Effect of temperature on the chain trajectory in thermoreversible gels and pregels of isotactic polystyrene: a preliminary investigation by neutron scattering

Marc Klein* and Jean-Michel Guenet†
‡Laboratoire d'Ultrasous et de dynamique des Fluides complexes, Université Louis Pasteur-CNRS URA 851, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France

and Annie Brûlet and François Boué
Laboratoire Léon Brillouin, CEN, Saclay 91191, Gif sur Yvette Cedex, France

(*Received 9 May 1990; revised 10 July 1990; accepted 17 July 1990*)

We report on preliminary investigations of the chain trajectory determined by neutron scattering, first, in the gel and the pregel state, and second, in the liquid state just after melting. For the gel state ($C_{pol} = 15\%$), only the system isotactic polystyrene (iPS)/*cis*-decalin has been investigated. Just after gel melting ($T = 66°C$), chain conformation is virtually unaltered: the chains possess nearly the same stiffness they had in the gel (worm-like statistics, with statistical length $b \simeq 8$ nm). In this sense, gel melting resembles a nematic–isotrope transition. Conformational change only occurs after subsequent annealing at this temperature in relation to the sample's crystallization (turbid sample). For the pregels ($C_{pol} \simeq 1\%$) at 66°C the chains still exhibit enhanced rigidity (worm-like conformation with $b \simeq 10$ nm) in iPS/*cis*-decalin solutions while in iPS/*trans*-decalin solutions this behaviour has vanished. From these results we conclude: chain rigidity does not arise from gelation but, on the contrary, gelation occurs due to the unusual chain rigidity; and the stabilization mechanism producing enhanced rigidity is thought to originate in helix solvation.

(Keywords: neutron scattering; chain trajectory; gels; pregels; chain rigidity)

INTRODUCTION

The gelation mechanism of isotactic polystyrene (iPS) solutions is a topical issue[1–5]. Molecular structure investigations have led to different models being proposed which are not described in detail here. Depending upon the model, gelation is regarded as either a crystallization phenomenon[1–3] or a nematic-like association of solvated helices[4]. To our knowledge the only study of the effect of temperature on the molecular structure is by Perez *et al.*[5]. Using nuclear magnetic resonance (n.m.r.) these authors did not observe any marked variation in chain mobility from the gel state to the liquid state but rather a progressive one. Accordingly they concluded that the melting process is distinct from the usual polymer crystal fusion.

The purpose of this paper is to report on preliminary investigations of the chain trajectory on either side of the gel melting point using small-angle neutron scattering. The study has been performed with gels ($C_{pol} = 15\%$) and pregels ($C_{pol} = 0.8$–1.6%). For the pregels the effect of solvent type (*cis-* or *trans*-decalin) has also been examined.

EXPERIMENTAL

Materials

Cis- and *trans*-decalin (protonated) were purchased from Merck. Deuterated *cis*-decalin (>99% deuterated) was obtained from Janssen. All the solvents were used without further purification.

Protonated iPS has already been used in other studies[6]: $M_w = 3.2 \times 10^5$, $M_w/M_n \simeq 2.8$.

Deuterated fractions have also been employed in previous studies[6]: $M_w = 7 \times 10^5$, $M_w/M_n = 1.2$; $M_w = 2.54 \times 10^5$, $M_w/M_n = 1.15$; $M_w = 0.65 \times 10^4$, $M_w/M_n = 1.1$.

Sample preparation

Pregels from the three different deuterated samples in protonated decalin (either *cis* or *trans*) were prepared in hermetic test tubes by heating at 170°C and then quenching in iced water for a minimum of 20 min. These pregels were stored for 1 week at room temperature prior to the neutron measurements. Gels containing ~1% deuterated chains (total polymer = 15%) were prepared in the same way.

