

## MOBILITY OF SPIN LABELLED POLY(ETHYLENE OXIDE) CHAINS GRAFTED ON SILICA

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**Abstract**—Samples of spin labelled poly(ethylene oxide) of average molecular weight 6000 and 400, grafted to extents of 20% and 15% by weight on silica gel, have been examined at various temperatures. EPR measurements at X-band frequency showed composite spectra, characteristic of two mobility states. A thermally activated process has been demonstrated. A two layer model is proposed.

### INTRODUCTION

Spin labelled polymers as mobility probes can be used to study the swelling or solubilization of poly(ethylene oxide) chains grafted on silica. Owing to the chemical preparation, the spin label is attached at the free end of the polymer chain grafted on silica. Consequently the EPR measurements are focused on the mobility of the tail. Influences of a solvent for the polymer and of molecular weight are thus manifest. The analysis is extended here to a wider temperature range than previously [1].

### MATERIALS

The materials and samples were as used previously [1]. The poly(ethylene oxide) (PEO) samples supplied by Merck were Polyethyleneglycol 6000 and 400 respectively. They were grafted on Silica as described by Utsugi *et al.* [2]. The extent of grafting was about 15% by weight for PEO 400 and 20% for PEO 6000. The grafted polymer was then spin labelled with 2,2,5,5 tetramethyl-3-pyrrolin-1-oxyl-3-carboxylic acid in its acid chloride form. The reaction was carried out in chloroform with pyridine. By washing chloroform, the unattached free radicals were removed.

### EVIDENCE FOR TWO POPULATIONS OF LABELS

As pointed out recently [1], the EPR spectrum of a grafted polymer has a special shape. We now reconsider this feature because it is of great importance for the interpretation of our data. In effect, as we extended the temperature range of study from  $-150^{\circ}$  to  $80^{\circ}$ , it became apparent that the superposition of two types of lines, already noted, was an essential feature of our spectra.

It is well known from theoretical work, e.g. by Freed *et al.* [3], that the EPR spectrum shape especially in the slow tumbling region is sensitive to the model of reorientation adopted for the label. Another hypothesis explains the special shape of our spectra as the result of a very anisotropic motion of the label, instead of analyzing it as a superposition. Therefore the theoretical and experimental spectra published by Mason *et al.* [4] and Wee *et al.* [5] for spin labels

subject to a very anisotropic reorientation were carefully examined: these spectra are generally similar to those due to an isotropic reorientation in our correlation time range except for the two extreme lines which are more or less distorted. On the other hand the lines of our spectra are much better separated into two types, so that this hypothesis can be rejected in our case.

It may be recalled that Robb and Smith [6] studied physical adsorption of a copolymer of vinyl pyrrolidone and allylamine at the silica-solution interface. Sistovaris *et al.* [7] have also studied the adsorption of polymeric compounds at a silica-solution interface. Both sets of authors could explain their results by assuming that there are two fractions of labelled polymers, one mobile and the other for which motion is restricted. The spectra appear then as a superposition of two types of lines, one with a great linewidth and a shape influenced by the anisotropic part of the Hamiltonian which is not wholly averaged in the slow tumbling region (Freed *et al.* [3]) and another with a small linewidth where three lines are well resolved, originating from the fast motion of the label (see Kivelson [9] for theory).

We shall adopt this picture for our problem but we propose to study the two fractions separately whenever possible. Towards the higher temperatures ( $50^{\circ}$ ), the spectrum corresponding to the fraction with a slow motion tends to disappear for the PEO 6000, whereas for the lower temperatures ( $-60^{\circ}$ ) only this part remains detectable. In an intermediate range, depending on the sample, the two fractions are simultaneously present and give a composite signal with sufficient intensities for both parts to be analysed. We have thus estimated the correlation times for both fractions as well as the relative proportions of each fraction at every temperature.

### ANALYSIS OF THE SPECTRA

Our method is illustrated in Fig. (1).

