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ORIGINAL CONTRIBUTION

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Unwinding of poly(ethylene oxide) chains grafted on silica under a shear flow of cyclohexane, observed by spin-labelling

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Abstract Poly(ethylene oxide) chains of molecular weight 2000 have been grafted on pyrogenic silica, spin-labelled at their free end and put into contact with cyclohexane. The electron paramagnetic resonance of the nitroxide free radical gives evidence of two specific environments: namely, trains adsorbed on the solid with a restricted motion and loops and tails protruding into solution with a high mobility. The dynamic parameters such as the rotational correlation time and the static ones such as the fraction of each population have been evaluated. Under a flow of solvent the unwinding of the chains has been observed with increasing flow rate in our experimental range. Some mechanisms are proposed to explain this behaviour.

Key words Solid/fluid interface processes · Amorphous and polymeric materials · Magnetic resonance and relaxation

Introduction

The equilibrium properties of polymers constrained at solid interfaces have been extensively studied over many years and substantial agreement between theoretical and experimental studies has been reached [1, 2]. More recently several studies have focused on non-equilibrium properties and particularly on the rheological behaviour in response to applied perturbations such as the frictional forces imparted by solvent flows in the neighbourhood of adsorbed or grafted layers [3–8]. The simplest method extensively used is the measurement of the reduction of volume flow in narrow capillaries coated with the polymer. Viscosity or volume flow determinations yield an average hydrodynamic thickness. The relationship between this parameter and the structural features of the adsorbed polymer is, however, not so clear. It seems therefore appropriate to investigate more precisely whether another technique giving molecular information on the chains at the surface cannot give more direct insight into the deformation, extension, stretching, unwinding or compression of the macromolecules.

Here the spin-labelling method is extended to situations where it can indeed give some experimental data on the fraction of loops and tails as a function of flow rate [9]. It is already established that the electron paramagnetic resonance (EPR) signal of nitroxide free radicals is very sensitive to the microscopic environment inside the surface layer and in particular lines characteristic of trains adsorbed on the surface and lines characteristic of loops and tails protruding in solution can be distinguished. It is tempting to investigate how these two parts of the concentration profile react to an external perturbation such as a shear flow of solvent. The system chosen is a layer of poly(ethylene oxide) grafted on silica and labelled at its free end and the flowing solvent is cyclohexane.

Experimental

Materials

The samples are similar to those used previously [9].

Silica

The silica was pyrogenic Aerosil 300 from Degussa (Degussa, Frankfurt a. M., Germany). Its specific surface area measured by nitrogen adsorption is 310 m^2/g. It is not porous on a molecular scale but consists of small aggregates of particles of about 10-nm diameter. This shape is probably important because it can influence the velocity field of the solvent around the solid. At the surface about 3.3 hydroxyl groups per nanometre are distributed more or less randomly and can further react with the polymer [10, 11].

Polymer

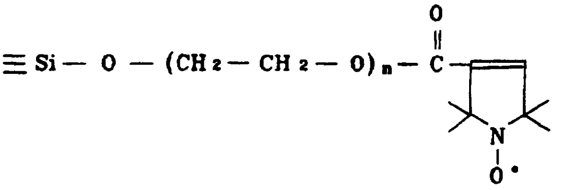
The polymer was poly(ethylene oxide) 2000 from Fluka (Fluka, Saint Quentin Fallavier, France). Its molecular weight is about 1880 g/mol and it bears about 1.6 terminal OH groups which can react both with the solid silica and with the free radical.

Grafting reaction

The grafting reaction was the direct esterification of the silanol groups of the silica by the OH groups of the polymer. The silica is dehydrated, agglomerated in acetone, and dried at 150 °C. It is then dispersed in a poly(ethylene oxide) solution to achieve the desired impregnation ratio. The solvent is evaporated, the silica dried in a vacuum of 2×10^{-3} Pa and maintained in a nitrogen atmosphere. It is kept at a temperature of 200 °C for 1 h. When the reaction is complete, the excess polymer is removed by a long extraction with acetone in a Soxhlet for 20 h. Finally, the grafted silica is dried in a dynamic vacuum of 0.1 Pa for 24 h at 60 °C. Four samples with the following grafting ratios determined by pyrolysis weight loss at 800 °C were prepared: 0.045, 0.057, 0.126 and 0.42 molecules/nm^2.

