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Solutions and gels of spin-labelled poly(octyl isocyanate) in non-polar hydrocarbon solvents

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Chain dynamics and the conformation of poly(octyl isocyanate) (POIC) in solutions and gels have been studied by electron paramagnetic resonance (e.p.r.) spectroscopy using a spin-labelled polymer. The polymer was dissolved in two non-polar solvents, isooctance and cyclohexane. The isooctane solutions form thermoreversible gels, whereas in cyclohexane viscous solutions are obtained. The e.p.r. spectra were analysed as combinations of various spectral modes, one of which reflects the restriction of the label motion by the carbonyl groups in the main chain. The other modes are due to the bending of the chain, i.e. due to chain flexibility. The temperature dependence of the chain flexibility is very different in the two solvents. Melting of the gel of POIC in isooctane is detected as a change from a broad immobilized e.p.r. spectrum to a motionally narrowed triplet spectrum with considerably broadened lines. Gel melting is accompanied by changes in the isotropic coupling constant, as well as by increasing dipolar interactions between the labels in the neighbouring chains. On the other hand, the spectra measured from the polymer dissolved in cyclohexane change only slightly with temperature.

(Keywords: poly(octyl isocyanate); gelation; spin labelling)

INTRODUCTION

Poly(alkyl isocyanates) are semiflexible helical polymers with interesting solution properties. Owing to the worm-like character of the polymer chains, poly(alkyl isocyanates) form lyotropic liquid-crystalline phases in concentrated solutions[1–4]. Recently, even lyotropic cholesteric phases have been obtained by doping a solution of poly(hexyl isocyanate) with optically active substances[5].

In solutions of poly(alkyl isocyanates), left- and right-handed helical conformations of the chain occur with equal probabilities. From optically active monomers, however, polyisocyanates with high optical activity may be prepared. It has been shown that even a small proportion of a chiral monomer in a poly(alkyl isocyanate) may have a considerable effect on the overall chain conformation and thus on the optical activity of the polymer[6,7].

Dilute solutions of poly(alkyl isocyanates) are interesting owing to the observed dependence of the persistence length of the polymer on the solvent polarity. The persistence length decreases with increasing polarity of the solvent. According to Cook *et al.*[8] this may be explained by a local interaction between the solvent molecules and the polymer backbone. A polar solvent affects the partial double-bond character of the amide group in the main chain and thus causes large torsional oscillations in the polymer backbone.

Poly(alkyl isocyanates) have been reported to form thermoreversible gels in certain solutions. Olayo and Miller[9] have studied the gelation of poly(butyl isocyanate) in benzene. Gels formed by poly(hexyl isocyanate) in some aliphatic solvents have also been described[10].

This paper discusses the solution properties of poly(octyl isocyanate) (POIC). Details of the chain dynamics have been studied by electron paramagnetic resonance (e.p.r.) spectroscopic measurements on a spin-labelled POIC. E.p.r. spectroscopy is an extremely suitable method for studies of the local dynamics of the chain segment close to the label group. In general, e.p.r. spectra of nitroxide radicals used as labels are sensitive to the rate and amplitude of the reorientational motion of the reporter groups. By careful analysis of the spectra, information on the motional model as well as possible anisotropy of the label motion may be obtained. Furthermore, the spectra are known to be sensitive to the polarity of the medium surrounding the label[11].

In the present case, the label (1-oxyl-2,2,5,5-tetramethylpyrrolidine) has been bound randomly to the

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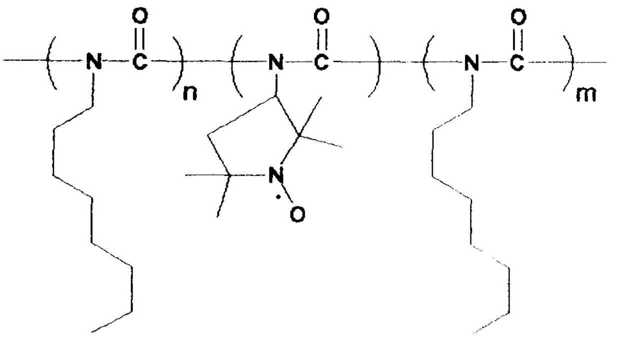
polymer main-chain nitrogen by a single covalent bond. This has been done by copolymerizing a nitroxide radical having an isocyanate function with n-octyl isocyanate. The structure of the polymer is shown below:



In the labelled POIC, the motion of the label is restricted by the main-chain carbonyls, and the label thus detects changes in the chain conformation. The spectra of the polymer have been shown to reflect the changes in the chain dynamics induced by the varying polarity of the solvent. However, the properties of the solutions are not determined only by the solvent polarity. In a recent study[12] it was observed that, when dissolved in two non-polar solvents, POIC forms a thermoreversible gel only in the other of the solvents. This paper describes the differences in the chain dynamics of POIC in two non-polar hydrocarbon solvents, cyclohexane and isooctane (2,2,4-trimethylpentane).

The method used to simulate the e.p.r. spectra of the labelled POIC is fairly complex and leads to a detailed and realistic description of the local chain dynamics. The theoretical background will be explained first. After this, the application of the method in the case of poly(octyl isocyanate) will be described. By comparing the dynamics of the polymer chain in two non-polar solvents, it should be possible to understand better the processes leading to the observed gelation of one of the studied solutions.

THEORETICAL BACKGROUND

The theoretical simulation of the e.p.r. spectra was performed according to the method developed by Timofeev *et al.*[13,14]. In this approach, an e.p.r. spectrum of a spin-labelled polymer is considered to be determined by nitroxide radicals involved in two types of motion, i.e. rapid anisotropic motion of the label with respect to the polymer and slow isotropic diffusion of the macromolecular carrier.