#### Fast motion

In this case the theoretical spectrum of the nitroxide label predicted by Kivelson [9] consists of three

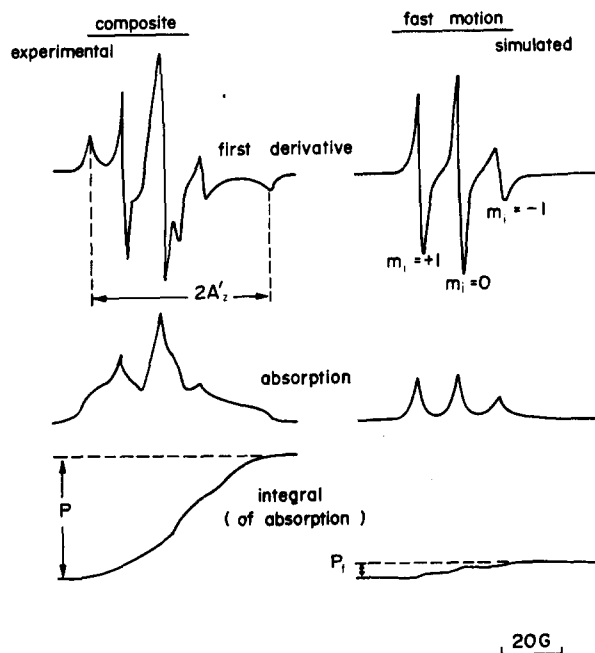


Fig. 1. Analysis of the EPR spectra.

Lorentzian lines with the following parameters:

$$T_2^{-1}(m_l) = A + B m_l + C m_l^2, \quad m_l = 1, 0, +1$$

where  $A$ ,  $B$  and  $C$  are constants related to the parameters of the spin Hamiltonian of the label and proportional to the rotational correlation time. We have simulated such spectra and have compared them with the experimental, focusing our attention on the two lines corresponding to  $m_l = \pm 1$  because the central line is evidently more complex. We are able to construct thus the "fast motion" spectrum.

#### Slow motion

The theory of Freed *et al.* [3] in the slow tumbling region, where the anisotropic part of the spin Hamiltonian is important, is not so easy to apply for simulation. We have preferred a simplified method, mentioned by McCalley *et al.* [10] and described by Freed [11] and Goldman *et al.* [8]. In fact we measure directly the distance between the two extreme peaks  $2A_z'$  on the experimental spectrum and use then the formula given by Freed:

$$\tau_c = a \left( 1 - \frac{A_z'}{A_{zz}} \right)^b$$

where  $A_z$  is the distance between the two extreme peaks for the rigid limit (i.e. the powder spectrum).

From the  $a$  and  $b$  values proposed by Freed, we have selected the following, taking into account the intrinsic linewidth of the Lorentzian components, for three hypotheses for the rotational reorientation:

$$\begin{aligned} a &= 5.4 \times 10^{-10} \text{ s} & b &= -1.36 \text{ (Brownian diffusion)} \\ a &= 1.1 \times 10^{-9} \text{ s} & b &= -1.01 \text{ (Free diffusion)} \\ a &= 2.55 \times 10^{-9} \text{ s} & b &= -0.615 \text{ (Strong jump)} \end{aligned}$$

It was not possible to select one model rather than another. Of course with such a method, the numerical

value obtained for the rotational correlation time cannot be very accurate. It does not matter for our study since we wish to consider the main features of the phenomenon. We have therefore only estimated the "slow motion" correlation time.

#### Superposition of two spectra

It is well known that the integral of the absorption EPR spectrum is proportional to the number of resonating spins. Thus integrating the simulated "fast motion" absorption spectrum, we obtain a number proportional to the "fast population". Integrating the experimental composite absorption spectrum, we obtain a number proportional to the whole population. As described by Jost and Griffith [12], the ratio of the "fast population" to the "slow" can be derived.