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 Organic Chemical (Rochester, New York, USA). This label in its acid chloride form was attached to the grafted chains. A typical chemical formula of a grafted labelled polymer chain is



It could be argued that the specific behaviour of the label greatly perturbs the conformations of the chains but it has been confirmed independently that the adsorption energy of a segment of poly(ethylene oxide) is higher than that of the label itself and, therefore, that the label follows the configuration adopted by the chains [12].

Solvent

The solvent was cyclohexane (Prolabo, Paris, France), which is a solvent of poly(ethylene oxide). Its boiling point is 60 °C. This solvent was also chosen for safety reasons because under flow conditions the set-up is more or less open.

EPR Spectroscopy

Samples and apparatus

In static conditions all the samples were prepared in Pyrex tubes of 4-mm diameter. The samples were degassed and sealed after repeated freeze–pump–thaw cycles. Under a flow of solvent the powders were kept in the middle of the EPR cavity over a bottleneck. This was made by melting an open spectroscopy tube also of 4-mm diameter. The driving force for the vertical flow was gravity and the force was adjusted through the height of liquid in the upper part of the tube.

The EPR spectra were recorded on a Varian E-4 (Varian, Palo Alto, USA) spectrometer operating in the X-band at 9.15 GHz. The temperature was regulated by a Bruker BV 2000 (Bruker, Karlsruhe, Germany) temperature controller and before recording each spectra 10 min was allowed for thermal equilibration of the sample.

Analysis of the EPR spectra

The shape of the EPR spectra of nitroxide free radicals is very well known and has been shown to be mostly sensitive to the molecular Brownian motion of the label [13]. The lines originate from transitions between the levels given by the spin Hamiltonian

$$H = SgB + IAS$$

where S is the spin of the unpaired electron, I the spin of the nitrogen nucleus, g the gyromagnetic tensor and A the hyperfine tensor. When the motion is fast (the rotational correlation time falls in the range 3×10^{-11}–3×10^{-9} s) the spectrum consists of three well-resolved Lorentzian lines explained by Kivelson theory [14]. This theory can be included in computer software relatively easily and the calculated spectrum can be adjusted to fit the experimental one. In the slow tumbling region (rotational correlation time above 3×10^{-9} s) the shape of the spectrum becomes influenced by the anisotropic part of the spin Hamiltonian and can be calculated using the more comprehensive Freed theory [15]. Here only the simplified approach of Freed has been used [13]. The most interesting region for our studies appears in an intermediate temperature range, where lines arising from the two extreme shapes distinguished before are displayed simultaneously. Using a simulation both contributions were extracted and the dynamical parameters, namely the rotational correlation times, and the statistical parameters, namely the fractions of each, were evaluated.

Results

Results in static conditions

A typical spectrum of the grafted labelled poly(ethylene oxide) samples in the dry state is shown in Fig. 1. This clearly shows a slow-motion shape indicating that the chains are closely constrained in the vicinity of the silica

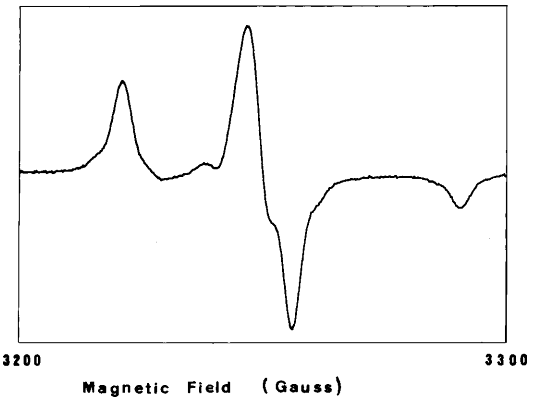


Fig. 1 Typical spectrum of the grafted labelled poly(ethylene oxide) in the dry state

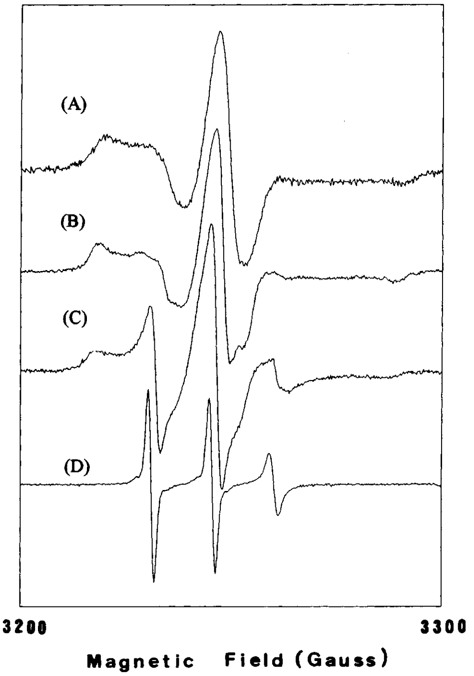


Fig. 2 Typical spectra of grafted labelled poly(ethylene oxide) in contact with cyclohexane at room temperature. The samples have the grafting ratios 0.045 (*A*), 0.057 (*B*), 0.126 (*C*), and 0.42 (*D*) molecules/nm^2

