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Solvent dependence of the chain flexibility, aggregation and gelation of spin-labelled poly(octyl isocyanate)

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A spin-labelled poly(octyl isocyanate) has been synthesized by copolymerizing a nitroxide radical having an isocyanate function, with *n*-octyl isocyanate. The electron paramagnetic resonance spectra of the labelled polymer in various solvents are sensitive to the local conformation and flexibility of the polyisocyanate chain. The motion of the label is less restricted in a polar solvent (chloroform) than in the non-polar hydrocarbons. Poly(octyl isocyanate) shows a tendency to form aggregates in certain solvents; in solvents with low polarity the aggregation leads to the gelation of the solution. A dipolar interaction between the nitroxide labels is observed in some of the samples. The proximity of the labels is suggested to be dependent not only on the solvent quality but also on the local ordering of the polymer chains.

(Keywords: poly(octyl isocyanate); chain flexibility; gelation)

INTRODUCTION

Poly(alkyl isocyanate)s are semiflexible polymers with an extended helical structure. The repeating unit of the polymers is (–NR–CO–), where R is an alkyl side chain. Owing to the worm-like character of the polymer chains, poly(alkyl isocyanate)s are known to form lyotropic liquid crystalline phases in solutions[1–4]. Poly(*n*-alkyl isocyanates), where the number of carbon atoms in the alkyl side chain, n, is $4 \leqslant n \leqslant 12$, also exhibit thermotropic liquid crystallinity; the temperature of transition from solid to a mesomorphic state decreases with increasing length of the alkyl side chain[5].

The amide bond in the polymer main chain has a partial double-bond character. An amide group in general tends to be planar, but for steric reasons the polyisocyanate chains are twisted into helical conformation. Polyisocyanates of relatively low molar mass are rod-like (degree of polymerization, $N < 1000$), but with increasing molar mass the chains take worm-like or, when $N > 10\,000$, even random-coil conformations[6].

The persistence length of poly(alkyl isocyanate)s is strongly dependent on the solvent polarity. The overall dimensions of poly(alkyl isocyanate)s in solution are observed to be smaller in polar than in non-polar solvents[7–9]. According to Cook *et al.*[9], the solvent effects are not explained by the occurrence of helix reversals along the chain but are merely due to a local interaction between the solvent molecules and the polymer backbone. According to these authors, a polar solvent causes larger torsional oscillations in the chain backbone than does a non-polar one. In an empirical force-field study of polyisocyanates, Lifson *et al.*[10] describe these polymers as helices that possess a degree of freedom of soft collective internal motion, in which the rotation per monomer around the polymer's helical axis varies considerably. In this description, the backbone torsional angles are free to fluctuate within a fairly wide amplitude.

Poly(alkyl isocyanate)s form physical, thermoreversible gels in certain hydrocarbon solvents. Recently, Olayo and Miller[11] have studied the gelation of poly(butyl isocyanate) in benzene. A uniform and birefringent gel was obtained by freezing and thawing the polymer solution, whereas at room temperature phase separation was observed. Dilute solutions of poly(hexyl isocyanate) in some aliphatic hydrocarbons have been shown[12] to gelate when stored at −20°C.

To understand the tendency of certain solutions of polyisocyanates to form gels it would be useful to find out how these solvent effects correlate with the gel formation. The flexibility and possible aggregation of the polymer chains are likely to be important factors affecting the formation of networks. It is known that thermoreversible gels may be formed by various mechanisms ranging from liquid–liquid phase separation to specific interactions (such as hydrogen bonding or crystallization) between the dissolved polymers[13,14].

To gain further understanding of the effect of various solvents on poly(alkyl isocyanate)s, a spin-labelled poly(*n*-octyl isocyanate) (POIC) has been prepared. Octyl isocyanate was chosen as a starting material instead of the more frequently used butyl or hexyl isocyanates because the corresponding homopolymer, POIC, has been reported to have interesting bulk properties[2]. The labelled polymer was synthesized by copolymerizing a nitroxide radical having an isocyanate function, with

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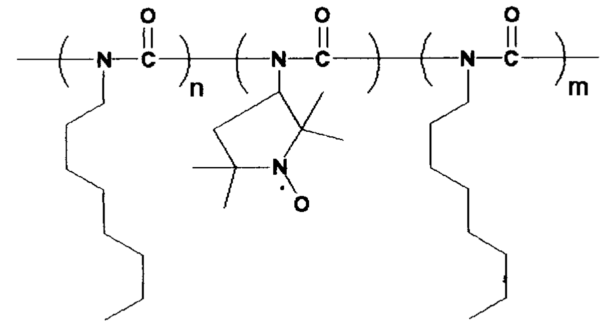
n-octyl isocyanate. The polymer thus has the following structure:



The synthesis of an end-labelled poly(butyl isocyanate) has been reported by Olayo *et al.*[15]. Electron paramagnetic resonance (e.p.r.) spectra showed the end group to possess considerable motional freedom in solutions. Spectra recorded of bulk polymers were typical slow motional spectra around room temperature; with increasing temperature the spectra were narrowed due to the increasing rate and amplitude of the reorientational motion of the nitroxide label. At 60°C, motionally narrowed three-line spectra were obtained.

