

Polymer Communication

Transport of a poly(ethylene oxide) solution through porous coated silica studied by spin labelling

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Abstract

Poly(ethylene oxide) (PEO) chains of molecular weight 4000 have been labelled at their free end by a nitroxide free radical and adsorbed on silica in cyclohexane. A solution of PEO 10 000 was allowed to flow through the impregnated silica in an Electron Paramagnetic Resonance spectrometer and the decay of the signal recorded as a function of time. The exchange of the short chains by the longer ones and the transport through the quenched disorder proceeds linearly with time. This observation could be characteristic of a diffusion mechanism similar to the Darcy law as the limiting factor of the whole process in the time regime used. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

By far most of the studies devoted to polymers at interfaces dealt with systems that were equilibrated. Practical situations like paints, adhesion or colloid stabilisation involve the building of a polymer layer on a solid surface. To give a rational explanation to each different application much fundamental work has been done on model systems, both experimental [1] and theoretical [2].

Yet it is also important to consider the dynamics of polymer chains. The exchange and transport through porous silica is of interest in the context of macromolecular separation by chromatography, electrophoresis, drainage for oil recovery, and also more fundamentally to elucidate the phenomenon of reptation. For the adsorption process itself and the exchange of chains many time scales are relevant [3,4]. Different other techniques have already been used to understand the kinetics of establishment of adsorption equilibrium, but here we investigate how the spin labelling method can be used for this purpose [5]. Poly(ethylene oxide) (PEO) chains of low molecular weight are labelled by a nitroxide free radical and adsorbed on silica. A fresh solution of higher molecular weight PEO is allowed to flow through the electron paramagnetic resonance (EPR) spectrometer and the decay of the signal is monitored as the short chains are desorbed and progressively replaced by the longer ones.

2. Experimental

2.1. Materials

2.1.1. Silica

Pyrogenic silica, Aerosil 200 from Degussa (Degussa, Frankfurt am Main, Germany) was used. It is prepared by the combustion of SiCl_4 in flame. It is composed of small particles of about 12 nm diameter aggregated in larger clusters and its specific surface area measured by nitrogen adsorption is $200 \text{ m}^2/\text{g}$. It bears about 2–4 OH per nm^2 which can be hydrogen bonded to the ether oxygen of the polymer [6,7].

2.1.2. Polymer

The polymers used are PEO from Fluka (Fluka, Saint Quentin Fallavier, France) with two molecular weights. PEO 4000 has a molecular weight of 4000 g/mol, a melting temperature of 59–61°C and a polymerisation index of 91. PEO 10 000 has a molecular weight of 10 000 g/mol, a melting temperature of 63–65°C and a polymerisation index of 227. These linear polymers are playing an increasingly important role in biomedical technology in part because of their newly found ability to render surfaces relatively inert to attack from the immune system.

2.1.3. Solvent

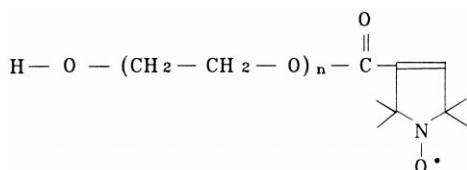
The solvent was pure cyclohexane (Prolabo, Paris, France) with a melting point of 6.5°C and a boiling

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temperature of 80.7°C. It has a relatively low dielectric constant and is appropriate for EPR measurements. Its toxicity is relatively low even if it should not be inhaled.

2.1.4. Spin labelling

The nitroxide free radical was 2,2,5,5-tetramethyl-3-pyrroline-1-oxyl acid from Eastman (Eastman Organic Chemical, Rochester, New York, USA). This radical was fixed in its acid chloride form on free end alcohols of the PEO 4000 chains. The typical chemical formula of a labelled PEO 4000 chain is:



2.1.5. Adsorption of the polymer

All the polymer solutions were prepared by stirring the polymer gently in the presence of cyclohexane, which appears as a relatively bad solvent. The remaining powder was removed and the supernatant was a nearly saturated solution of less than 0.5 mg/ml concentration. First the PEO 4000 solution was brought into contact with silica in the EPR tube and a steady flow achieved the desired coverage. It is probable that it corresponds roughly to the plateau value of the adsorption isotherm. Previous experiments have given relatively strong evidence that the presence of the label does not perturb the adsorption process on silica [5] much. Of course if the nitroxide free radical had a high affinity for the solid the picture would be very different as it would act as an anchor and the polymer as a buoy [8]. The silica was then completely washed with pure cyclohexane to remove all unattached chains until the EPR signal was constant. After that the PEO 10 000 solution was allowed to flow at a constant rate through the sample and it replaced progressively the PEO 4000, an exchange that was followed through the decay of the EPR signal.