The contributions of the two types of motion can be experimentally determined by measuring the separation between the outer extrema in the e.p.r. spectrum of the labelled polymer ($2A'$) as a function of temperature and solvent viscosity. The total shift of the outer extrema is denoted as Δ and may be defined as follows:

$$\Delta = 2A_Z - 2A' = (2A_Z - 2\bar{A}) + (2\bar{A} - 2A') = \Delta^S + \Delta^\tau \tag{1}$$

Here, $2A_Z$ is the separation between the extrema in the rigid limit spectrum; and $2\bar{A}$ is an extrapolated value for the extrema separation in the limit where the rotational diffusion of the macromolecule has the correlation time $\tau = \infty$. At this limit the detailed shape of the spectrum is determined only by the reorientation of the label with respect to the polymer. The extrapolation procedure is described in ref. 14.

The first term on the right-hand side of equation (1) (Δ^S) represents the level of averaging of the Z component of the magnetic tensor A as a result of the fast motion of the label covalently bound to the polymer. The partial averaging may be expressed by an experimentally obtainable dimensionless order parameter S:

$$S = (\bar{A} - a_0)/(A_Z - a_0) \tag{2}$$

where a_0 is the isotropic coupling constant. (Throughout this text, $A_\parallel$ is simply written as A, and A_{ZZ} is written as A_Z.)

The second term on the right-hand side of equation (1) (Δ^τ) describes the shift of the outer extrema of an e.p.r. spectrum due to the Brownian diffusion of the macromolecule in solution. This shift can be expressed using the order parameter S and the correlation time τ (in nanoseconds) of the diffusion of the macromolecule:

$$\tau = (197/S)(\Delta^\tau/S)^{-1.39} \tag{3}$$

It should be emphasized that τ in this case refers to the reorientational motion of the whole macromolecular carrier, and not to that of the label.

In general, when the label bound to a polymer has a degree of motional freedom independent of the polymer, the rapid tumbling of the label has a much more profound effect on the shape of the e.p.r. spectrum than does its slow diffusion together with the macromolecule. The reorientational motion of the label is principally a random process and needs to be discussed further.

In case of the fast anisotropic reorientation of the label, an e.p.r. spectrum represents a continuous set of the possible space positions of the label. Within the time gate of the spin label method, i.e. the minimum period during which it is possible to register the anisotropy of A and g tensors[15], all the registered states or space positions of the nitroxides are averaged. In fact, it is more correct to use the term ‘double averaging’. Then, the first averaging applies to a single nitroxide and a large number of its reorientational jumps (200–600 within the e.p.r. time gate), and the second one to the whole number of labelled molecules in the sample. The mathematical result of this process is the averaging of the components of A and g tensors.

In the present approach the random process of label reorientation is approximated with more simplified model processes. These simple processes are easy to describe, like e.g. the anisotropic rotation of the nitroxide z axis around a preferential space axis, or the oscillations of the nitroxide relative to one of the molecular coordinate axes.

Several models exist to describe the partial averaging of the components of the A and g tensors. If it is possible to approximate the reorientations of a group of nitroxides as a rotation of a single radical around a certain space axis, then the averaged magnetic tensors will have an axially symmetrical form. On the other hand, if the rotational oscillation of a nitroxide relative to one of the molecular coordinates is taken as an approximation of the random anisotropic motion of the label, then the model of averaging will be different and the magnetic tensors will be transformed into an unsymmetrical form. A stationary picture of the processes may be represented as a number of nitroxides grouped around a preferential space axis of rotation or as a group of nitroxides oscillating around a certain axis in the molecular coordinate system. These groups of nitroxides are called here *clusters*.

In the axially symmetrical case, the averaging of the **A** and **g** tensor components may be expressed as:

$$\begin{aligned} \bar{A} &= a_0 + \tfrac{2}{3}\Delta\bar{A} \\ \bar{A} &= a_0 - \tfrac{1}{3}\Delta\bar{A} \end{aligned} \qquad (4)$$

where:

$$\begin{aligned} \Delta\bar{A} &= \Delta A S - \delta A(1-S)\kappa \\ \Delta A &= A_Z - (A_X - A_Y)/2 \\ \delta A &= (A_X - A_Y)/2 \end{aligned}$$

Here, S is the order parameter; κ will be defined further below.

For a certain moment of time t the z axis of the nitroxide radical may be expressed relative to the laboratory coordinates by the Eulerian angles:

$$\cos^2\alpha(t) + \cos^2\beta(t) + \cos^2\gamma(t) = 1 \qquad (5)$$

Then, the axis of the motional averaging in the axially symmetrical case may be defined in a space fixed by an order parameter axis system (S_X, S_Y, S_Z) such that:

$$S_X + S_Y + S_Z = 0 \qquad (6)$$

Equation (6) defines a plane in the coordinates of the order parameters; every point in this plane corresponds to a possible space position of the z axis of the nitroxide. If S_Z in equation (6) is written simply as S, then S_X and S_Y may be expressed with S and κ as follows:

$$\begin{aligned} S_X &= \tfrac{1}{2}[-S - (1-S)\kappa] \\ S_Y &= \tfrac{1}{2}[-S + (1-S)\kappa] \end{aligned} \qquad (7)$$

In the case where the nitroxide may be assumed to oscillate around one of the molecular axes, the averaging of the magnetic tensors leads to:

$$\begin{aligned} \bar{A}_X &= A_X + (A_Z - A_X)P/2 \\ \bar{A}_Y &= A_Y \\ \bar{A}_Z &= A_Z - (A_Z - A_X)P/2 \end{aligned} \qquad (8)$$

Here it has been assumed that the nitroxide oscillates symmetrically relative to the y axis, within an angle $\pm\alpha$. In equations (8), $P = 1 + \sin(2\alpha)/2\alpha$.

The conclusions pertinent for the analysis of the experimental e.p.r. spectra are the following. First, the number of molecules in a cluster (n_{ij}) is proportional to the probability of the corresponding state (ρ_{ij}) of the nitroxide in a stationary process leading to the averaging of the magnetic tensors:

$$\rho_{ij} = n_{ij}/N \qquad (9)$$

Here, N is the total number of molecules in the sample. Secondly, each cluster is expected to produce its own typical e.p.r. spectrum. And thirdly, the experimental spectrum is a superposition of the spectra obtained from each of the clusters in the sample. The number of molecules in each cluster inevitably varies and thus the subspectra need to be summed with different weights.