In the present case, the nitroxide labels are located randomly along the polymer chain, and the cyclic labels are connected to the main chain nitrogen by just one covalent bond. The motion of the label is expected to be severely restricted not only by the slow motion of the macromolecular carrier but also by the close proximity of the carbonyl groups in the main chain. The purpose of this paper is to show that this type of label is an extremely sensitive reporter group giving information on the local conformation and flexibility of a polyisocyanate chain.

The polymer has been observed to form rigid, thermoreversible gels in toluene and isooctane (2,2,4-trimethyl pentane). In cyclohexane or chloroform, no gel formation could be detected. Time- and temperature-dependent changes due to aggregation and gelation have been studied by e.p.r. spectroscopy.

This paper describes the synthesis of the spin-labelled poly(octyl isocyanate) and discusses the chain flexibility, aggregation and gelation of the polymer in various solvents.

EXPERIMENTAL

Synthesis of the paramagnetic isocyanate monomer

1-Oxyl-2,2,5,5-tetramethylpyrrolidine-3-carboxylic acid (**1**) was synthesized from 2,2,6,6-tetramethyl-4-oxopiperidine by the methods of Rozantsev[16]. Compound **1** was converted to the corresponding acyl chloride (**2**) by treating it with a 1.25-fold excess of oxalyl chloride in dry ether containing pyridine. After slowly adding oxalyl chloride to the ether solution at 0°C, it was left stirring at room temperature to complete the reaction in 2 h. The resulting pyridinium salt was filtered off, after which the unreacted oxalyl chloride and the solvent were distilled under reduced pressure. The acyl chloride was dissolved in dry cyclohexane; to this solution a 1.25-fold excess of activated sodium azide was added and the mixture was refluxed for 2 h. The precipitate was filtered off and cyclohexane was distilled under reduced pressure. The product (**4**) was identified from its i.r. spectrum[17] which shows the absorption characteristic to isocyanate at 2265 cm^{-1}. See *Scheme 1.*

Synthesis of polymers

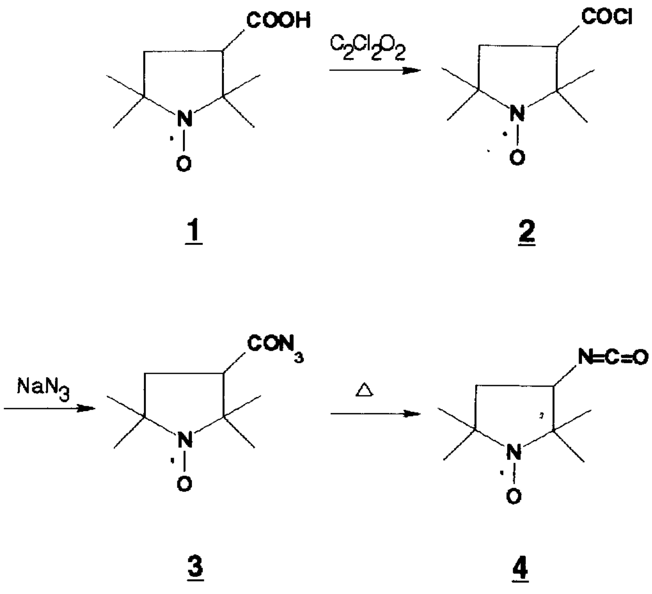
Poly(octyl isocyanate) and its spin-labelled analogue were prepared by anionic polymerization according to Shashoua *et al.*[18]. The monomer, *n*-octyl isocyanate, was synthesized by the Curtius reaction from the corresponding acyl chloride.

Spin-labelled polymer. 1-Oxyl-2,2,5,5-tetramethylpyrrolidine-3-isocyanate (75 mg) and freshly distilled octyl isocyanate (7.5 g) were dissolved in 45 ml distilled *N,N*-dimethylformamide (DMF). The polymerization was carried out under argon atmosphere near the freezing point of the solvent (−58°C) with continuous stirring. The reaction was initiated with 2 ml of a suspension of sodium cyanide in DMF (0.5 g/10 ml). After 70 min the reaction was terminated with methanol. The product polymer was precipitated with methanol and purified by repeated reprecipitations with methanol from chloroform solutions. Yield was 42%. From g.p.c. calibrated with polystyrene standards, polydispersity M_w/M_n was determined to be 3.97. The value of M_w, obtained from light scattering, was 90 000. Part of the polymer was fractionated into 28 fractions with a Sephacryl HR 400S (Pharmacia) gel column using tetrahydrofuran as an eluent.

Homopolymer POIC. Pure poly(octyl isocyanate) was prepared by the same method as described above. Yield was 83%. Polydispersity from g.p.c. was 2.19. The value of M_w, measured by light scattering, was 300 000. The light-scattering measurements will be described in detail in a forthcoming report.