In order to match the coherent signal from the hydrogenated polymer the solvent was a mixture of deuterated and protonated *cis*-decalin (19.8% v/v of the deuterated species)[6]. Gels of identical concentration but

---

* Present address: LACERM S.A., 27 rue Mimosas, 68400 Riedisheim, France

† To whom correspondence should be addressed

‡ Formerly: Laboratoire de Spectrométrie et d'Imagerie Ultrasonore

0032-3861/91/111943-05

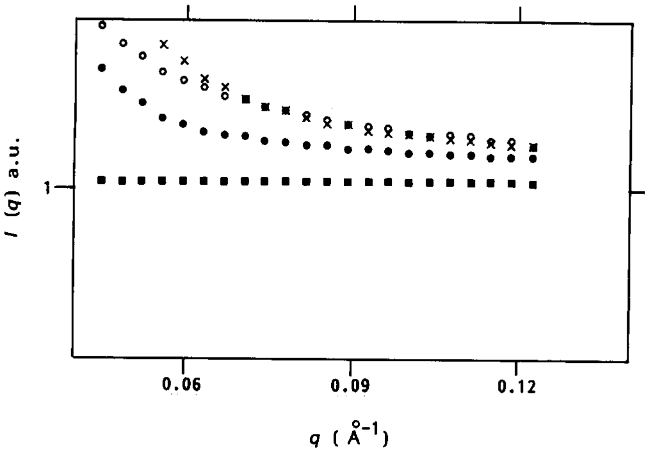

Figure 1 Neutron scattering data only corrected for transmission, thickness and normalized by decalin spectrum. ■, Protonated *cis*-decalin at 17°C. The following are iPSD/*cis*-decalin dilute systems: ●, $M_w=2.5\times10^5$, $C_D=0.8\times10^{-2}$ g cm^{-3}, $T=66$°C; ×, $M_w=6\times10^4$, $C_D=1.6\times10^{-2}$ g cm^{-3}, $T=17$°C; ○, $M_w=6\times10^4$, $C_D=1.6\times10^{-2}$ g cm^{-3}, $T=66$°C. The spectrum of *cis*-decalin at 66°C after the above correction is not given since it differs from the one at 17°C by ~1%

with no deuterated chains were also produced to be used as blanks.

Pieces of gel were then introduced into rectangular amorphous silica cells (inner thickness 1 mm). These cells were hermetically sealed and the gel was molten and reformed in the cell under the same conditions as described above.

The scattered intensity was measured at 17, 37, 66 and 95°C for the gels and at 17, 66 and 95°C for the pregels.

Experimental set-up and signal processing

All the experiments were performed at the Laboratoire Léon Brillouin (CEN Saclay, CNRS-CEA) using PAXY small-angle camera. This camera is equipped with a two-dimensional position-sensitive counter. The available scattering vectors q, where $q=4\pi/\lambda \sin\theta/2$ (λ = neutron wavelength and θ = scattering angle), were in the range $0.015\leqslant q(\text{Å}^{-1})\leqslant 0.13$ (for $\lambda=5$Å).

The samples were placed onto a sample holder that was kept at the desired temperature to within ±1°C. The temperature was measured in a companion reference cell containing only oil. Pure *cis*-decalin was used for normalization of the counter since this solvent gives off only incoherent scattering (decalin's coherent scattering amplitude A_{dec} is even smaller than that of protonated water: $A_{dec}=-7\times10^{-14}$ cm compared to $A_{H_2O}=-18\times10^{-14}$ cm). The intensity scattered by the deuterated chains was obtained from the following expression:

$$I_N(q)=\frac{\dfrac{I_s(q)}{T_s\delta_s}-(1-X_D)\dfrac{I_0(q)}{T_0\delta_0}}{\dfrac{I_{dec}(q)}{T_{dec}\delta_{dec}}-\dfrac{I_{ec}(q)}{T_{ec}\delta_{ec}}} \qquad (1)$$

where subscripts s = sample, 0 = blank sample, dec = *cis*-decalin and ec = empty cell, $I(q)$, T and δ are the intensity, transmission and thickness respectively, and X_D is the proportion (v/v) of deuterated species in the sample.