2.2. EPR spectroscopy

2.2.1. Samples and apparatus

All the experiments in a flow of solvent or solutions were performed in the spectrometer, in a Pyrex tube of 4 mm diameter except in the middle of the cavity where a bottleneck prevented the silica from falling out. The flowing of pure cyclohexane checked that this was indeed not the case. The EPR spectra were recorded on a Varian E-4 (Varian, Palo Alto, CA) spectrometer operating in the X-band at 9.15 GHz.

2.2.2. Analysis of the spectra

The spectra of nitroxide free radicals are very well known [9]. Depending on the molecular mobility of the label they

have different shapes. If the motion is fast then the three well-resolved Lorentzian lines explained by the Kivelson theory [10] are expected. If the motion is slow then the anisotropic part of the spin Hamiltonian is not averaged and broader peaks shifted relative to the previous ones appear. They are explained by the much more comprehensive Freed theory [11]. In fact in our case the spectra were always typical of a superposition of the two kinds motions attributed, respectively, to the trains immobilised on the solid and of loops and tails mobile in solution. However no attempt was made to analyse more precisely the information contained in these components. They indicate, at least, that the chains spread onto the surface and adopt a relatively flat conformation. The relevant quantity, which was recorded, was the total surface area of each spectrum evaluated in arbitrary units but in a coherent manner to allow some comparisons. Indeed as is usual in magnetic resonance experiments it can be shown that this surface, which is proportional to the total magnetisation M , is also proportional to the number of resonating spins following the expression

$$M = N \frac{g^2 \beta^2 S(S+1) H_0}{3k_B T}$$

where N is the number of spins, g the spectroscopic splitting factor, β the Bohr Magneton, S the spin, T the temperature and H_0 the magnetic field.

3. Results

A typical spectrum obtained for labelled PEO 4000 adsorbed on silica is shown in Fig. 1. As has already been mentioned it consists of two major components [5]: three relatively narrow lines caused by the tails protruding into solution and experiencing a fast motion; and a broader component caused by the trains in contact with the solid with a hindered motion. Therefore the chains are indeed adsorbed on the solid and moreover the slow motion part being larger as they are spread on silica, and adopt a relatively flat conformation, indicating that there is indeed strong adsorption. It has been checked that this spectrum is not altered by a flow of pure solvent. It could then be concluded that the chains were nearly irreversibly fixed and could not be displaced by the small molecules of cyclohexane. Similarly the reverse experiment trying to displace the PEO 4000 by a smaller non-labelled PEO chain did not show any detectable effect. All the experiments have been conducted at room temperature (22°C), as it is more difficult to have a flow of the solvent and a thermal regulation simultaneously.

The situation is no longer the same when a flowing solution of PEO 10 000 is passed through the sample. The integrated intensities of the EPR signals in three different experiments are reported in Figs. 2–4 as a function of time. A few remarks about the set-up are in place here. A very

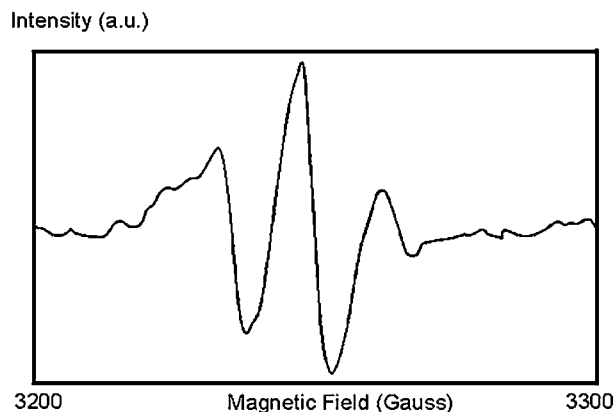


Fig. 1. Typical EPR spectrum of labelled PEO 4000 adsorbed on silica in a steady state flow of cyclohexane.