Conformational energy analysis

The motional freedom of the nitroxide label was investigated by molecular mechanics and molecular



Scheme 1

dynamics simulations which were carried out with the Biosym INSIGHT II/DISCOVER program package using the consistent valence force field (CVFF)[19,20].

A segment of poly(methyl isocyanate) consisting of three repeating units was constructed to find out the most favourable helical conformation of a poly(alkyl isocyanate). The torsional angles of two successive amide bonds were independently rotated by 10° increments. After each increment, the torsional angles were held stationary and the rest of the segment was allowed to relax to its minimum energy. The energy contour map was calculated as a function of the rotations. In this way, the conformation with the lowest energy could be found for the trimeric model.

Using the low-energy conformation obtained for the trimer, right-handed helices consisting of 15 repeating alkyl isocyanate units were constructed with varying alkyl side chains, and thus polymers of methyl, *n*-butyl, and *n*-octyl isocyanate could be compared. Each chain was allowed to relax to its minimum energy after which one of the alkyl chains in the middle of the segment was replaced by a nitroxide label. The rotational energy profile of the label was calculated by rotating it around the bond connecting the cyclic label to the main-chain nitrogen in 10° increments. After every increment, the torsional angle of the nitroxide (ABCD, see *Figure 1*) was held constant and the rest of the structure was allowed to move freely to its minimum energy.

Molecular dynamics was used to confirm the reliability of the energetically favourable conformation which was originally found for the trimer with molecular mechanics. The molecular dynamics simulation of an isolated labelled poly(octyl isocyanate) was carried out in vacuum at 300 K for a 20 ps period.

Measurements

Thermal analysis. Polymer solutions and gels were studied calorimetrically with a Perkin Elmer DSC 7. Samples were prepared by weighing the polymer directly to the aluminium sample pans. After the known amounts of solvent were added, the sample pans were closed and kept at 60–70°C for several days to assure the dissolution of the polymer. Samples were allowed to gelate at −22°C. The thermograms were recorded with a heating rate of $10^\circ C\ min^{-1}$.

E.p.r. measurements. The e.p.r. spectra were recorded with a Varian E-4 instrument. Samples were prepared in glass capillaries which were sealed and held for at least 24 h at 60°C to dissolve the polymer. Prior to the measurement, samples (except those dissolved in chloroform) were heated for a short time in a boiling water bath.

RESULTS AND DISCUSSION

An essential step in the synthesis of a polyisocyanate is the purification of the isocyanate monomers, which is most conveniently done by distillation. Although the nitroxides are thermally reasonably stable, attempts to distil the radical **4** were observed to lead to a partial decomposition of its paramagnetic centre. It was decided to use **4** without distillation, with the risk that the impurities remaining after the initial purification (see Experimental section) could disturb the anionic polymerization. For example, Zuen and Gandini[21] have shown that homopolymerization of totally unpurified 2-furyl isocyanate prepared by the Curtius reaction from an azide gives mainly low molar mass oligomers. In the present synthesis of a spin-labelled polymer, however, the amount of the unpurified monomer was less than 1 mol% of the whole monomer feed. Consequently, it was assumed that the amount of impurities in the monomer mixture is low enough not to prevent the polymerization.

The yield of the labelled polymer was only half of that of the pure POIC and also the molar mass distribution was fairly broad. This is due to the chain transfer and termination reactions caused by the impurities.

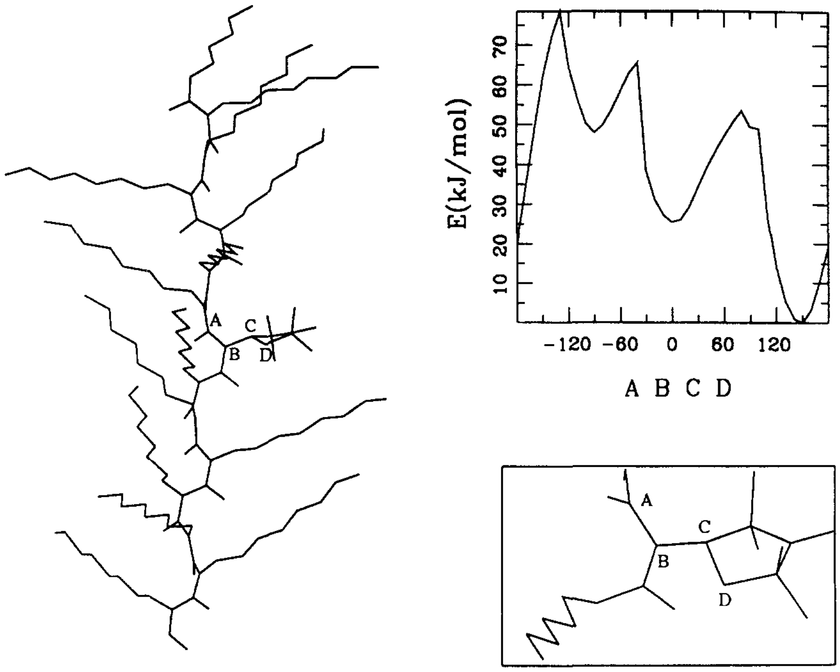


Figure 1 Part of the labelled segment of poly(octyl isocyanate) in its optimized conformation (left). The energy of rotation of the torsion angle ABCD is shown in the upper right corner. The angle ABCD is defined below the graph

However, the molar mass of the product is satisfactorily high. In this molar mass regime, the e.p.r. spectra are sensitive to the local motion of the polymer segments, in addition to the label's fast reorientation relative to the macromolecule[22].