The normalized intensity in the Zimm approximation is:

$$I_N(q)=KC_DM_w[P_D(q)-2A_2C_DP_D^2(q)] \qquad (2)$$

where M_w is the weight average molecular weight of the deuterated species, $P_D(q)$ their form factor and A_2 the virial second coefficient. The calibration constant K is given by:

$$K=4\pi\delta_{dec}N_A(a_D-y_{HD}a_H)^2/(1-T_{dec})m_D^2 \qquad (3)$$

where a_D and a_H are the scattering amplitudes of the species, y_{HD} the ratio of their molar volumes ($y_{HD}=v_D/v_H$) and m_D the monomer molecular weight.

Although the noise (incoherent signal) is larger with pure decalin, this effect is compensated for by the high contrast of polystyrene in this solvent ($A_{iPSD}-A_{dec}=10.8\times10^{-12}$ cm compared to $A_{iPSD}-A_{gel}=8.4\times10^{-12}$ cm). In particular, we could use solutions of concentrations slightly <1% without serious problems. At the largest angles the ratio signal/noise is about 1.16 for $C_{pol}=0.8\times10^{-2}$ g cm^{-3}. Between $q=0.06$ Å^{-1} and 0.09 Å^{-1} this ratio varies from 1.34 to 1.19 for $C_{pol}=0.8\times10^{-2}$ g cm^{-3} and 1.58 to 1.33 for $C_{pol}=1.6\times10^{-2}$ g cm^{-3} (*Figure 1*).

The statistical dispersion $N^{-1/2}$, where N is the number of counts, is <2%. Accordingly, as far as statistical error is concerned, error bars are of the order of the size of the symbols used to represent the experimental intensities.

RESULTS AND DISCUSSION

Results obtained on the gels are plotted in *Figure 2* by means of a Kratky representation ($q^2I(q)$). As can be seen, at 17°C a result previously published is obtained[6], namely the chain statistics can be described by a worm-like conformation for which the statistical length b is ≃8 nm. As shown in *Figure 2*, this conformation is practically unaltered at 66°C, a temperature located above the gel melting temperature ($T_m\simeq50$–60°C). The virtually unaltered chain rigidity leads one to assume that gel melting takes place through a disorientation process reminiscent of a nematic–isotropic transition as in liquid crystalline polymers but not through helix fusion as in crystallized polymers. The temperature must be raised to 95°C to observe a significant discrepancy with the gel state (*Figure 2*).

The chain conformation is however, not stable at 66°C.

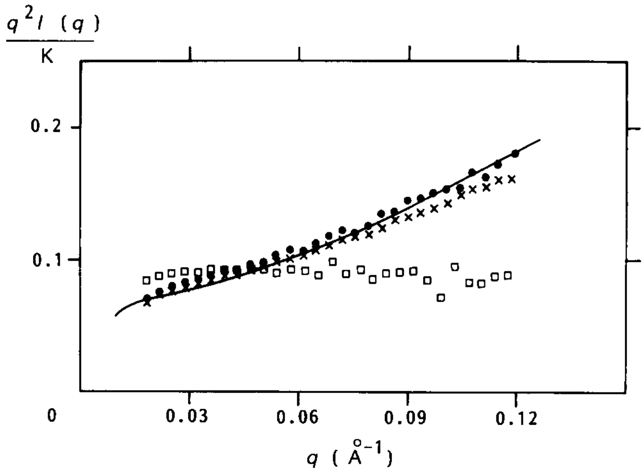

Figure 2 Kratky plot $q^2I(q)$ *versus* q for a 15% gel prepared at 0°C and then heated at different temperatures: ($C_D=1.05\times10^{-2}$ g cm^{-3}, $M_w=2.5\times10^5$) ×, 17°C; ●, 66°C; □, 95°C. The solid line is calculated from Yoshisaki and Yamakawa's function[9] for a worm-like chain with $b=10$ nm