## RESULTS

Typical results for the mobility of polymers (PEO 400 and PEO 6000 with an excess of  $C_6D_6$ ) are shown in Figs 2 and 3. When the polymer is not grafted but simply swelled in presence of solvent in excess without silica, the correlation time changes drastically when the solvent freezes (m.p. of  $C_6D_6$ : 6.7°). On the contrary when it is grafted, we find two populations and as the temperature changes from  $-150^\circ$  to  $+80^\circ$  the variation of both correlation times is very smooth. But it cannot be shown in such a figure that the relative proportion of both populations actually varies very much and moreover that, generally in the solvent freezing region, the signal of one of the two populations is no longer detectable. However there exist a temperature range where both populations can be studied simultaneously.

The minor variation of grafted polymer mobility at the solvent freezing point can be explained by the assumption that the solvent does not make up a host

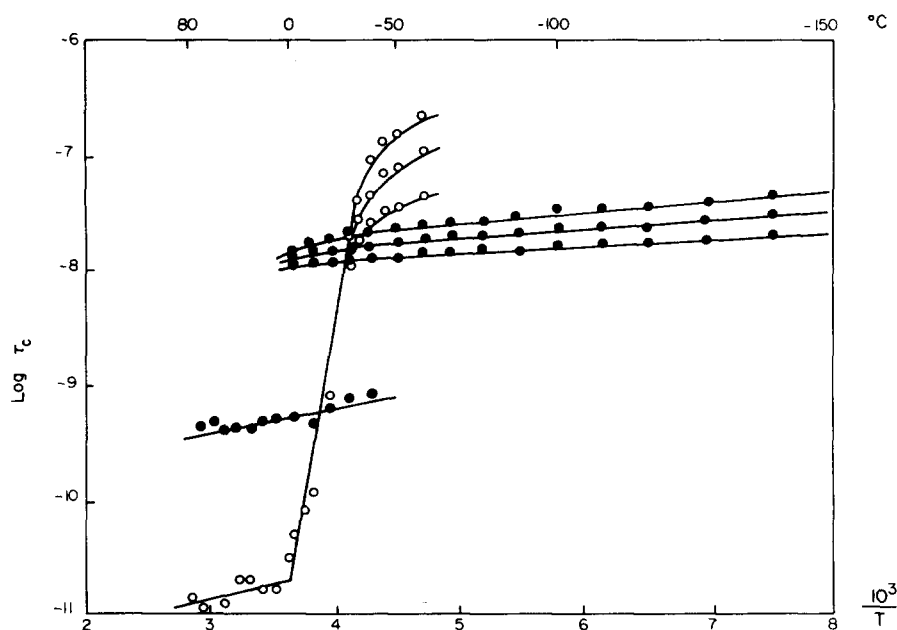


Fig. 2. Dependence on temperature of the rotational correlation time of the label for PEO 400 not grafted, with an excess of  $C_6D_6$  (○); grafted, with an excess of  $C_6D_6$  (●). For estimating slow-motion correlation times, three models were used.

matrix as strongly bonded as that without silica. The evolution of the two populations of label, discussed below, indicates that the density distribution of the free end does not change drastically after freezing. But it seems probable that the swelling of our grafted polymer is not exactly of the same type as that of free polymer [13]. The correlation time change is of more than one order of magnitude greater when we go from the free polymer to the fast fraction of the grafted polymer. The comparison between the fast fraction of

PEO 400 and PEO 6000 shows that the latter is more mobile. The fact that the correlation times of the slow fraction do not depend on the molecular mass or on the solvent suggests that the motion involves only short segments of the chain, for the same reason as that proposed by Lang *et al.* [14].

