^{4,5} These authors studied by ¹H and ¹³C n.m.r. the motion of unlabelled macromolecules. Particularly, the measure of the longitudinal relaxation time T_1 , by a sequence of inverse-recovery-Fourier transform, has confirmed that there are indeed two distinct populations of different mobilities. Moreover, the fact that the exchange time between the two possible states for a monomer unit exceeds 0.5 s,⁵ ensures that our evaluation method of the relative proportion of the two fractions and their corresponding label relaxation time is valid. The distribution of segments evaluated will therefore be near the statistical equilibrium.

The spectra for all the studied oligomers and polymers, $M = 44, 88, 132, 176, 400, 600, 2000$, at 15°C are shown in Figure 2.

The spectra for the shortest chains are the most difficult to interpret because the two linewidths are not very different. Therefore a typical spectrum for grafted ethylene oxide at 16°C and one for grafted diethylene oxide at 11°C are shown in Figure 3. From them we infer that starting from the diethylene oxide the two-state model is valid for these highly flexible chains.

The plot of the logarithm of the ratio of the fast

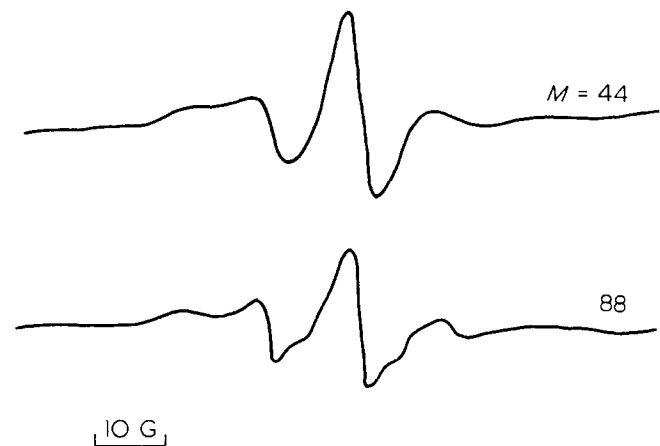


Figure 3 Enlarged spectra of grafted ethylene oxide at 16°C and of grafted diethylene oxide at 11°C showing the appearance of the composite two-state shape

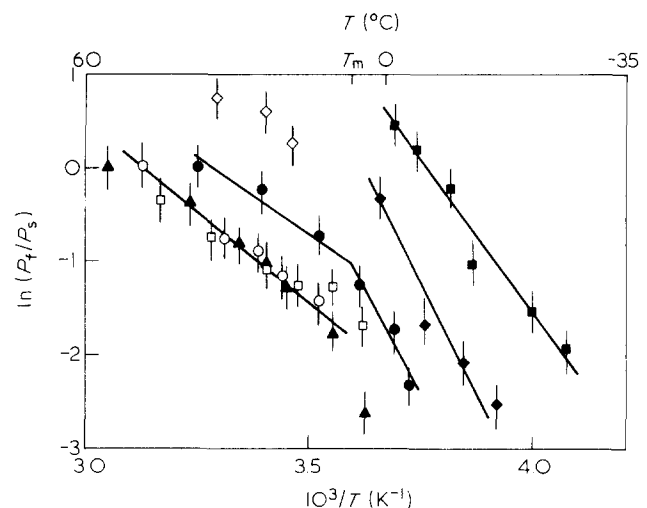


Figure 4 Dependence of the ratio of the two populations on temperature for grafted PEO in C_6D_6 ; molecular mass 44 (\diamond), 88 (\circ), 132 (\square), 176 (\blacktriangle), 400 (\bullet), 600 (\blacklozenge), 2000 (\blacksquare). T_m is the melting point of the solvent

Table 3 Experimental values for the *A* and *B* parameters characterizing the evolution of the two populations