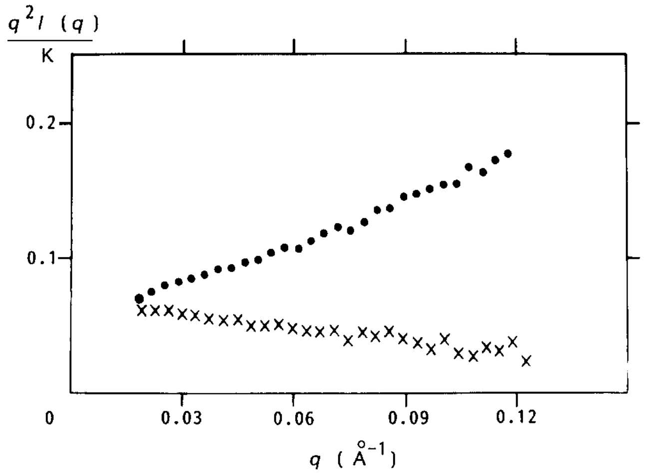

Figure 3 Kratky plot for the same gel as in *Figure 2*. ●, Gel at 66°C (3 h maximum at this temperature); ×, gel annealed 24 h at 66°C then stored for 1 week at room temperature

As expected the sample develops turbidity on ageing at 66°C for 24 h and then 1 week at room temperature which indicates that crystallization eventually takes place under these conditions. Correspondingly, the chain trajectory is significantly modified as shown in *Figure 3*. A behaviour of the type q^{-n} with n slightly larger than 2 is found which is markedly different from the one observed in the gel. Such behaviour is reminiscent of that found for single crystals prepared at high undercoolings[7,8]. We shall not discuss this point further here.

From these experiments we conclude that gel melting takes place by a mechanism reminiscent of the nematic–isotrope transition as in liquid crystalline polymers. This implies a similarity in structure with that of nematic liquid crystalline polymers, which agrees with previous conclusions[4,6]. The absence of helix fusion and correspondingly no significant change in chain internal mobility may be linked to the n.m.r. findings of Perez *et al.*[5]. This melting process also suggests that some kind of helix stabilization impedes helix fusion. Does there remain some chain–chain interaction (for instance two parallel chains forming a kind of double-stranded structure) or is the stabilization process inherent in the chain (special helical form or solvation)? Since only a few chains are labelled, we cannot confirm or invalidate the former hypothesis. Investigations carried out on the pregels shed further light on this question.

Results obtained on the pregels are plotted by means of a Kratky representation ($q^2I(q)$) in *Figure 4* for *cis*-decalin and *Figure 5* for *trans*-decalin.

Cis-*decalin pregels*

Pregels prepared in *cis*-decalin exhibit different types of behaviour depending upon temperature (*Figure 4*):
(1) At room temperature chains are aggregated as shown by the strong upturn at small scattering angles. At larger scattering angles, the q^{-1} behaviour occurs again. These results suggest that the pregels are composed of worm-like chains aggregated at random (possibly possessing a fractal structure) rather than regularly (forming fibres for instance). In the latter case one would not expect to observe the q^{-1} behaviour unless the chains in the aggregate were greatly spaced from one another (considering the value q^* at which this behaviour occurs suggests a distance of about $2/q^* \approx 3.3$ nm).
(2) At 66°C aggregation has vanished which is expected since the system is well above its melting point and yet the rod-like behaviour is still seen. A statistical segment of about 10 nm can be estimated both from a fit with Yamakawa's analytical function for worm-like chains[9] and from Rawiso *et al.*'s criterion[10], $q_0 b \simeq 7$, where q_0 is the transfer momentum at which it is estimated that the q^{-1} behaviour is effectively reached.

What allows chain rigidity to be maintained above the melting temperature of both the gel and the pregel? Undoubtedly some helical stabilization must take place.