Actually the physical explanations given in the preceding paper [1], limited to high temperatures and relatively fast motion, hold very well, but we prefer now to express them in terms of the two population

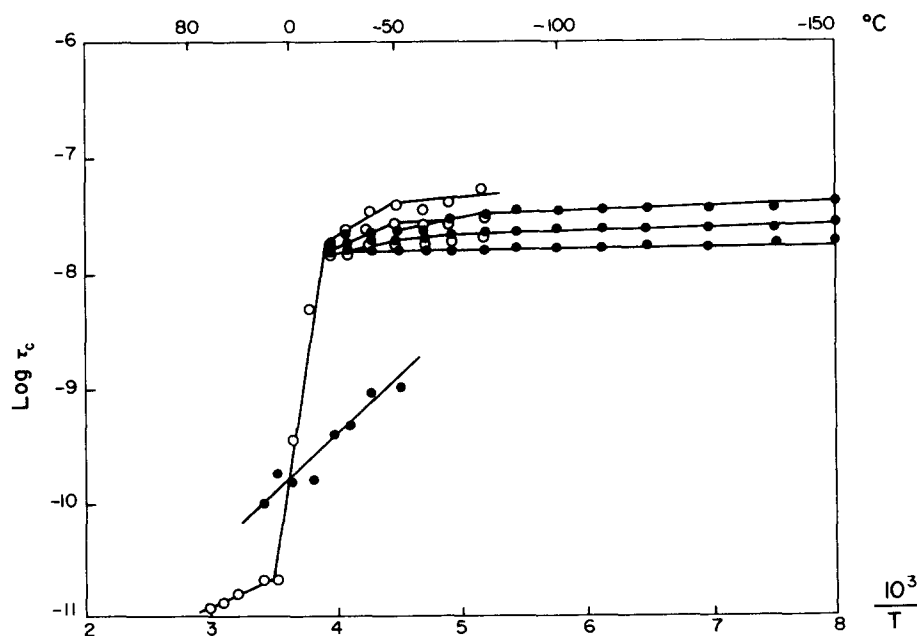


Fig. 3. Dependence on temperature of the rotational correlation time of the label for PEO 6000 not grafted, with an excess of  $C_6D_6$  (○); grafted, with an excess of  $C_6D_6$  (●). For estimating slow-motion correlation times, three models were used.

Table 1. Activation energies (kJ) (Estimated precision 10–20%)

	Fast motion	a	Slow motion b	c
PEO 400				
not grafted, in C <sub>6</sub> D <sub>6</sub>				
–20–40°		52	36	21
grafted, in C <sub>6</sub> D <sub>6</sub>				
0–40°	3	4	4	3
PEO 6000				
not grafted, in C <sub>6</sub> D <sub>6</sub>				
10–10°	33			
–10–40°		12	10	5
–40–80°		< ~4	< ~3	< ~2
grafted in C <sub>6</sub> D <sub>6</sub>				
0–50°	7	3	3	3

(a) Brownian diffusion; (b) Free diffusion; (c) Strong jump.

scheme. Of course the numerical values given for the correlation time, in particular at low temperatures, must be corrected [15].

A few activation energies of the motion are given in Table 1. In particular it can be clearly seen that they are much weaker for the grafted polymer (particularly the slow fraction) than for the free polymer in the same temperature range. The surface molecular motion is expected to look like the segmental motion of macromolecules at low temperatures, responsible for activation energies of the same order. It is the case for PEO 6000 where enough data are available but it seems that the grafted polymer does not exhibit the phase transition which occurs in the free polymer.

#### Evolution of the two populations

The ratio of the “fast” population to the “slow” is plotted vs (absolute temperature)<sup>–1</sup> (Figs 4 and 5). The experimental results fit the Arrhenius law:

$$\ln \frac{P_f}{P_s} = \frac{A}{T} + B.$$

The numerical values are given for PEO 6000 and PEO 400 in Table 2. The estimated precision is 10%.

In our temperature range, the fast fraction is rather small. The slope of the straight lines depends mainly on the nature of the solvent. For the region of interest, C<sub>6</sub>D<sub>6</sub> (m.p. 6.7°) is frozen whereas C<sub>6</sub>F<sub>6</sub> (m.p. –13°) is liquid. The discussion of the effect of the solvent is therefore not straightforward. The ratio of the two populations is molecular weight dependent: at a given temperature, the immobilized fraction of PEO 400 is relatively more important than that of PEO 6000.