According to the present approach, the simulation of the experimental e.p.r. spectra is performed as a search of:

(i) the model of the averaging of the components of **A** and **g** tensors in the clusters; and
(ii) the density probability distribution of the clusters in the sample, i.e. weighted contribution of each spectrum of a corresponding cluster.

The weight of the contribution of each spectrum of a corresponding cluster may be clarified with the following equations:

$$\begin{aligned} \rho_{ij} &\approx \exp\{-[(S_i - S_0)/\sigma_S\sqrt{2}]^2\} \\ &\quad \times \exp\{-[(\kappa_j - \kappa_0)/\sigma_\kappa\sqrt{2}]^2\} \\ \rho_n &\approx \exp\{-[(\alpha_n - \alpha_0)/\sigma_\alpha\sqrt{2}]^2\} \end{aligned} \qquad (10)$$

Here, ρ_{ij} is the weight of the spectrum of the cluster ij representing the axially symmetric model of averaging, written as a two-dimensional Gaussian function; S_0 and κ_0 define the preferential position of the nitroxide z axis in the space of the order parameters; and σ_S and σ_κ give the dispersion of S and κ. The term $2\bar{A}$ in equation (1) (and also used in equation (4)) corresponds to the situation where $S = S_0$. Finally, ρ_n, α_n and α_0 have essentially the same meaning as above, but they refer to the case of the oscillational model of averaging.

Finally, the simulated spectra are obtained:

$$\begin{aligned} Sp^l_{\mathrm{ax}} &= \sum_{ij} \rho_{ij} Sp(S_i, \kappa_j) \\ Sp^m_{\mathrm{osc}} &= \sum_{n} \rho_n Sp(\alpha_n) \\ Sp_{\mathrm{res}} &= \sum_{l} w_l Sp^l_{\mathrm{ax}} + \sum_{m} w_m Sp^m_{\mathrm{osc}} \end{aligned} \qquad (11)$$

In the following discussion, Sp^l_{ax} as well as Sp^m_{osc} will be referred to as spectral modes. Sp^l_{ax} is the simulated spectrum obtained from several axially symmetric clusters, and Sp^m_{osc} is that from the oscillational ones.

The resulting simulated spectrum Sp_{res} therefore is a sum of the axial and oscillational modes, weighted with w_l and w_m, which are chosen in the process of the simulation to give the best possible fit with the experimental spectra.

EXPERIMENTAL

Spin-labelled poly(octyl isocyanate) was synthesized by anionic polymerization from n-octyl isocyanate and 1-oxyl-2,2,5,5-tetramethylpyrrolidine-3-isocyanate. The polymerization was carried out in *N,N*-dimethylformamide at −58°C under argon atmosphere. Sodium cyanide was used as an initiator. The synthesis is described in detail elsewhere[12]. The M_W of the polymer determined by light scattering was 90 000.

The number of nitroxide groups per single chain was estimated by comparing the intensity and width of the central line of the e.p.r. spectrum of a solution of the labelled polymer to those of a reference solution with known nitroxide concentration. A single chain was determined to contain two or three nitroxide groups.

Samples for the e.p.r. measurements were prepared by dissolving the polymer in the appropriate solvent at 60°C for several days. Then, the solutions were briefly heated in a boiling water bath and kept at −5°C overnight before the measurements. Prior to the measurement, samples were transferred into a flat quartz cell. The e.p.r. spectra were measured with a Varian E-104A spectrometer.

RESULTS AND DISCUSSION

The e.p.r. spectra of the spin-labelled POIC have been shown to be sensitive to changes in the flexibility of the main chain. In this investigation, solutions with low concentration have been studied in order to find out the details of the local dynamics of the polymer in two non-polar solvents. Isooctane (2,2,4-trimethylpentane) and cyclohexane were chosen as the solvents for the following reasons. The isooctane solutions of POIC have been detected to form thermoreversible gels when stored at −20°C, whereas in cyclohexane POIC does not form gels but highly viscous solutions. In a previous study[12] it was observed that fresh solutions of the labelled POIC in isooctane and cyclohexane ($50\,\mathrm{mg\,ml^{-1}}$) give almost identical e.p.r. spectra at room temperature. However, upon standing at room temperature, phase separation slowly occurs in isooctane solution, whereas the cyclohexane solution is stable.

Samples for the present investigation were prepared in such a way that the isooctane sample was in a gel state when the measurements were started. First, samples with the concentration $30\,\mathrm{mg\,ml^{-1}}$ were studied.

Spectra of a cyclohexane solution at temperatures ranging from 10 to 60°C are shown in *Figure 1*. The spectra are typical for spin-labelled polymers in solution; the outer extrema are broad and much less intense than the triplet lines. A noticeable feature in these spectra is the slight temperature dependence of their shape. This is clearly seen in *Figure 2*, where the spectra at 10 and 60°C are redrawn and superimposed. The intensity of the high-field line of the nitrogen hyperfine triplet is seen to increase with temperature. The separation of the outer extrema $2A'$ is constant, 54 G over the whole temperature range. This indicates that the system under study is extremely complex and the simulation of the e.p.r. spectra is not easy.

As explained in the preceding discussion, it would be advantageous to evaluate separately the effects on $2A'$ of the slow diffusion of the macromolecule and the fast reorientations of the nitroxide. The estimation of the correlation time of the polymer segment is not a straightforward task owing to the semiflexible nature of the polyisocyanate chain. The estimation may be possible by studying the temperature–viscosity dependence of the spectra. From this dependence, the order parameter S (equation (2)) as well as the parameters Δ^S and Δ^τ are obtained. However, to get a useful range of solvents with varying viscosities, solvent mixtures are needed. Knowing the sensitivity of the present polymer to the solvent properties, this experiment had to be omitted.