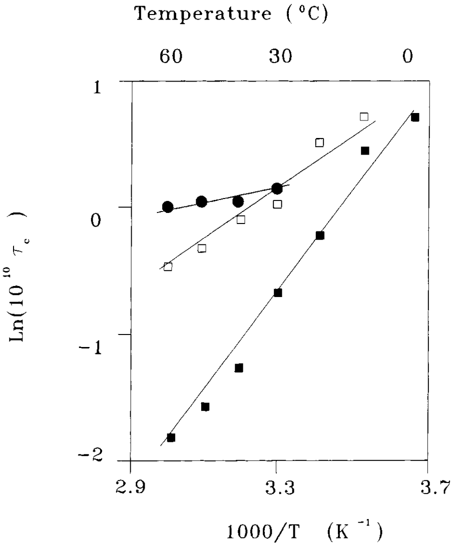


Fig. 3 Evolution of the rotational correlation times of the fast fraction of labels as a function of the inverse of absolute temperature for the samples with the grafting ratios 0.057 (●), 0.126 (□) and 0.42 molecules/nm^2 (■)

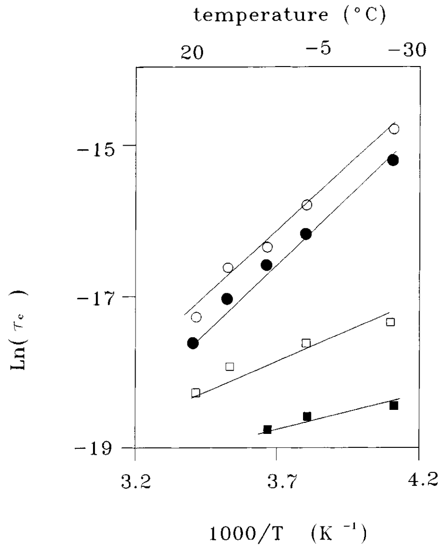


Fig. 4 Evolution of the rotational correlation times of the slow fraction of labels as a function of the inverse of absolute temperature for the samples with the grafting ratios 0.045 (○), 0.057 (●), 0.126 (□), and 0.42 molecules/nm^2 (■)

with little molecular motion. In Fig. 2 typical spectra for the four grafting ratios at room temperature in contact with cyclohexane are shown. They evolve regularly: when increasing the grafting ratio the fast fraction of labels also increases. The fast fraction of labels has been attributed to tails (or could also be loops) protruding into solution. The slow-motion fraction of labels has been attributed to trains with restricted mobility due to the hindrances caused by the solid silica. From the shape of the spectrum an indication of the concentration profile can therefore be extracted. When the coverage increases the chains interact with each other, repel each other and extend into solution where the label has a faster motion. The evolution of the rotational correlation times of the fast fraction as a function of the inverse of the absolute temperature is shown in Fig. 3. When increasing the temperature this time becomes shorter and the mobility increases due to thermal agitation. Moreover the slope of the lines can be explained assuming an Arrhenius law, as an effective activation energy; this slope becomes greater as the grafting ratio increases, indicating that at low coverage the barrier to be overcome to reach another position is relatively small, whereas at high coverage the interactions between segments render it higher. At a given temperature the rotational correlation time is shorter the greater the grafting ratio, a trend in line with what has been explained previously on the interactions between chains extending into solution. The evolution of the rotational correlation times of the slow fraction of labels as a function of the inverse of the absolute temperature is shown in Fig 4. The general trends are rather similar to those observed previously. It is remarkable to see that the influence of the solvent on the mobility is even felt in the contact region with the solid which suggests that cyclohexane is not such a bad solvent for these chains in these conditions. Again the mobility increases when the temperature increases and at a given temperature increases when the grafting ratio increases. From this point of view, even if the EPR spectra distinguish clearly between loops and tails on one hand and trains on the other, the overall picture is rather homogeneous over all the concentration profile. The evolution of the ratio of the population of labels in solution over the population of labels adsorbed is shown in Fig. 5. When the temperature increases the fraction of labels in solution increases. The thermal agitation competes with the adsorption energy of surface sites and fewer segments remain held by the solid. At a given temperature the fast fraction increases with grafting ratio: the chains interact more with their neighbours and protrude in solution going from a mushroom conformation to a stretched brush.