#### Discussion

Thermodynamical interpretation of the Arrhenius law experimentally observed leads to consideration of the system of all the labelled polymers, without interaction, which can be found in two states of respective energies  $E_f$  and  $E_s$  ( $E_f > E_s$ ). Partition functions  $Z_i$  must be introduced to take into account the respective internal states of motion.  $P_f$  and  $P_s$  being the respective numbers of labels in each state, the rough approximation of an ideal gas leads to an equilibrium condition:

$$\ln \frac{P_f}{P_s} = -\frac{E_f - E_s}{kT} + \ln \frac{Z_{if}}{Z_{is}}.$$

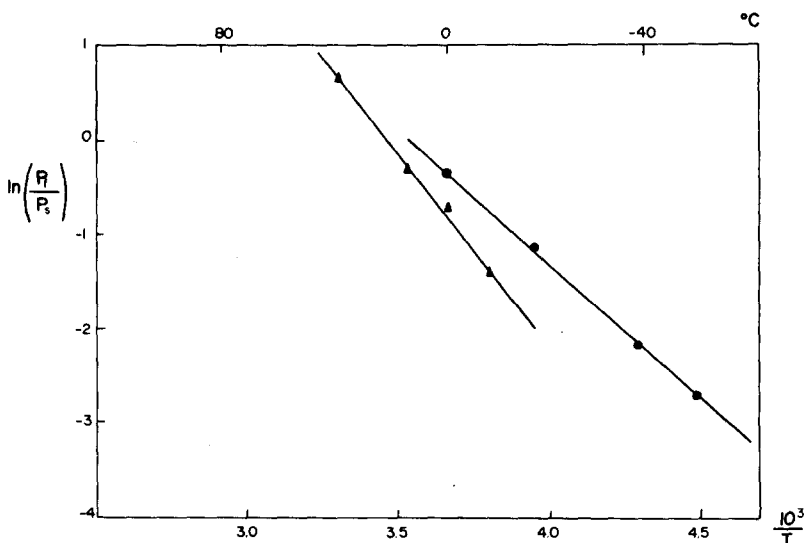


Fig. 4. Dependence of the ratio of the two populations on temperature for grafted PEO 6000 (●) with C<sub>6</sub>D<sub>6</sub>, (▲) with C<sub>6</sub>F<sub>6</sub>.

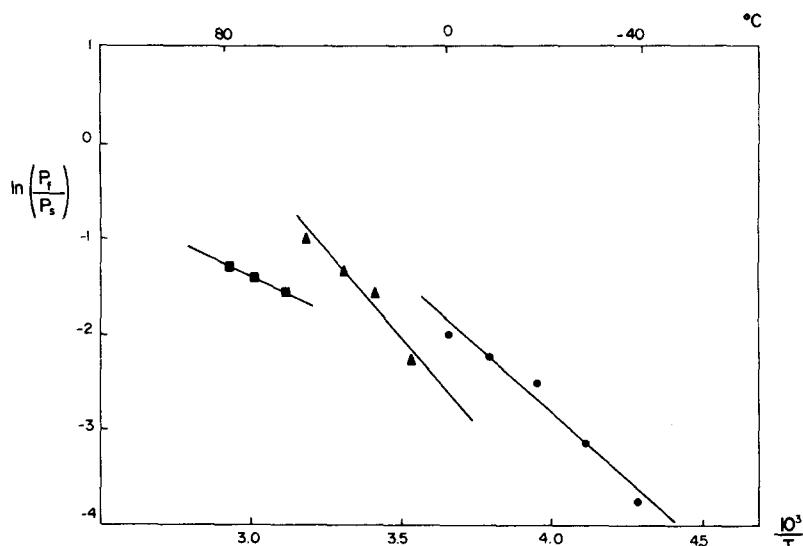


Fig. 5. Dependence of the ratio of the two populations on temperature for grafted PEO 400 (●) with  $C_6D_6$ , (▲) with  $C_6F_6$ , (■) without solvent.