A part of the labelled polymer was fractionated into several small fractions in a g.p.c. column to check the influence of the polydispersity on the shape of the e.p.r. spectra. Various fractions, either in bulk or dissolved in 2,2,4-trimethyl pentane, gave essentially identical spectra. This finding indicates that although the polydispersity is known to affect the solution properties of a polymer, such as phase separation and gelation, this effect is hardly detectable when one observes the immediate surroundings of the reporter group bound to a close proximity of the polyisocyanate main chain.

By theoretical considerations based on molecular mechanics, it has been shown that the motional freedom of the nitroxide label is strongly affected by the rigidity of the main chain, The analysis of a poly(alkyl isocyanate) chain was started by studying a trimeric model of poly(methyl isocyanate). The optimum helical structure for the model was concluded to be that with approximate torsional angles of (−30°, 160°). Taking these values as a starting point, the torsional angles in the polymeric methyl, *n*-butyl and *n*-octyl isocyanate chains were determined as (−29°, 153°), (−36°, 155°) and (−40°, 160°), respectively. A slight distortion of the angles is observed in the chain with the longest alkyl side groups.

The energy barrier of the rotation about the backbone amide bonds was determined to be 29 kJ mol^{-1}. Because the partial double-bond character of the polyisocyanate main chain is not taken into account in the molecular mechanics simulation, the value needs to be critically evaluated. Based on both theoretical and experimental reasoning, Lifson *et al.*[10] use a value of 52 kJ mol^{-1} (12.5 kcal mol^{-1}). This indicates that in the present model, the flexibility of the polymer chain has been somewhat exaggerated.

A part of the labelled segment of poly(octyl isocyanate) in its energetically most favourable conformation is shown in *Figure 1*. In this conformation, the torsion angle ABCD is of the order of 145°. Thus, the 2pπ orbital of the nitroxide nitrogen is oriented approximately along the helix long axis. The energy barrier for the rotation of the nitroxide (also shown in *Figure 1*) was calculated to be 78 kJ mol^{-1}. The value was observed to be about the same in the cases of poly(methyl isocyanate) and poly(butyl isocyanate). The average thermal energies within the temperature limits of the e.p.r. measurements are of the order of 1.4–2.9 kJ mol^{-1}. It is obvious that the energy barrier shown in *Figure 1* may not be overcome if the polymer main chain is held in the conformation shown in the figure.

According to the molecular dynamics simulation, only small fluctuations of the torsion angle ABCD take place during 20 ps. The angle varied in the range 142 ± 9°. With this simulation, the stability of the helical conformation was also observed; only a small fluctuation of the main-chain torsional angles could be detected.

To conclude, the simulations indicate that even when too much flexibility is allowed for the polyisocyanate main chain, the rotation of the nitroxide is considerably restricted by the substituents in the polymer backbone.

Because the properties of polyisocyanates are known to be critically dependent on the solvent polarity, four solvents were used in the e.p.r. measurements. Three of these were non-polar hydrocarbons and the fourth was chloroform. The solvents and some of their properties relevant to this discussion are listed in *Table 1*.

Fresh solutions of the polymer in toluene or isooctane (2,2,4-trimethyl pentane) were detected to form turbid gels when stored at −20°C overnight. The toluene gel melts below room temperature, whereas the isooctane gel is stable at ambient temperature. In cyclohexane, poly(octyl isocyanate) does not gelate but forms highly viscous solutions. No gel formation was observed in chloroform.

E.p.r. spectra of solutions with a concentration of 50 mg ml^{-1} were measured at room temperature to detect possible time-dependent changes of the samples. Fresh solutions were equilibrated at room temperature and the spectra were recorded. The samples were left at room temperature and the measurement was repeated the following day and after 2 weeks. All the other samples were clear solutions but that in isooctane was slightly opaque. A slow phase separation started in the isooctane solution when it was kept at room temperature.

The nitrogen hyperfine coupling constant (a_N) was larger in chloroform than in the non-polar hydrocarbons, as is usual. No time-dependent changes in a_N could be detected at room temperature; the values of the coupling constant are shown in *Table 1*.