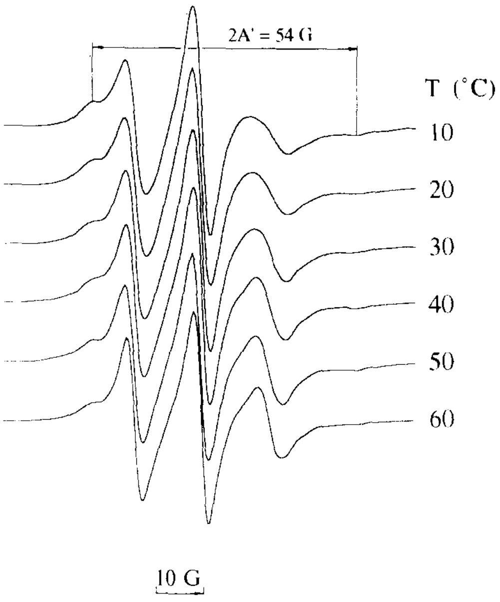


Figure 1 E.p.r. spectra of the labelled POIC dissolved in cyclohexane ($30\,\mathrm{mg\,ml^{-1}}$) measured as a function of increasing temperature

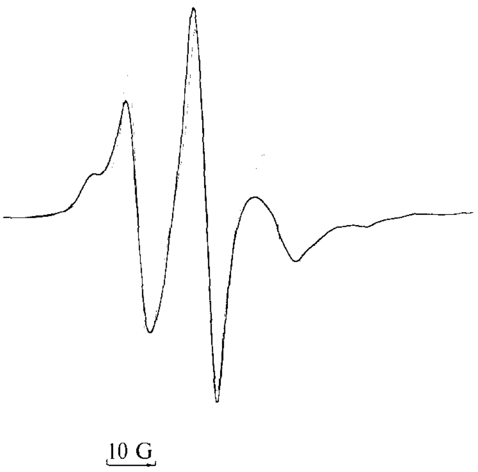


Figure 2 Comparison of the spectra from the cyclohexane solution at 10°C (thick curve) and 60°C (thin curve)

Approximate values of S and τ are needed to start the simulation; they should be chosen such that $\Delta^S + \Delta^\tau = 2A_Z - 2A' = 13\,\mathrm{G}$ and the simulated spectra are close to the experimental ones. The value $2A_Z = 67\,\mathrm{G}$ was obtained from the rigid limit spectrum measured at 77 K. From the observed constancy of $2A'$ it was concluded that τ must be considerably high. Also the amplitude of the fast angular reorientation of the label shows only a minor temperature dependence; the value of S must be nearly constant. Therefore, the estimation of the first initial simulations led to the following parameters. The shift of the outer extrema (Δ^τ) due to the diffusion of the polymer ($\tau \approx 100\,\mathrm{ns}$) is of the order of 1–2 G and the order parameter $S = 0.7$. From the latter value one obtains $\Delta^S = 11.6\,\mathrm{G}$ and $\Delta^\tau = 1.4\,\mathrm{G}$. Thus, the starting input parameters for the simulation were: $\tau \approx 100\,\mathrm{ns}$, $S_0 = 0.7$, isotropic coupling constant $a_0 = 14.0\,\mathrm{G}$, $A_Z = 33.5\,\mathrm{G}$, $g_Z = 2.0022$.

Table 1 The components of *A* and *g* tensors of the spin-labelled POIC (exp: experimental values)

Set of parameters	Sample: solvent, concentration, temperature	A_X (G)	A_Y (G)	A_Z (G)	a_0 (G) exp	$2A_Z$ (G) exp	g_X	g_Y	g_Z	g_0
1	cyclohexane, 5–30 mg ml^{-1} 10–60°C	5.0	3.5	33.5	14.0	67	2.0095	2.0063	2.0022	2.0060
	isooctane, 5 mg ml^{-1} 10–60°C									
	isooctane, 30 mg ml^{-1} 55°C									
2	isooctane, 30 mg ml^{-1} 10°C	7.0	5.0	36.3	16.1		2.0099	2.0068	2.0022	2.0063

Table 2 Parameters used to simulate the e.p.r. spectra of the labelled POIC

T (°C)	Mode	S_0	σ_S	κ_0	σ_κ	w[a]	Parameter set[b]	Linewidth (G)
Cyclohexane, 30 mg ml^{-1}								
10	1	0.70	0.10	−0.5	0.05	0.50	1	2.6
	2	0.35	0.10	1.0	0.05	0.25		
	3	−0.30	0.25	0.0	0.05	0.25		
60	1	0.65	0.12	−0.5	0.05	0.50	1	2.6
	2	0.15	0.05	1.0	0.05	0.25		
	3	−0.15	0.08	0.0	0.05	0.25		
Isooctane, 30 mg ml^{-1}								
10	1	0.60	0.21	−0.5	0.05	0.50	2	5.2
	2	0.80	0.13	−1.0	0.05	0.50		
55	1	0.55	0.05	1.0	0.05	0.40	1	9.0
	2	0.30	0.44	1.0	0.23	0.60		
Cyclohexane, 5 mg ml^{-1}								
20	1	0.70	0.05	−0.5	0.05	0.50	1	2.6
	2	0.10	0.16	1.0	0.05	0.35		
	3	−0.10	0.05	0.0	0.05	0.15		