Assuming the second term does not depend strongly on temperature in the range considered, we find a law of the form found experimentally. The experimental values of  $A$ , of the order of magnitude of a heat of physical adsorption, may correspond to the term  $(E_f - E_s)/kT$ , characteristic for an effective adsorption of the labelled polymer on the surface silica. The second term  $B$  may be associated with the term  $\ln(Z_{if}/Z_s)$ . In our experimental temperature range, we do not observe a variation of this term. It means, as  $Z_i$  depends on the degrees of translation, rotation and vibration of the labelled polymer, that the responding sublevels of energy are tightly spaced compared with  $E_f - E_s$ . In these limits, the ratio  $Z_{if}/Z_s$  becomes more simply the ratio of both states degeneracies. Another point is the relatively important value of the pre-exponential factor  $\exp(B)$ , which implies an important increase of the degrees of freedom for the "fast" population. This analysis supports our assumption, attributing the fast and slow phases to the ends of adsorbed and not adsorbed labelled polymer.

#### PHYSICAL MODELS

At this point of our analysis, some models describing conformation of grafted polymers can be examined. The case of physically adsorbed polymers, more intensively studied, suggest some of them. The two cases usually distinguished [16] are uniform

adsorption and specific adsorption of the end segment of the chain. In the case of weak physical adsorption, De Gennes [17] has demonstrated theoretically that the only equilibrium surface state has a relative low surface density; the chains are spread out and can be described as a semi-dilute two dimensional solution. The radius of a chain is always much larger than the layer thickness. The experimental results of Howard [18] and Killman [19] on poly(ethylene oxide) and of Eirich [20] on various polymeric compounds show that the adsorbed molecules form a monolayer and that PEO adopts a nearly flat conformation but that there is moderate looping into the solution phase.

About the dominant adsorption of the label, it can be noted that Robb and Smith [5] have not observed a difference between adsorption isotherm using both labelled or unlabelled copolymers, within experimental errors. On the other hand Lozos *et al.* [21] have shown the differences between the low field and high field extremes ( $2A_{zz}$ ) of the rigid limit spectrum to be sensitive to a hydrogen bonding of the NO group. In our case this constant does not change when the polymer is grafted, and hydrogen bonding can be excluded as an adsorption mechanism for the label. At last we cannot completely exclude another adsorption mechanism for the label (Fig. 6a).

A more specific model for grafted polymers was proposed by Papirer *et al.* [22], based on the maximum experimental rate of grafting for this kind of material. The coverage of the whole surface is done by

Table 2. Experimental values for the  $A$  and  $B$  parameters characterizing the evolution of the two populations

	$A$		$B$
	(K)	(kJ)	
PEO 6000 grafted with $C_6D_6$	-2800	-21	10.0
PEO 400 grafted with $C_6D_6$	-2800	-21	8.4
PEO 6000 grafted with $C_6F_6$	-4000	-30	14.0
PEO 400 grafted with $C_6F_6$	-3700	-27	10.8
PEO 400 grafted without solvent	-2000	-15	4.8

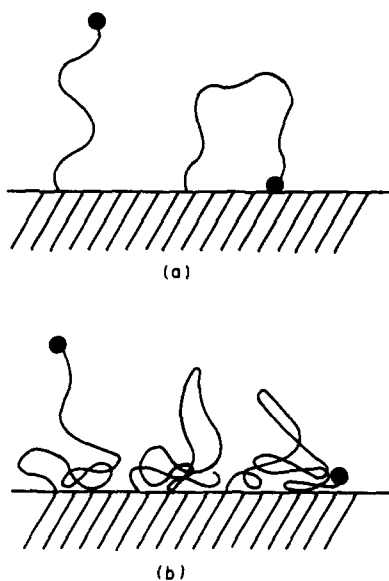


Fig. 6. Physical models: (a) for selective adsorption of the label; (b) for uniform adsorption of the polymeric chain.

Gaussian coils as in dilute solution, and the average molecule can be considered just isolated. It is noticeable that the required lateral extension of the coils on the surface is smaller than for physical adsorption. This picture can be true for chemical preparation but as the solvent is changed it must be modified. We expect that the polymer conformation is the result of a competition between surface attraction and chain repulsion. The probable consequence is that the fast population would be more important than predicted for physical adsorption.