The e.p.r. spectra of isooctane and cyclohexane solutions of the labelled POIC are shown in *Figure 2*. As may be seen from the figure, the spectra of fresh solutions are very similar. The existence of two outer maxima with a separation of around 55 G, as well as the broadness of the three hyperfine lines, indicates that the motion of the label is restricted in both samples. Spectra of this type are often obtained from solutions of spin-labelled polymers where the nitroxide labels are involved in two

Table 1 Properties of the solvents

Solvent	Melting point (°C)	Viscosity (10^{-5} Pa s)	Dipole moment (10^{-30} Cm)	δ^a (MPa$^{1/2}$)	$a_N{}^b$ (G)
Isooctane (2,2,4-trimethyl pentane)	−107	51	0	14.0	13.7
Cyclohexane	6.5	96	0	16.8	13.7
Toluene	−95	59	1.20	18.3	13.7
Chloroform	−63	57	3.37	18.7	14.7

[a] Hildebrand solubility parameter from ref. 25

[b] Nitrogen hyperfine coupling constant measured from 50 mg ml^{-1} solutions

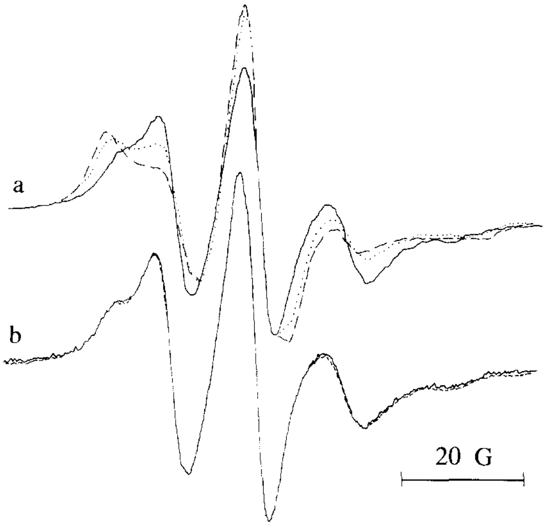


Figure 2 E.p.r. spectra of 50 mg ml^{-1} solutions of the labelled polymer in (a) isooctane and (b) cyclohexane. ——, Spectra of the fresh solutions, ····, spectra measured after 1 day; – – –, spectra measured after 2 weeks

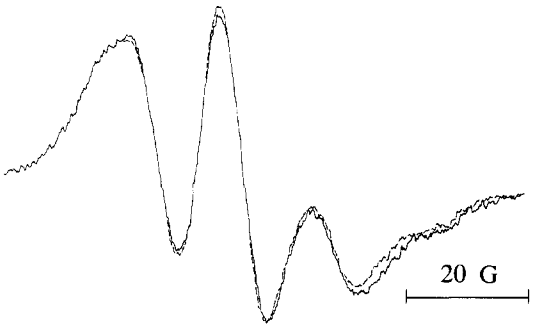


Figure 3 E.p.r. spectra of a 50 mg ml^{-1} solution of the labelled polymer in toluene, ——, Spectrum of the fresh solution; – – –, spectrum measured after 2 weeks

types of motion: the fast anisotropic reorientation relative to the polymeric carrier, and the slow diffusion of the macromolecule. The simulation of the spectra is not a straightforward task and it will be described in detail in a separate report. Owing to the phase separation of the isooctane solution, the spectra of this sample change from a shape typical of a solution closer to that typical of a solid polymer. During the period of 2 weeks, the cyclohexane solution seemed to be stable. The similarity of the spectra obtained from the fresh solutions in isooctane and cyclohexane is noteworthy when one considers the difference in the viscosities of the solvents. The fact that the viscosity of cyclohexane is almost twice the viscosity of isooctane justifies the conclusion that the motional freedom of the spin label is determined not by the solvent as such but by the flexibility of the polymer chain in this particular solvent.

The toluene solution of the labelled POIC was clear and stable at room temperature. The e.p.r. spectrum from a fresh solution is similar to that measured after 2 weeks (see *Figure 3*). These spectra are very different from those displayed in *Figure 2.* The spectrum from a toluene solution may be characterized as a superposition of a nitroxide triplet and a broad singlet. Spectra of this type are typically obtained from solutions with a relatively high nitroxide concentration and are due to an interaction between the nitroxides, either dipolar interaction or spin exchange. The exchange interaction is essentially a contact interaction and is dependent on the molecular collision rate[23]. Thus, spin exchange is probable in non-viscous solutions but may not be in the case of a fairly concentrated solution of poly(octyl isocyanate). The spectra in *Figure 3* indicate that in a toluene solution the local concentration of nitroxide radicals is higher than in the isooctane or cyclohexane solutions. Although toluene has been regarded here as a non-polar solvent, it of course differes from the aliphatic hydrocarbons (see *Table 1*). The small difference between the polarity of the aliphatic solvents and toluene may be sufficient to cause the observed differences between the e.p.r. spectra. Also, the differences between the solvents are clearly seen from the values of the solubility parameters. Poly(hexyl isocyanate), which has been extensively studied during the past 20 years, is generally considered to be molecularly dispersed in dilute toluene solutions. However, this is not necessarily the case with poly(octyl isocyanate) in the present experimental conditions. Increased local nitroxide concentration may follow either from the aggregation of the polymer chains or from the lateral arrangement, i.e. local ordering of the polymer chain segments in toluene. Experimental evidence of aggregation of poly(*n*-hexyl isocyanate) in toluene has been reported[24]; however, if the dipolar interaction were a consequence of an aggregation process it should also be seen in the spectra of isooctane solutions in *Figure 2.*