[a] Weight
[b] From *Table 1*

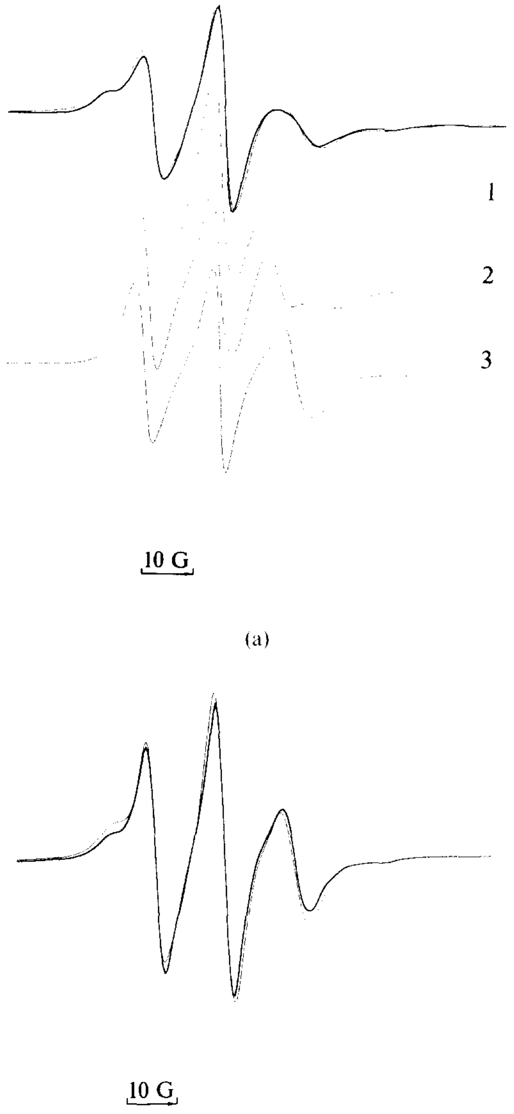
The simulation process was performed according to the following scheme:

(1) Adjustment of the components of the *A* and *g* tensors.
(2) Calculation of a set of 155 spectra with $\tau = 100$ ns.
(3) Initial simulation—finding the major spectral mode (equations (10) and (11)).
(4) Recalculation of the set of 155 spectra (if required) with varied values of τ and the linewidth.
(5) Evaluation of all possible spectral modes.
(6) Variation of all parameters in each mode ($\sigma_S, \sigma_\kappa, S_0, \kappa_0$) and the weight w_i for each mode.

All the parameters used to obtain the final simulated spectra are shown in *Tables 1* and *2*.

In *Figure 3*, the experimental spectra of the labelled POIC in cyclohexane (30 mg ml^{-1}) at 10 and 60°C are compared with the calculated ones. The simulated spectra are composed of three basic spectral modes (shown as 1–3 in *Figure 3a*) having weights 0.5, 0.25 and 0.25, respectively. All the spectra studied in this work could be sufficiently simulated using only axially symmetric averaging of the components of the magnetic tensors.

It has been shown already that the motion of the label connected to the helical POIC is severely hindered by the carbonyl groups in the main chain. To allow the rotation of the nitroxide bound to the main-chain nitrogen, a certain amount of flexibility has to be introduced into the helix structure. This general idea is in good accordance with the observation that the motion of the nitroxide is less restricted in a polar solvent (chloroform) than in non-polar ones[12]. In several investigations the persistence length of poly(alkyl isocyanates) has been shown to decrease with increasing polarity of the solvent. It is concluded that the first spectral mode shown in *Figure 3a* is an expression of the motional hindrance felt by the label due to the polymer chain in its equilibrium helical conformation. The fluctuation of the torsional angles, which produces the flexibility of the polymer chain, also increases the motional freedom of the label. Thus, the flexing of the main chain is the origin of the second and third spectral modes seen in *Figure 3a*. The first mode



(b)

Figure 3 (a) Experimental (thick curve) and simulated (thin curve) spectra of the labelled POIC in cyclohexane at 10°C are compared at the top. The components of the simulated spectrum, curves 1–3, are shown below. (b) Experimental (thick curve) and simulated (thin curve) spectra of the cyclohexane solution of the labelled POIC at 60°C

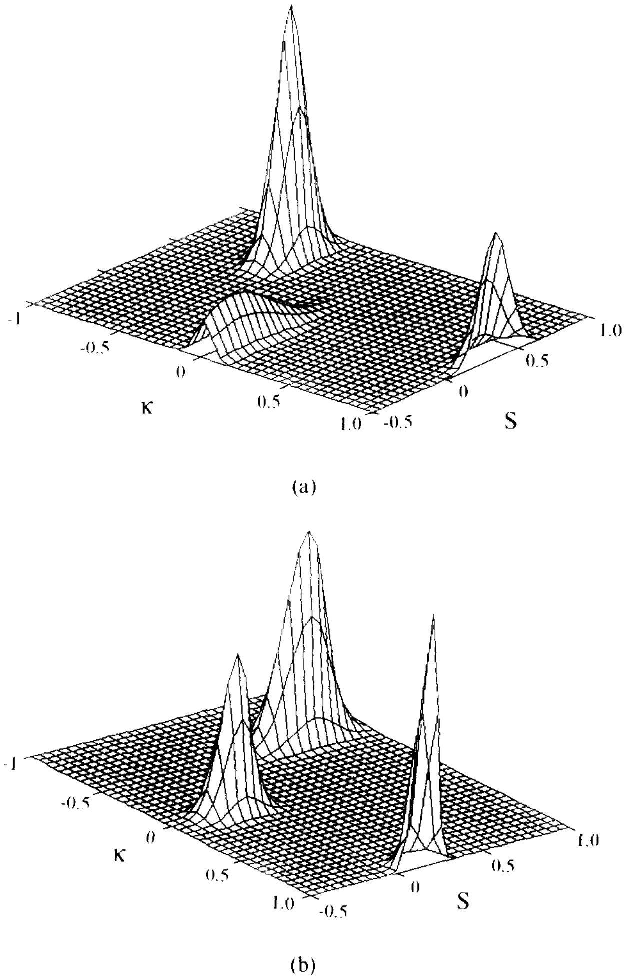


Figure 4 (a) Density probability distribution of the parameters S and κ corresponding to the simulated spectrum in *Figure 3a*. (b) Distribution of S and κ corresponding to the simulated spectrum in *Figure 3b*

does not respond to variations in temperature, whereas the second and third modes are considerably affected by temperature (see *Table 2*).