The picture which accounts for our results may be that given on Fig. 6(b) of partially collapsed coils on the surface (slow population) and loops or tails (fast population).

#### CONCLUSION

Experimental studies of EPR spectra, observed at a frequency of about  $10^{10}$  Hz, of spin labelled poly(ethylene oxide) grafted on silica have shown special behaviour, distinct from that of the bulk polymer, due to the presence of this solid adsorbent.

Over an appreciable temperature range, two mobility states are observed, from the point of view of the free labelled tail of the polymer. The change with temperature of the ratio of the statistical populations of those two states obeys an Arrhenius law. Values of the activation energy are not extremely dependent on the molecular weight but increase as hexafluorobenzene replaces benzene. The pre-exponential factor

takes relatively large values, which signifies noticeable restriction of degrees of freedom from one state to the other; it is greater, the higher the molecular weight. It increases with activation energy, when replacing one fluid in contact with the other.

A two layer model is assumed to account for the experimental results. One layer is in the vicinity of the surface where the mobility is highly restricted to local motions of a few monomer units. In the other layer, mobility is much higher. The observed correlation times indicate a more restricted mobility than in the bulk for the high temperature range.

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#### REFERENCES

1. H. Hommel, L. Facchini, A. P. Legrand and J. Lecourtier, *Eur. Polym. J.* **14**, 803 (1978).
2. H. Utsugi, H. Horikoshi and T. Matsuzawa, *J. Colloid Int. Sci.* **50**, 154 (1975).
3. J. H. Freed, G. V. Bruno and C. F. Polnaszek, *J. phys. Chem., Ithaca* **75**, 3385 (1971).
4. R. P. Mason, C. F. Polnaszek and J. H. Freed, *J. phys. Chem., Ithaca* **78**, 1324 (1974).
5. E. L. Wee and W. G. Miller, *J. phys. Chem., Ithaca* **77**, 182 (1973).
6. I. D. Robb and R. Smith, *Eur. Polym. J.* **10**, 1005 (1974).
7. N. Sistovaris, W. O. Riede and H. Sillescu, *Ber. Bunsenges. Physik. Chem.* **79**, 882 (1975).
8. S. A. Goldman, G. V. Bruno, C. F. Polnaszek and J. H. Freed, *J. chem. Phys.* **56**, 716 (1972).
9. D. Kivelson, *J. Chem. Phys.* **33**, 1107 (1960).
10. R. C. McCalley, E. J. Shimshick and H. M. McConnell, *Chem. Phys. Lett.* **13**, 115 (1972).
11. J. H. Freed, *Spin Labelling Theory and Applications* (Edited by L. J. Berliner), p. 53. Academic Press, New York (1976).
12. P. Jost and O. H. Griffith, *Spin Labeling Theory and Applications* (Edited by L. J. Berliner), p. 251. Academic Press, New York (1976).
13. J. Lecourtier, R. Audebert and C. Quivoron, *Macromolecules* **12**, 141 (1978).
14. M. C. Lang, C. Noël and A. P. Legrand, *J. Polym. Sci. Polym. Phys. Ed.* **15**, 1329 (1977).
15. H. Hommel, Thèse 3ème cycle, Université P. M. Curie, Paris oct. 26 (1978).
16. S. Alexander, *J. Phys.* **38**, 983 (1977).
17. P. G. De Gennes, *J. Phys.* **37**, 1445 (1976).
18. G. J. Howard and P. McConnell, *J. phys. Chem. Ithaca* **71**, 2974 (1967).
19. E. Killmann, *Polymer* **17**, 864 (1976).
20. F. R. Eirich, *J. Colloid Int. Sci.* **58**, 423 (1977).
21. G. P. Lozos and B. M. Hoffman, *J. phys. Chem., Ithaca* **78**, 2110 (1974).
22. E. Papirer, J. B. Donnet, G. Riesz and V. T. Nguyen, *Angew. Macromolek. Chem.* **19**, 65 (1971).