Results under a flow of cyclohexane

First, the sample best suited for study under flow was selected. The percentage of labels with a fast motion at room temperature is given as a function of the grafting ratio in Table 1. It was checked that this qualitative picture did not change drastically when the samples were under a flow of solvent. When the grafting ratio is low the chains lie rather flat on the surface and are little affected by the solvent running outside the layer whatever the flow rate. When the grafting ratio is high the chains are extended and only labels with a fast motion are detected and therefore the eventual extension of the polymers cannot be measured. The sample displaying the most complete set of data subject to variations when changing the flow rate is that with a grafting ratio of 0.126 molecules/nm^2 and the following discussion is restricted to it. Second, it appears that the starting point for the experiment could not be reproduced exactly each time. The process of filling the tube with cyclohexane in the experimental set-up has a certain importance: progressive and gentle filling can have an influence on the conformations of the chains at the beginning which is different from that obtained with instantaneous addition of the solvent. It is apparent that better control of these conditions is required in the future. However, as we wanted to highlight the main features of the phenomena and to investigate the qualitative behaviour as well as the feasibility of the measurement this uncertainty was not completely reduced. The evolution of the rotational correlation time of the fast fraction of labels as a function of the flow rate is shown for a first measurement in Fig. 6. It decreases as the flow rate increases. The more solvent passes through the chains the greater the mobility. The corresponding percentage of the fast fraction of labels as a function of flow rate is shown in Fig. 7: it increases as the flow rate increases. The solvent pulls the chains and they extend more into solution. The same kind of measurement was repeated giving the rotational correlation time (Fig. 8) and the percentage of the fast fraction of labels as a function of the flow rate (Fig. 9). The trends are the same even if the numerical values are somewhat different. At this point it is appropriate to recall that the silica powder is packed above a bottleneck in the tube. Each time the packing can be slightly different. Moreover the flow of the solvent through the

Table 1 Percentage of the labels with a fast motion at room temperature as a function of the grafting ratio

Grafting ratio (molecules/nm^2)	Percentage of labels with a fast motion
0.045	~0
0.057	~0
0.126	22
0.42	100

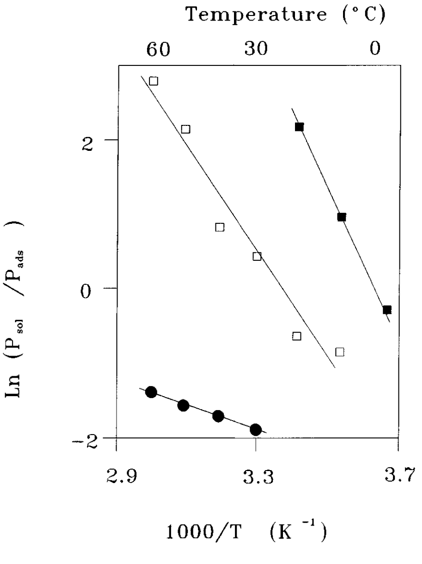


Fig. 5 Evolution of the ratio of the population of the fast motion labels over that of the slow motion labels as a function of the inverse of absolute temperature for the samples with the grafting ratios 0.057 (●), 0.126 (□) and 0.42 molecules/nm^2 (■)

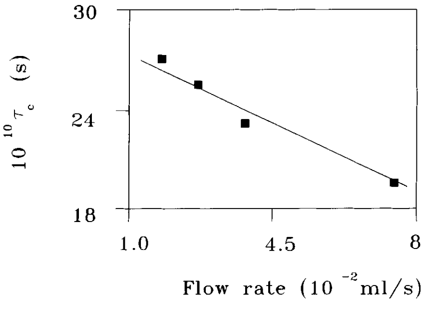


Fig. 6 Evolution of the rotational correlation times of the fast fraction of labels as a function of the flow rate for the samples with the grafting ratio 0.126 molecules/nm^2 (first experiment)