Grafted compound	<i>A</i>		<i>B</i>
	(kJ)	(eV)	
(Above $T_m = 6.7^\circ\text{C}$)			
Ethylene oxide	22	0.25	10.0
Diethylene oxide	26	0.30	10.6
Triethylene oxide			
Tetraethylene oxide			
PEO of molecular weight 400	25	0.28	10.5
(Below $T_m = 6.7^\circ\text{C}$)			
PEO of molecular weight 400	68	0.78	31.4
600	60	0.69	28.8
2000	49	0.57	24.6

population to the slow one versus the inverse of absolute temperature shows that the experimental results fit a Van't Hoff type of law² (Figure 4) for all the oligomers and polymers studied ($M = 44, 88, 132, 176, 400, 600, 2000$) in both regions of the diagram delimited by the melting temperature of the solvent:

$$\ln\left(\frac{P_f}{P_s}\right) = -\frac{A}{T} + B$$

At a given temperature the ratio P_f/P_s is highest for ethylene glycol, and is one order of magnitude lower and independent of the chain length for di-, tri- and tetraethylene glycol and increases again for PEO 400, 600 and 2000.

The values of the parameters *A* and *B* are shown in Table 3.

DISCUSSION

Statistical distribution of the end segment

We define $p(N, z)$ as the probability that the end segment of a grafted chain of N links is at a distance z from the surface. The fast population is then given by

$$P_f = \int_a^\infty (N, z) dz$$

and the slow one by

$$P_s = 1 - P_f$$

where a is the length of a link. The integration limits will be realistic if we assume that the main hindrance to motion is due to adsorption. Furthermore the fast isotropic motion of the label must be sensitive mainly to the motion of a short segment¹¹ and must not depend on the distance from the surface for a given molecular weight.

Influence of the label

Let η be the adsorption energy of the label on the silica surface. The label concentration on the surface differs from the concentration in the solution by the factor $e^{\eta/kT}$.

The measured quantity P_f/P_s is of course dependent on the specific adsorption of the label, but in a well known way. Indeed it can be shown that if ϵ is the adsorption energy of a monomer unit, the ratio of the populations for

unlabelled chains $P_f/P_s(\epsilon, N)$ is connected to that for labelled chains $P_f/P_s(\epsilon, \eta, N)$ by the relation:

$$\left.\frac{P_f}{P_s}(\epsilon, N)\right|_{\text{unlabelled chains}} = \left.\frac{P_f}{P_s}(\epsilon, \eta, N)\right|_{\text{labelled chains}} e^{\eta/kT} \times e^{-\epsilon/kT}$$

$$\text{or } \ln\left(\frac{P_f}{P_s}(\epsilon, N)_{\text{unlabelled}}\right) = \ln\left(\frac{P_f}{P_s}(\epsilon, \eta, N)_{\text{labelled}}\right) + \frac{\eta - \epsilon}{kT}$$

In the temperature range studied, the experimentally observed law for the labelled chain is:

$$\ln\left(\frac{P_f}{P_s}(\epsilon, \eta, N)\right) = -\frac{A}{T} + B$$

Therefore it is predicted that the unlabelled chain should follow a law:

$$\ln\left(\frac{P_f}{P_s}(\epsilon, N)\right) = -\frac{A'}{T} + B'$$

where

$$A' = A - \frac{\eta - \epsilon}{k}$$

$$B' = B$$

We make this assumption, and thereafter the experimental results can be compared directly with the theoretical models of the configurations of unlabelled chains at a solid-liquid interface. In particular, it must be noted that the analytical form of the law in this temperature range is not modified and, if *A* and *B* are functions of *N* only, the same is true for *A'* and *B'*.

Isolated chains

For the discussion of our results we take as reference the random walk model proposed for long polymeric chains which do not depend on the detailed chemical nature of the molecules considered. There exist today many approaches for handling the problem of the configurations at an interface^{18,19}. Among these we shall use mainly the continuous mean field theories.

The simplest and oldest theories deal with the configurations of an isolated ideal chain at an interface²⁰⁻²³. They predict an end segment distribution decaying exponentially. In the formulation of Lepine and Caille²³:

$$p(N, z) = \text{constant} \times \frac{12(\theta - \theta_c)}{a} \exp\left(-\frac{12(\theta - \theta_c)z}{a}\right)$$

where $\theta = \epsilon/kT$ and ϵ is the adsorption energy of a monomer adsorbed at the interface. In the regime where $\theta > \theta_c$ one can indeed deduce a law of the form:

$$P_f/P_s = \exp[12(-\theta + \theta_c)]$$

This result is consistent with our experimental result, if it is recalled that the model assumes many approximations and is not realistic enough for an exact comparison of the numerical values. For example, the effects of self-exclusion of the chain are not taken into account²⁴.