simple procedure was adopted. The solution flowed at a constant overall rate of about 3 ml/h in our tube of 4-mm diameter moved only because of the influence of gravity. In fact the gravity drainage is now recognised as an important method for oil recovery from heavy oil and depleted oil reservoirs, which has been modelled with sand columns [12]. This does not at all imply that the flow was really uniform and laminar at a molecular scale. It must be recalled that to ensure a sufficient surface area to give coverage detectable by the EPR signals it was necessary to use a silica powder, which is highly irregular, and the shape of the solid network through which it is percolating affects the flow of solvent. Some places are subject to a strong and fast flow in a direction parallel to the solid, some others experience a slower flux and perhaps somewhat tilted following another orientation than strictly vertical. Finally some points may even be stagnation points. All the details of the ways followed by the solvent are lost in the overall picture given by the integrated intensity. Here the interaction of polymer molecules with the solid surface takes place

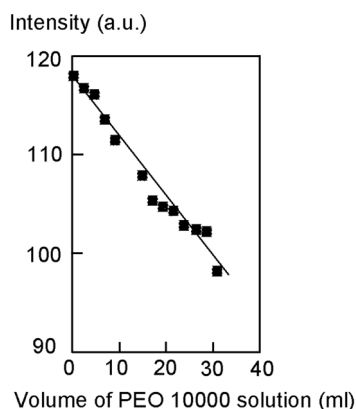


Fig. 2. Evolution of the amount of labels and therefore also of the amount of adsorbed PEO 4000 as a function of the volume of the PEO 10 000 solution having flown through the sample. Two successive points are separated by 16 min (first experiment).

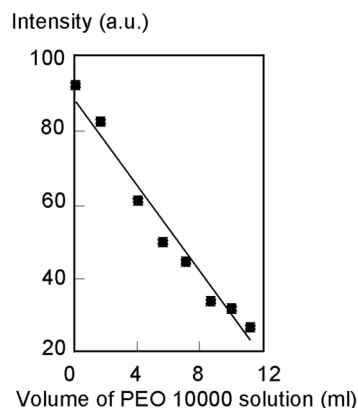


Fig. 3. Evolution of the amount of labels and therefore also of the amount of adsorbed PEO 4000 as a function of the volume of the PEO 10 000 solution having flown through the sample. Two successive points are separated by 16 min (second experiment).

under the application of an external flow field. The flow field deforms the polymer molecules and further enhances the conformational changes in the interfacial region. An investigation of the flow through loops and tails has indeed been presented in Ref. [1], but of course the relevant parameters describing the system are not necessarily the same here.

It is all the more remarkable that our experimental results fall into a very simple scheme. The geometry of the system is such that transport rates cannot easily be estimated, so that it is not possible to correlate the conclusions with a definite rate-determining step. However it is apparent from Figs. 2–4 that the signal in all the three cases, differing in the packing of the silica powder, is decaying linearly with time. This result seems very well documented by our data, the correlation coefficients of the linear regression being always higher than 0.92 and sometimes than 0.97. The slopes and origin of the lines can be different but the qualitative

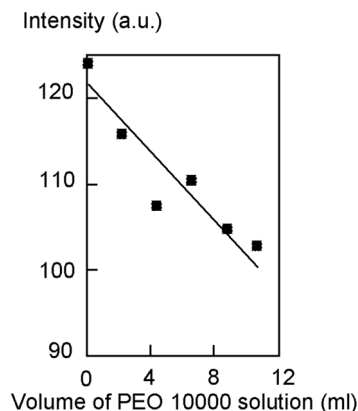


Fig. 4. Evolution of the amount of labels and therefore also of the amount of adsorbed PEO 4000 as a function of the volume of the PEO 10 000 solution having flown through the sample. Two successive points are separated by 16 min (third experiment).

behaviour remains identical. It is therefore the major result, which holds regularly. The similarities (linear variation with time) and differences (in slope for example) between Figs. 2–4 show clearly that the exponent is more firmly established and that the other parameters cannot be completely explained. As will be discussed below, this is not completely unexpected in view of the literature, but the fact that it has been established by the EPR spectroscopy seems promising to the best of our knowledge and appears to open a new method of investigation of these phenomena.