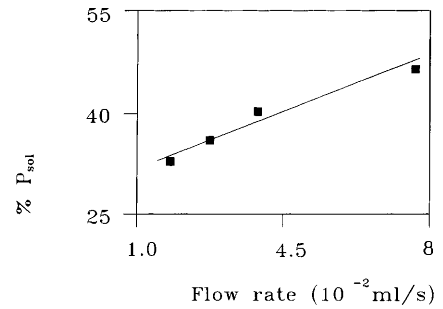


Fig. 7 Evolution of the percentage of the fast fraction of labels as a function of the flow rate for the samples with the grafting ratio 0.126 molecules/nm^2 (first experiment)

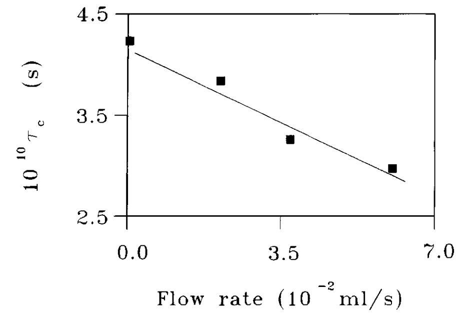


Fig. 8 Evolution of the rotational correlation times of the fast fraction of labels as a function of the flow rate for the samples with the grafting ratio 0.126 molecules/nm^2 (second experiment)

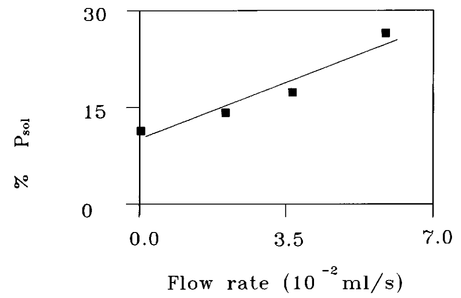


Fig. 9 Evolution of the percentage of the fast fraction of labels as a function of the flow rate for the samples with the grafting ratio 0.126 molecules/nm^2 (second experiment)

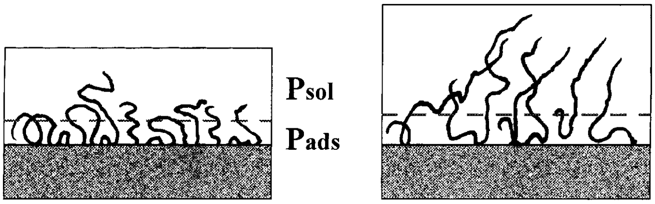


Fig. 10 Unwinding of the statistical coils under the flow of solvent

pores can be highly heterogeneous with places corresponding to a vertical opening with much solvent going through fast whereas other places can even be local stagnation points. EPR spectroscopy is relatively sensitive but it gives a signal which is the sum of the contributions of about 10^{17} spins which again can be in very different environments. The measured overall flow rate does not precisely describe all the different situations which are present in different proportions. It is all the more remarkable that the average result of chains elongated by the flow and experiencing a faster motion holds well under our experimental conditions.

Discussion

Expected phenomena

The concentration profile of a macromolecular layer on a solid surface has been extensively studied experimentally as well as theoretically in static conditions. Mean field [1] and scaling [2] models have been developed. Even if the end segment does not have specific interactions with the solid [12] it seems likely that long dangling tails which contribute mostly to the outer thickness of the layer [16–18] exist and that these should be the most sensitive to the flow of solvent.

Some theoretical models involve the application of shear to polymer brushes and investigate the crossover between low-shear linear elastic behaviour to a nonlinear regime in which the brush swells [19]. Since the flow does not penetrate into the brush, only the free ends are submitted to solvent friction. However, the opposite case of a few or even ideally of one tethered chain deformed in strong flows has also been considered and the deviation from a coil shape has been calculated [20]. Not only the steady state but also the transients, i.e. the unwinding of ideal or swollen chains subjected at a time $t=0$ either to a force or to a flow of the solvent, have been studied [21]. When the flow velocity is allowed to vary weakly spatially it can cause a coil–stretch transition, a situation which is often encountered in practice [22]. It has also been suggested that the thickness of polymer brushes can increase in flow leading to novel normal forces between brushes in shear flows. This is the basis of a recent proposal to utilise polymers grafted to the walls of porous media to produce novel pressure-sensitive microvalves. This is the situation in strong permeation flows when the polymer grafted to a permeable surface is subject to hydrodynamic pressure gradients normal to the polymer layer [23]. Another typical industrial problem, encountered in fabric softening, has been addressed through mesoscale computer simulation of the effect of coating two opposite walls with amphiphilic molecules on the fluid structure, friction and viscosity of a pure solvent [24].