The density probability distributions of the parameters S and κ for the simulated spectra at two temperatures are shown in *Figure 4*. The three spectral modes and their contributions to the final calculated spectra are clearly resolved.

Next, the spectra of the labelled POIC in isooctane ($30\,\mathrm{mg\,ml^{-1}}$) are to be considered. The spectra were measured as a function of increasing temperature; spectra at temperatures varying from 10 to 55°C are shown in *Figure 5*. The sample in isooctane was in a gel state when the measurements were started and it melted during heating. The spectra in *Figure 5* differ noticeably from those measured in cyclohexane. The immobilized spectra obtained at low temperatures change at higher temperatures into motionally narrowed three-line spectra. This finding as such shows that the change in the

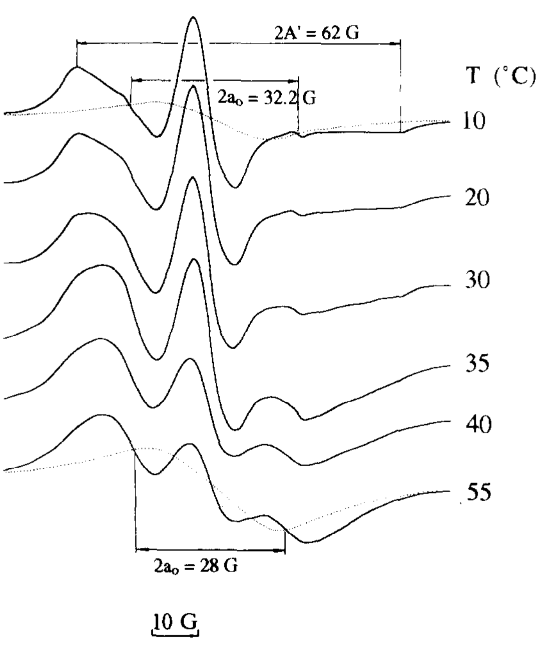


Figure 5 E.p.r. spectra of the labelled POIC dissolved in isooctane ($30\,\mathrm{mg\,ml^{-1}}$) at various temperatures

mobility of the label with temperature is greater in isooctane than in cyclohexane. The lines of the spectra measured at higher temperatures are considerably broadened. Furthermore, a strong distortion of the baseline is observed. The distortion is due to a broad singlet, shown as a dotted line in *Figure 5*. The line broadening as well as the presence of the broad singlet at high temperatures confirm the occurrence of a very strong dipole–dipole interaction between the nitroxides of the neighbouring chains. This interaction is seen to increase with increasing temperature. The sudden change from the broad immobilized spectra to the three-line spectra occurs in the temperature range (30–35°C) where the gel starts to melt.

The spectra measured in isooctane turned out to be more complex to simulate than those of the cyclohexane solutions. This is not only because of the quite dramatic change of the shape of these spectra with increasing temperature, but also because of the difference in the widths of the spectra of the cyclohexane and isooctane samples. The extrema separation at 10°C is 54 G and 62 G in cyclohexane and isooctane, respectively (*Figures 1* and *5*). In the non-polar solvents used in this work, the isotropic coupling constants a_0 should be equal. This was observed to be the case at high temperature (at $T \geqslant 55°C$, $a_0 = 14.0\,G$ in both solvents). However, the attempt to simulate the spectra of the isooctane samples with the same parameters as in the case of cyclohexane samples failed. To obtain spectra with $2A'$ equal to 62 G, very high values for the order parameter ($S = 0.9$) and correlation time ($\tau = 300\,ns$) had to be used. Even with these parameters the shapes of the calculated spectra were far from the experimental ones.

The key to the understanding of the spectra shown in *Figure 5* is the weak sharp lines detectable at 10 and 20°C. These lines are from a three-line spectrum, the origin of which most probably are the labels located at or close to the mobile chain ends. Because this spectrum is rather weak, a separate spectral mode was not added to reproduce its shape. The isotropic coupling constant of the weak three-line spectrum is much larger ($a_0 = 16.1\,G$) than that of the spectra measured in cyclohexane or in isooctane at high temperature ($a_0 = 14.0\,G$). This indicates that in the isooctane sample at low temperature the nitroxide is located in a more polar surrounding than it is at higher temperatures. The polarity results from the aggregation of the polymer, the main chain of which is highly polar. The decrease of the polarity of the medium around the label with increasing temperature is due to the melting of the aggregates acting as network junctions in the gel.

To simulate the spectra measured in isooctane, new input parameters had to be defined for the gelled samples; spectra measured above the melting temperature of the gel could be theoretically reproduced with the same parameters as in the case of cyclohexane (see *Tables 1* and *2*). The simulated spectra together with the experimental ones at two temperatures are shown in *Figure 6*. The linewidth at 10°C is 5.2 G, and increases during the melting of the gel to 9.0 G. The broadness of the lines is an indication of the dipolar interaction between the nitroxides, strengthening with temperature. It can be concluded that the polymer chains aggregate also at high temperatures but the structure of the aggregates changes with temperature.

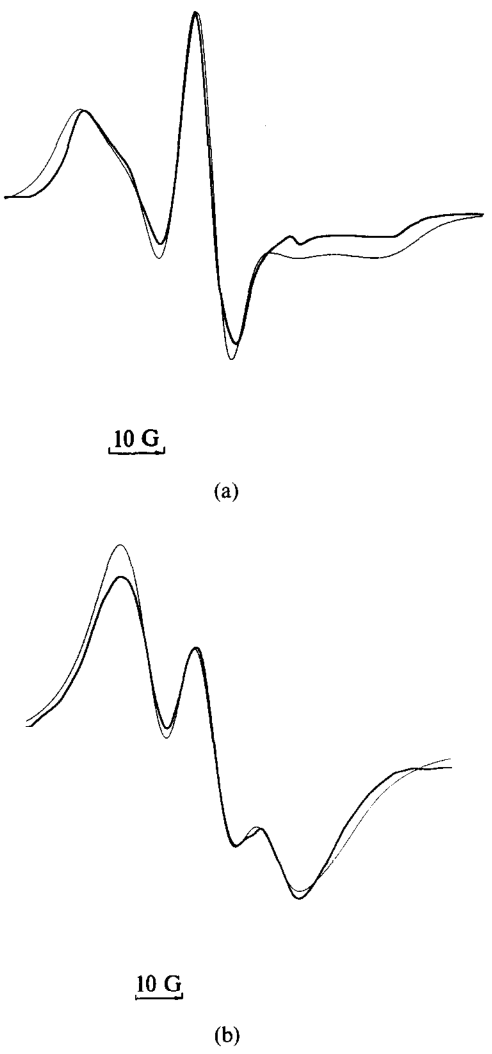


Figure 6 Experimental (thick curve) and simulated (thin curve) spectra of the polymer in isooctane (30 mg ml^{-1}) at (a) 10°C and (b) 55°C