The sharpness of the three nitrogen hyperfine lines in the spectra obtained from the chloroform solution with a concentration of 50 mg ml^{-1} (*Figure 4*) indicates that the motion of the label is faster and less restricted in chloroform than in the non-polar solvents. The large torsional oscillations of the polymer backbone in the polar solvent increase the motional freedom of the label. It is interesting to note that time-dependent changes also occur in the chloroform solution. In *Figure 4* only two spectra are displayed, that of a fresh solution and that recorded on the following day; the increase in the linewidth is obvious. In the spectrum recorded 2 weeks later the linewidth was further increased. The third spectrum has been excluded from *Figure 4* owing to its low signal-to-noise ratio. The label degrades upon standing in a chloroform solution.

The e.p.r. spectra of the solutions of the labelled POIC were also measured as a function of temperature. In these measurements, two concentrations were used: 50 and 200 mg ml^{-1}. The higher concentration was chosen

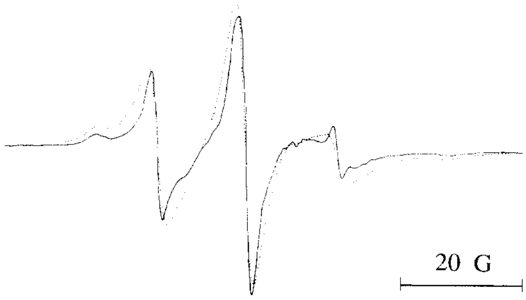


Figure 4 E.p.r. spectra of a 50 mg ml^{-1} solution of the labelled polymer in chloroform. ——, Spectrum of the fresh solution; ····, spectrum measured on the following day

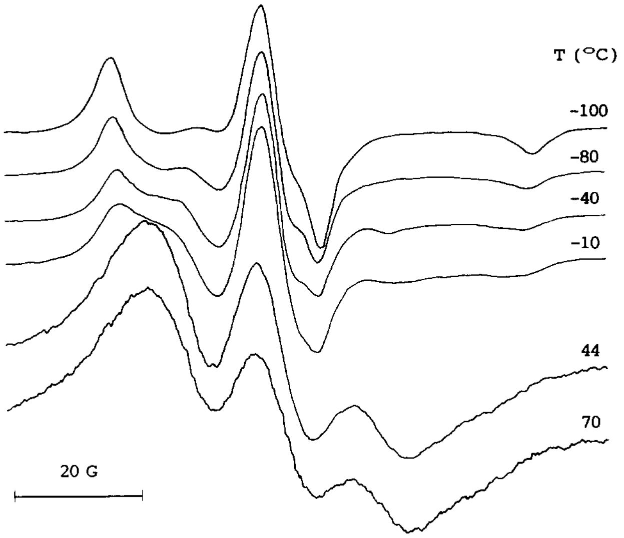


Figure 5 Spectra of a concentrated toluene solution (200 mg ml^{-1}) measured as a function of temperature

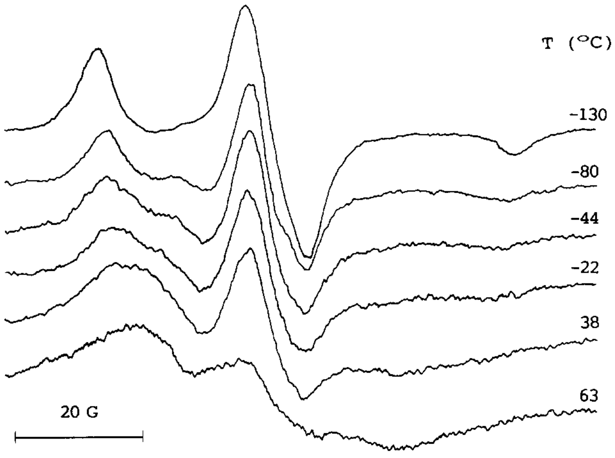


Figure 6 Spectra of a concentrated isooctane solution (200 mg ml^{-1}) measured as a function of temperature

because it was assumed to be in the regime where the solutions show lyotropic liquid crystalline behaviour. The liquid crystallinity of the samples was verified after the e.p.r. measurements with a polarizing microscope; all of the more concentrated samples were birefringent. Because the gelation of the solutions was of interest, care was taken to assure a similar thermal history for every sample. It is known that some polymer solutions form gels upon freezing[13–15] and thus all the samples were frozen in the cavity of the spectrometer prior to the measurements.