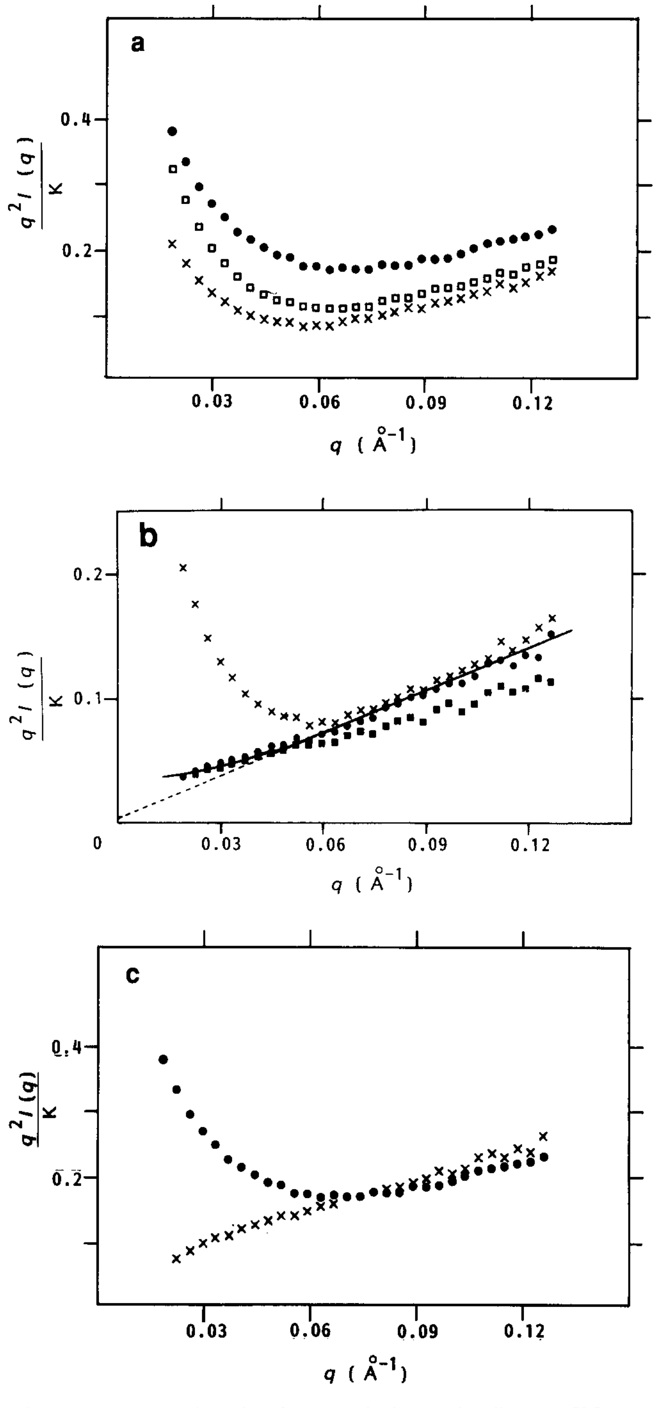

Figure 4 (a) Kratky plot for pregels in *cis*-decalin at 17°C. ×, $M_w = 2.5\times10^5$, $C_D = 0.8\times10^{-2}$ g cm^{-3}; □, $M_w = 7\times10^5$, $C_D = 1.05$ g cm^{-3}; ●, $M_w = 6\times10^4$, $C_D = 1.6\times10^{-2}$ g cm^{-3}. (b) Effect of temperature on iPSD/*cis*-decalin pregels ($M_w = 2.5\times10^5$); ×, 17°C; ●, 66°C; ■, 95°C. Solid line calculated as in *Figure 2*. (c) Effect of temperature on iPSD/*cis*-decalin pregels ($M_w = 6\times10^4$): ●, 17°C; ×, 66°C