The observed strengthening of the dipolar interaction between the labels with increasing temperature is somewhat surprising. However, the fact that the polymer at low temperature forms a network (gel) instead of precipitating out from the solution means that the chains are just partially aggregated. Knowing that a single chain contains only two or three nitroxide units, it can be understood that during the gelation only a small fraction of nitroxides are brought close to each other. When temperature increases and the gel melts, the nitroxide side groups in the polymer chains can more freely approach each other.

The density probability distributions of S and κ corresponding to the spectra in *Figure 6a* and *6b* are displayed in *Figures 7a* and *7b*. Two spectral modes were used to simulate the spectra. The first mode representing the stiff helix structure ($S = 0.6$–0.55) is only slightly dependent on temperature. The second mode, however, shows very strong temperature dependence. At 10°C, the motion of the label described by the second mode is strongly restricted ($S = 0.8$) but gains considerable freedom ($S = 0.3$) at 55°C. In very general terms it may be stated that the flexibility of POIC increases with temperature in both solvents used in this work. However,

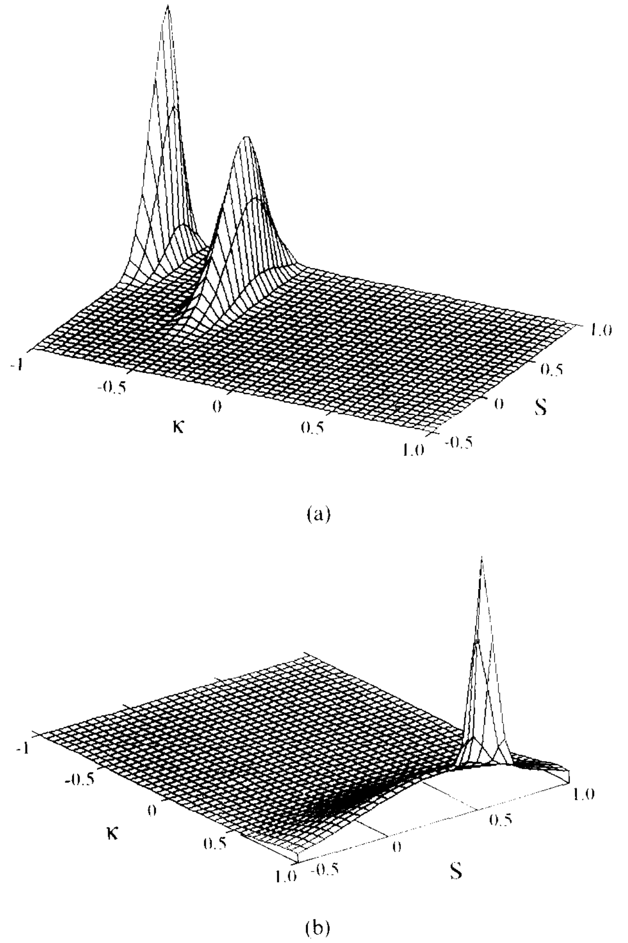


Figure 7 (a) Density probability distribution of S and κ corresponding to the simulated spectrum in *Figure 6a*. (b) Distribution of S and κ corresponding to the simulated spectrum in *Figure 6b*

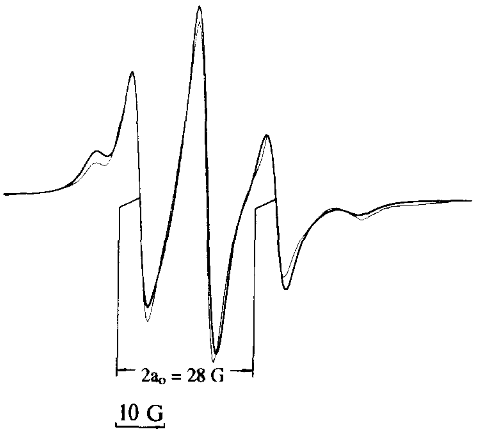


Figure 8 Experimental (thick curve) and simulated (thin curve) e.p.r. spectra of diluted solution (5 mg ml^{-1}) of the polymer in cyclohexane at 20°C

the increase of flexibility is much more profound in isooctane.

Some evidence supporting the above conclusions was obtained by diluting the samples to the concentration 5 mg ml^{-1}. A few spectra of these samples are shown in *Figures 8* and *9*.

Lowering the concentration of POIC in cyclohexane has nearly the same effect on the chain dynamics as the increase of temperature of a more concentrated solution. In *Figure 8*, the e.p.r. spectrum of a 5 mg ml^{-1} solution of POIC in cyclohexane at 20°C is compared with its simulated counterpart. The spectrum is closely similar to that measured from the more concentrated sample at 60°C, cf. *Figures 1* and *2*. As can be seen from *Tables 1* and *2*, the spectrum could be simulated with almost the same parameters as the concentrated sample at high temperature. Lowering of the concentration leaves the first spectral mode practically unaffected, whereas the second and third modes change considerably, showing the increase of the chain flexibility. The observed dependence of the chain flexibility on concentration indicates that strong polymer–polymer interactions occur in the studied concentration regime. Aggregation of the polymers seems to be inevitable in non-polar solvents.