E.p.r. spectra measured as a function of increasing temperature reveal profound differences between the various solutions of POIC in the solvents used. In the spectra of the more concentrated toluene and isooctane samples (*Figures 5* and *6*), a strong interaction between the nitroxides is observed at temperatures above the ambient. On the other hand, in the cyclohexane solution (*Figure 7*) no such effect can be detected. In this respect the spectra of the more dilute solutions are similar; dipolar interaction is seen in the isooctane and toluene samples but not in cyclohexane. In chloroform solutions, the dipolar interaction is observed only in the more concentrated sample. The spectra of the chloroform solutions are not reproduced here.

The broadening of the e.p.r. lines due to the interaction between the nitroxide radicals is illustrated in *Figures 8–10* by plotting the peak-to-peak width of the central line ($m_I = 0$) of the e.p.r. spectra against temperature. Cyclohexane samples behave as expected for a true non-associating solution: the linewidth decreases with increasing temperature, the decrease being greatest around the melting point of the solvent. In the isooctane and toluene solutions, the spectral lines are broad over the whole temperature range and start to broaden during the melting of the gels. Indeed, it has been observed by d.s.c. that the isooctane gels melt in the temperature range 30–50°C ($\Delta H \approx 2$–$5\,\mathrm{J\,g^{-1}}$), whereas the toluene gels melt

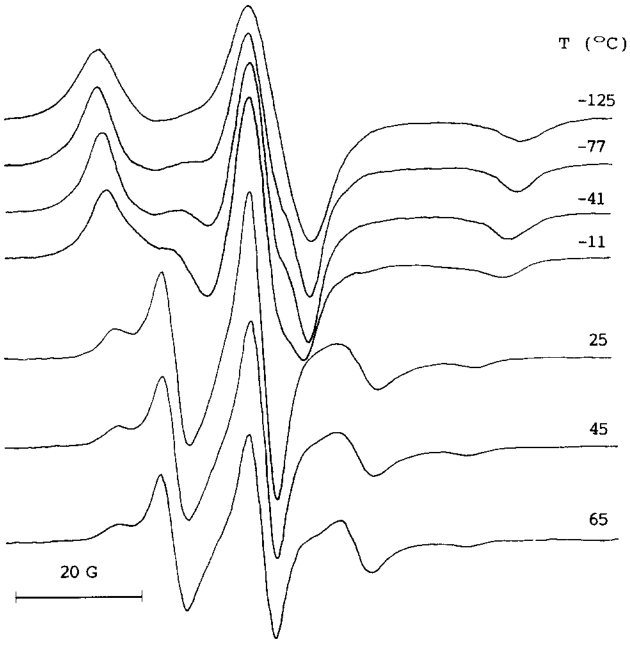


Figure 7 Spectra of a concentrated cyclohexane solution (200 mg ml^{-1}) measured as a function of temperature

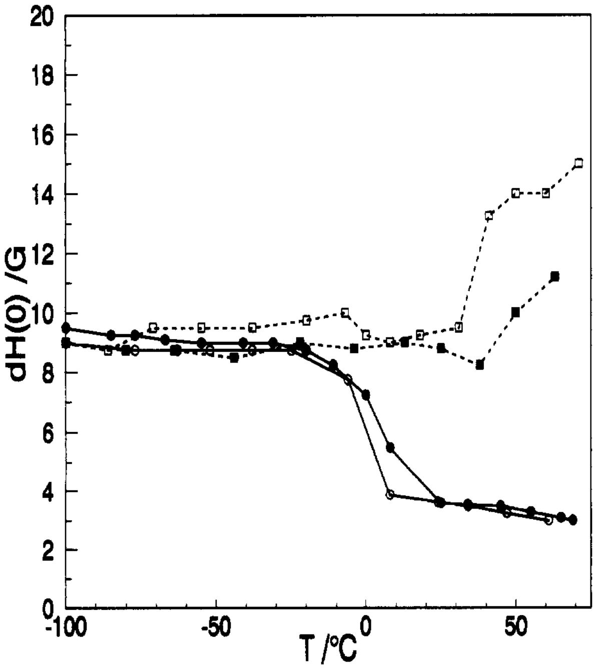


Figure 8 Width of the central e.p.r. line (dH(0), in Gauss) of the cyclohexane (circles) and isooctane (squares) solutions as a function of temperature. Open symbols: 50 mg ml^{-1}; solid symbols: 200 mg ml^{-1}