With optical tweezers plus fluorescent labels it is now possible to force, and to observe, the stretching and the relaxation of a single polymer chain. The chains can be subjected to a force [25] or to a flow of the solvent [26]. Extension and manipulation of individual biopolymers is generally performed by first anchoring one end of the molecule at a solid matrix; stretching may then be achieved by viscous drag, electrophoresis or optical forces. DNA has proven to be an efficient molecule for this purpose. In another process called "molecular combing" molecules attached at one end to a solid surface were extended and aligned by a receding air–water interface and left to dry on the surface [27].

More globally the relationships between the molecular dimensions of polymers adsorbed on solid surfaces and the "hydrodynamic thickness" obtained by viscosity or flow rate measurements through capillaries have been approached by solving the corresponding Navier–Stokes equation. An exponential density distribution of polymer segments in the vicinity of the adsorbing interface was used [3, 4], which corresponds to the mean field profile of loops and is not completely representative of the actual profile. Some authors proposed that inhomogeneous adsorption on the surface may produce a circulating velocity pattern, in regions of low adsorption, as though these act as cavities in the side of the flow channel. This circulation was speculated to push polymer segments perpendicular to and away from the wall [5]; however, there is relatively little evidence for the "spotty" adsorption proposed. In general the effective hydrodynamic thickness is found to be much larger than the root-mean-square end-to-end distance of the free macromolecules in solution. Sometimes in certain regimes it can also decrease with increasing shear stress [6]. It is suggested that there exists a critical shear rate above which the hydrodynamic thickness decreases with increasing shear rate. Below this critical shear rate, shear-induced disentanglement of subloops and the detachment of weakly anchored trains may be responsible for the rise in hydrodynamic thickness [7]. A different explanation has also been proposed. There seems to be no shear-thickening if the pores are straight with smooth walls, i.e., in pure shear flow. Variations in cross-sectional area of channels or wall rugosities in straight pores are necessary to produce solvent flow perpendicular to the surface, i.e., a local elongational flow [8].

Observations

The results of our measurements can be qualitatively compared with predictions and earlier results using other techniques. Clearly in our regime we observe a thickening of the layer when increasing the overall flow rate. Our samples are indeed prepared in such a way, by packing silica powder over a bottleneck in a tube, that channels with some irregularity or nonuniformity in mean-cross-sectional area appear in the porous medium. Such channels introduce both extensional straining components into the local velocity gradient tensor and velocity components perpendicular to the boundary surfaces, which can easily stretch macromolecules perpendicularly to the walls. Moreover the EPR signal is the sum of the contributions of about 10^{17} molecules/g and many different situations for each individual chain should be taken into account. Even if the overall trend is relatively similar, it should not be confused with the conceptually simpler case of a single chain reacting to an external field. For the physicist DNA resembles an ideal chain, is a molecule with a relatively high molecular weight and is well suited for such studies. Here, by spin-labelling, the behaviour of many different chains could be investigated in heterogeneous environments and the situation is much more comparable to what is observed in most practical systems. To extend the range of use of the EPR spectrometer, whose feasibility has been demonstrated, it would probably be appropriate to better control the overall flow rate with a convenient pump, and to improve the packing process to render it more reproducible. Knowing the complexity of the shape of silica particles [10, 11], even this last requirement does not seems so easy to satisfy. On the other hand, the more the system is purely defined and characterises each parameter well, the less it bears resemblance to most problems encountered in applications where the limiting factor can be completely different. Therefore with its advantages and drawbacks the spin-labelling technique can indeed add to our knowledge of the conformation and mobility of macromolecules at interfaces under a flow of solvent, and it gives an overall picture which is simultaneously derived from the signals of individual chains and from their integration over a large ensemble, providing a balanced view between specificity and generality.

Conclusion

The conformation and the mobility of poly(ethylene oxide) chains grafted on silica in contact with cyclohexane have been investigated in static conditions. They have been compared with what is observed under a flow of solvent. The unwinding of the chains, or more precisely the thickening of the layer, has been observed with increasing flow rate. This result is consistent with the existence of local elongational flows originating from irregularities in the packed silica powder. Spin-labelling has demonstrated its efficiency in these unusual conditions of flow of solvent through the EPR cavity and should be considered as a useful investigative technique in this case.

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