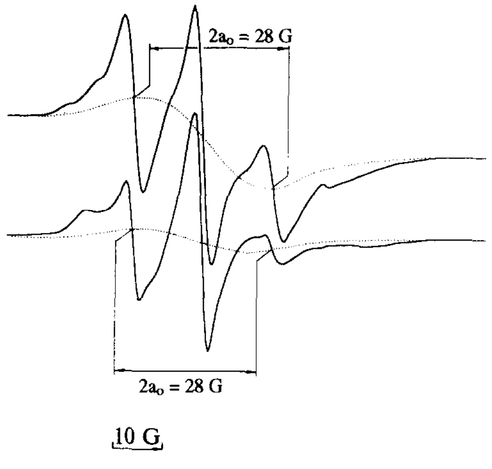


Figure 9 The e.p.r. spectra of the diluted solution (5 mg ml^{-1}) of the polymer in isooctane measured at 55°C (top) and 20°C (bottom)

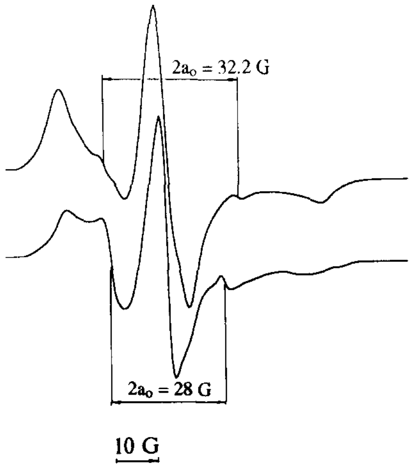


Figure 10 Spectra from the isooctane solutions of the polymer measured at temperatures below ambient: (top) polymer concentration 30 mg ml^{-1}, temperature −22°C; (bottom) polymer concentration 5 mg ml^{-1}, temperature −18°C

The spectra of the dilute solution of the labelled POIC in isooctane at 20 and 55°C are shown in *Figure 9*. The dilution of the solution is seen to increase the flexibility of the chain and thus the motional freedom of the label also in this case. The spectra in *Figure 9* resemble the spectra of the concentrated cyclohexane solutions. The distortion of the baseline due to the dipolar interaction is detectable also in this case, and it becomes stronger with increasing temperature. Isooctane is probably a thermodynamically poor solvent for POIC in the temperature range studied in this work. Even at temperatures above the melting temperature of the gel, polymer–polymer contacts tend to be favoured instead of polymer–solvent contacts. However, the dynamic state of the polymer is strongly affected by concentration and it seems possible that molecularly dispersed solutions may be obtained only at concentrations even lower than were used in this work. The simulation of these spectra is not done here. The complexity of the simulation comes from the fact that the spectrum is a superposition of at least two spectra, one with broadened lines (linewidth dH of the order of 5 G and more) and the other with sharper (d$H \approx$ 2.6 G) lines.

Isooctane has a very low melting point, and the spectra of the isooctane solutions could be measured also at temperatures well below ambient. Spectra of the samples with low and high concentration measured at temperatures around −20°C are shown in *Figure 10*. Two outer lines of the weak triplet spectrum, seen already in *Figure 5*, are detectable in both curves. The isotropic coupling constant measured from the weak sharp lines is 14.0 and 16.1 G in low and high concentration, respectively. As a comparison, it should be mentioned that the free label dissolved in isooctane and cyclohexane has $a_0 = 14.0$ G in both solvents. Because increasing polymer concentration favours the aggregation of the polymers, the solvent and concentration dependence of a_0 observed during the measurements can certainly be concluded to be due to aggregation at low temperatures.

CONCLUSIONS

Analysis of the e.p.r. spectra of the spin-labelled POIC revealed clear differences in the dynamic behaviour of the polymer when dissolved in cyclohexane and isooctane, respectively. The shape of the spectra measured from cyclohexane solutions changes only moderately with increasing temperature, whereas the spectra from isooctane solutions change from broadened immobilized ones into motionally narrowed three-line spectra.

The spectra of the polymer dissolved in cyclohexane have been characterized as combinations of three distinct spectral modes. The first mode describes the motion of the label, which is strongly restricted by the main chain. The second and third modes are due to much less restricted motion, and are interpreted as a result of the oscillation of the torsional angles in the main chain, i.e. of the flexibility of the chain. The spectra of the isooctane solutions have been analysed using two spectral modes, these having the same origin as in the case of cyclohexane solutions. In both cases, the first mode has been shown to be only slightly dependent on temperature, whereas the other modes respond strongly to temperature. The flexibility of the chain has been shown to increase with temperature, the increase being much more dramatic in isooctane than in cyclohexane.

Decreasing the polymer concentration from 30 to 5 mg ml^{-1} has nearly the same effect on the chain dynamics at room temperature as was observed when heating the more concentrated samples. This observation indicates that frequent polymer–polymer contacts occur in the studied concentration regime in both non-polar solvents.

The e.p.r. spectra of the spin-labelled POIC have also been shown to be sensitive to the gelation of the isooctane solutions; melting of the gel is detected as a change from broad immobilized spectra to motionally narrowed three-line spectra. The linewidth in the motionally narrowed spectra of the isooctane samples is high owing to the dipole–dipole interaction between the labels in the neighbouring chains. The partial aggregation of the polymers at low temperatures, the formation of the polymer network, is accompanied by an increase of the isotropic coupling constant of the nitroxide radical due to the increased polarity of the medium surrounding the radical. The spectra of the labelled POIC in cyclohexane differ considerably from those measured in isooctane. In cyclohexane, no gel formation was observed. Consequently, no changes in the isotropic coupling constant were detected. The dipolar interaction was not observed in cyclohexane.

The results indicate that at high temperatures (50–60°C) the polymer is more flexible in isooctane than in cyclohexane. The situation is reversed, however, with decreasing temperature. The gelation observed in isooctane may thus be understood as a frozen-in phase separation of the stiff polymer.

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