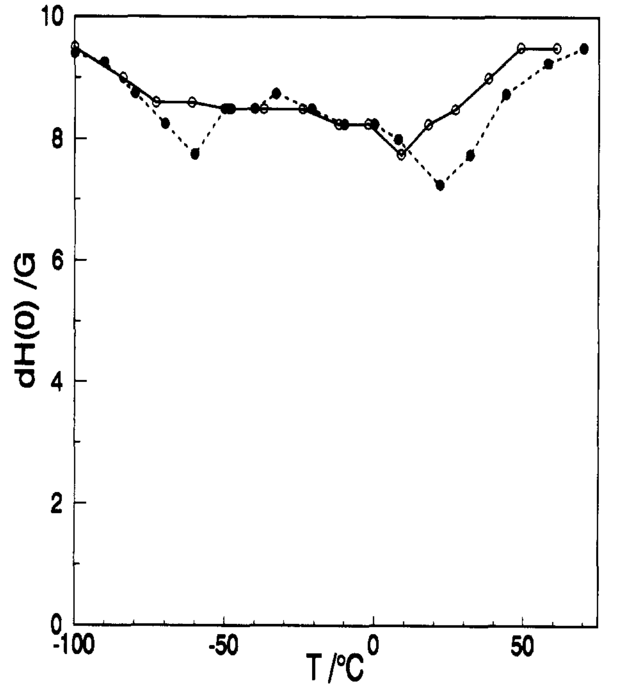


Figure 9 Width of the central e.p.r. line of the toluene solutions as a function of temperature. Open circles: 50 mg ml^{-1}; solid circles: 200 mg ml^{-1}

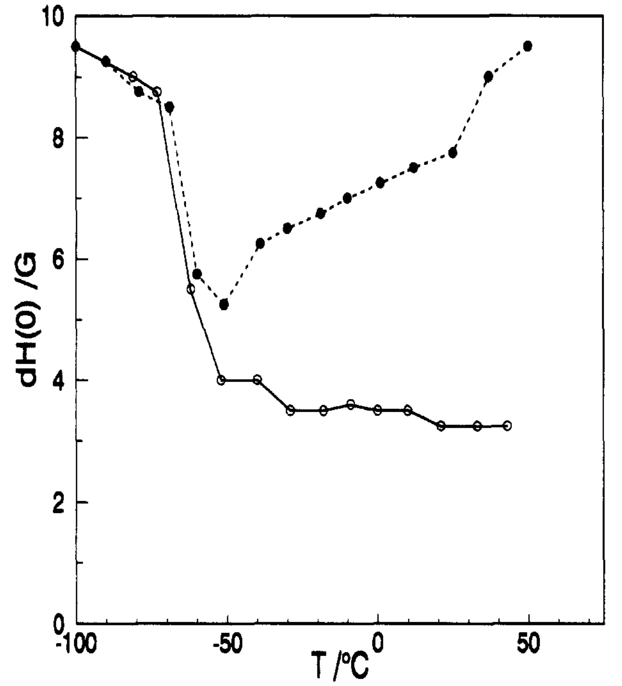


Figure 10 Width of the central e.p.r. line of the chloroform solutions as a function of temperature. Open circles: 50 mg ml^{-1}; solid circles: 200 mg ml^{-1}

between 10 and 20°C ($\Delta H \approx 2\,\mathrm{J\,g^{-1}}$). It can be concluded that in these samples the network forms during freezing by partial aggregation of the chains. From this conclusion it follows that the mutual alignment of the polymer chain segments, which was suggested to be the reason for the observed dipolar interaction, is to a certain extent prohibited by the network junctions and thus becomes apparent only after the melting of the gel.

In *Figure 10*, the width of the central e.p.r. line of the chloroform solutions is shown as a function of temperature. The more dilute solution behaves like the cyclohexane sample, i.e. the decrease of the linewidth is fastest around the solvent melting point. However, in the concentrated sample the interaction between the paramagnetic labels becomes apparent soon after the melting of the solvent. In the curve representing the linewidth of the concentrated sample there is an upturn above room temperature. When the same sample is melted in d.s.c., a small endothermic peak may be detected at about 25°C ($\Delta H \approx 0.1$–$0.2\,\mathrm{J\,g^{-1}}$). The polymer is concluded to aggregate in chloroform but to a much lower extent than in isooctane and toluene (see also *Figure 4*). The liquid crystalline order in the more concentrated solution increases the possibility of the nitroxides moving close to each other.

To conclude, it has been shown that the e.p.r. spectra of the spin label bound to the poly(octyl isocyanate) chain are sensitive to solvent-dependent differences in the flexibility of the polymer main chain, Poly(octyl isocyanate) has a tendency to form aggregates in solutions, not only in the non-polar solvents but also in chloroform. In isooctane and toluene the aggregation leads to gel formation (at temperatures below the ambient); gelation was not observed in chloroform. No aggregation or gelation was detected in cyclohexane. Cyclohexane is the only solvent used in this study where no interaction between the spin labels was detectable, even in the concentrated liquid crystalline samples. Thus, the dipolar interaction (proximity of the labels) is not only due to the alignment of the polymer chains, but also depends on the solvent quality. Cyclohexane seems to be a good solvent for poly(octyl isocyanate); it is capable of keeping even the oriented chains well apart, and, the high viscosity of cyclohexane may be important in this.

The investigation is to be continued by a systematic thermal analysis of the gels and solutions of POIC, as well as by a detailed analysis of their e.p.r. spectra.

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