4. Discussion

4.1. Expected phenomena

The solvent from which they were adsorbed cannot usually readily desorb polymers. In a practical sense, the adsorption is thus irreversible. However they may readily exchange against the polymer molecules coming from the solution and there is a steady-state traffic of macromolecules between the adsorbed state and the unadsorbed state. Pioneering theory, experiments, and simulations by Pefferkorn, Varoqui and co-workers endeavoured to understand the kinetics of establishment of adsorption equilibrium [13–17]. Some very simple limiting cases can be described. If diffusion is the controlling step, the coverage Γ should vary with the time t like $t^{1/2}$. If simultaneously the convection is present then the solution given by Leveque [18] is $\Gamma \sim t$; and if the mechanism is rather a chemical kinetic with surface sites then again $\Gamma \sim t$. Only a comprehensive study made with varying velocity gradient can therefore discriminate between these different mechanisms. Moreover it is quite possible that here several adsorption and desorption processes take place successively as for the plateaux in a chromatography column. Experimentally the exchange of short PEO chains by long ones was also investigated by means of reflectometry [19]. The short ones adsorb initially. Granick et al. have emphasised the role of the topological constraints on the displacement process [20].

The transport behaviour of a polymer chain itself is generally studied by analysing the time dependence of the mean square displacement of a monomer of a chain (here the label) and that of the centre of mass of the chain molecule. A common practice in such analysis is to look for the leading power-law dependence of these displacements described by the exponents ν , $< R^2 > \sim t^\nu$. The magnitude of these power law exponents is well known in the melt from the short to the long time regimes, i.e. for a monomer motion $\nu = 1$ (diffusion), $1/2$ (Rouse), $1/4$ (constrained Rouse), $1/2$ (reptation) and 1 (diffusion) while for the centre of mass $\nu = 1$, $1/2$ and 1 . Heterogeneity because of quenched barriers of a porous medium makes the problem more difficult altering the local and global motion of the chains as well as their conformations. In the absence of quenched barriers the field drives the chain to drift and

one would expect a crossover from a diffusive behaviour at short time-scales to a drift-like motion in the long time regime [21]. One may expect not only the crossover behaviour to change but also the exponents for the power-law dependence may be altered as the field begins to compete with the barriers [22–24]. In addition to the Rouse and reptation models, there is a third regime (entropic trapping) where large open spaces in the medium can cause the polymer chains to slow down more than that anticipated on the basis of reptation (elucidated by Muthukumar and Baumgartner [25–28]).

4.2. Observations

Our experimental results clearly show a linear behaviour of the amount desorbed with time $\sim t$. This simple result can be explained by many of the different laws exposed above. The overall flow of solvent certainly implies convection even if the velocity gradient can be different from place to place due to the packing of the silica powder. Although the simple kinetics observed is consistent with the diffusion/convection model, which could also apply for small molecules, the exchange mechanism must be fundamentally different. Whereas small molecules are released at once, the displacement into a polymer solution must have proceeded zip like, a small number of segments at a time and finally the exchange of PEO molecules, which are very flexible, should be relatively fast [19]. In fact it seems rather that the detailed microscopic behaviour, which is now under clarification as shown in the above references, has no direct influence on the overall evolution with time. At present it is still not possible to attribute this outcome to the limitation of the range of experimental parameters for the packing, or to a limiting rate due to a specific step in the phenomena. It is tempting to search for a phenomenological law like the Darcy law, which would describe this outcome whatever, the underlying complex microscopic data.

The practicability of the method of spin labelling is demonstrated and valuable information could be obtained similarly in other situations. The spin-labelling method is sensitive to about 10^{17} spins/g and in a range depending on the mobility of the label of about four decades, which gives a sufficient window of observation. The time necessary to record a spectrum can vary between a few minutes and an hour. It seems indeed interesting to investigate further the potential of this spectroscopy for such studies, for example by varying the flow rate in a larger range with the help of a pump. In such conditions it seems well possible that other regimes will be accessible.

5. Conclusion

The exchange of short chains of PEO by longer ones has been followed by the spin labelling technique. The decay of the signal characteristic of the short chains has been shown to be linear with time and among the models proposed

several individual mechanisms are consistent with this observation. A simple overall result like this Darcy law suggests that many molecular details of the desorption process are not rate limiting in this case or that other experiments in conditions where the velocity gradient and other parameters can more easily be varied could discriminate between the different molecular steps involved.

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