On the other hand, it is interesting to note that in this regime of appreciable adsorption ($\theta > \theta_c$) the theoretical models for isolated chains do not predict a variation of the ratio P_f/P_s with the molecular weight.

Interacting chains

In contrast, the more comprehensive theories which take into account, even approximately, the interactions between chains or more exactly the surface density of polymer segments^{8,18,19,25,26} indeed predict an appreciable variation of $p(N,z)$ with N . For example, in the formulation of Jones and Richmond²⁶, although $p(N,z)$ has a more complicated analytical form than previously, it still decreases exponentially for large z and depends on N through a factor $N\sigma(1-2\chi)$ where σ is the grafting ratio (in molecules/nm²) and χ the well known parameter of interaction between solvent and polymer introduced by Flory.

Comparison with the experimental results

When comparing these predictions with our experimental results it appears that the measured ratio P_f/P_s does indeed vary according to Van't Hoff law. A can therefore be considered as an adsorption energy and B as a mean entropy loss by a monomer unit. Facchini⁵ has confirmed that in our temperature range the grafted unlabelled PEO chains were strongly adsorbed in the presence of C₆D₆ (more than 90% of the segments), i.e. we are actually in a regime where $\epsilon/kT \gg 1$.

Thus, it is the interpretation of the variation with the molecular mass which is critical.

The spectra and the P_f/P_s values for grafted labelled monoethylene glycol clearly suggest that the chosen spectral analysis is not pertinent in this case.

The fact that the ratio of populations does not depend on the chain length for the other oligomers, like di-, tri- and tetraethylene glycol, suggests that the latter adopt a conformation where the monomers of the grafted molecules do not compete with each other and with the label for surface site. Moreover since there is no variation of P_f/P_s as a function of the surface segment density, the models founded on random flight appear completely impracticable for the description of these short chains.

In contrast, for the longer chains a behaviour typical for interacting polymer is observed: the ratio P_f/P_s depends on N in the expected order. When the surface density of segments increases, the layer extends into the solution. Indeed the values of the parameters (Table 1) give

PEO 400	$N\sigma = 5.4$ segments/nm ²
PEO 600	$N\sigma = 7.0$ segments/nm ²
PEO 2000	$N\sigma = 9.0$ segments/nm ²

Thus a behaviour typical for oligomers is clearly distinguished from another typical for polymers, with these very flexible molecules.

The experimental values of the adsorption energies (Table 3) are rather high, especially those below the melting point of the solvent. However, comparison with the published adsorption enthalpies²⁷ is difficult because our integral enthalpy results from the adsorption enthalpy of polymer segments, the simultaneous desorption energy of the solvent from the surface and the solute/solvent energy variation. Below the melting point of the solvent, they decrease with the molecular weight and the surface density of segments.

Our measurement on the concentration profile should also be compared with the small-angle neutron scattering studies by Vincent and coworkers²⁸. Currently the mea-

sured probability for the tails to be away from the surface is compared with the provisions of the theories^{18,19}.

CONCLUSION

The values of the ratio of fast to slow populations of label have been measured for poly(ethylene glycol) chains of different molecular masses grafted onto silica.

The measured values in the given temperature range suggest that one can distinguish between two different behaviours, one for the oligomers, the other for the polymers. The oligomer chains do not interact appreciably with each other, a fact which is consistent with a representation of flexible 'brush bristles'. The polymer chains, however, do interact with each other in a manner consistent with the random walk models, and a representation of the layer as an array of weakly overlapping partly collapsed coils.

ACKNOWLEDGEMENTS

The authors thank L. Facchini for many helpful and stimulating discussions and C. Noel for her constant interest. This work was partly supported by the Marcel Boll Award for Research 1980.

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