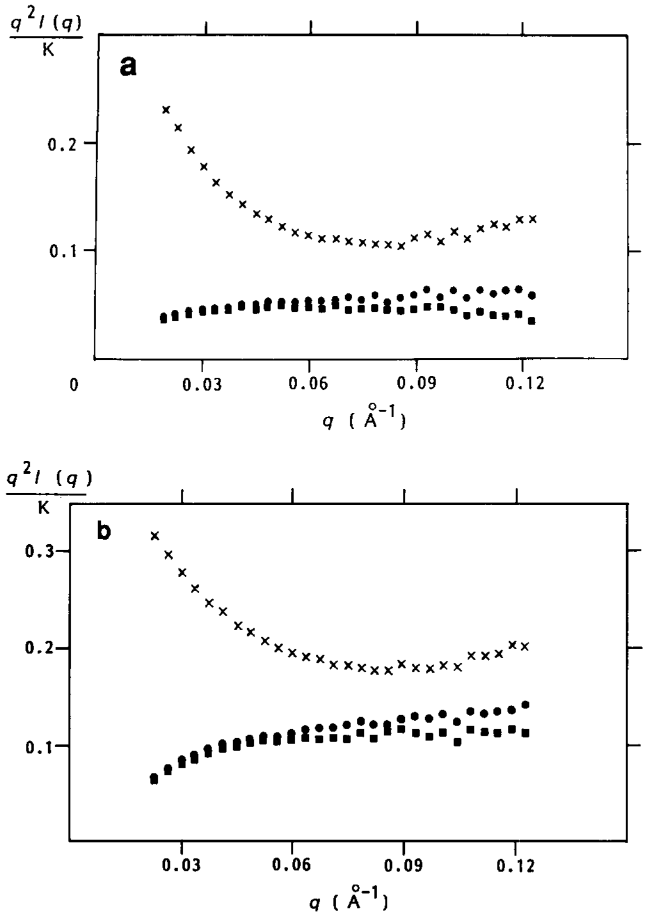

Figure 5 Kratky plot for pregels in *trans*-decalin. ×, 17°C; ●, 66°C; ■, 95°C. (a) $M_w=2.5\times10^5$, $C_D=0.9\times10^{-2}$ g cm^{-3}; (b) $M_w=6\times10^4$, $C_D=1.46\times10^{-2}$ g cm^{-3}

Given that all the chains here are labelled means that the double or multi-stranded structure hypothesis can be invalidated. As a matter of fact, the linear mass, μ_L, can be estimated from the slope of the q^{-1} behaviour in the Kratky representation for worm-like chains[11]:

$$\frac{q^2I(q)}{KC_D}=\pi\mu_L q+\frac{4\mu_L}{3b} \tag{4}$$

This yields $\mu_L\simeq480\pm40$ g mol^{-1} nm^{-1}, a value close to what is expected for a single chain (for deuterated chains $\mu_L=505$ g mol^{-1} nm^{-1} for a 3_1 form and $\mu_L=439$ g mol^{-1} nm^{-1} for a 12_1 helix). This implies that stabilization is internal in the chain. So far there are two explicit molecular models: either the chain adopts a 12_1 form as proposed by Keller *et al.*[1,2] or the chain adopts a solvated near-3_1 form as proposed by one of us[4]. Since there is strong evidence against the presence of the 12_1 form in the nascent gel[4,12,22] we shall assume this is so for the pregels and accordingly dismiss it (note that the experimental linear mass μ_L, although of limited accuracy, is in better agreement with the 3_1 form). This leaves the hypothesis of solvated near-3_1 helices unless another model can better account for the results obtained in this system.

That chains rigidity remains unchanged despite the fact they are now independent has far-reaching consequences regardless of the stabilization mechanism. The gel formation mechanism can be thought of as the reverse of the gel melting mechanism. Such a symmetry in melting and formation means that enhanced chain rigidity probably does not arise from gelation, but, on the contrary, that gelation is due to the existence of rigid chains (isotrope–nematic type transition). Since it may be assumed that enhanced rigidity prevents the formation of tight loops and correspondingly chain-folding, this might mean that gelation occurs because chain folding cannot take place.

(3) Finally, as in the 15% concentrated systems, the chains, at 95°C, lose their worm-like conformation. However, the exponent found in the final regime of $I(q)$ is 1.5, a value different from what would be expected with chains in a good solvent $(5/3)$[13,14].

At this point it is worth reminding that Reiss[15] had already noted a conformational transition at ~80°C which he interpreted as a transition from a 3_1 form to a disordered form[16]. We further suggest that the 3_1 form is stabilized at lower temperature by solvation.

Trans-*decalin pregels*

Trans-decalin pregels exhibit a scattering pattern contrasting, to some extent, with the one observed for *cis*-decalin pregels (*Figure 5*):

(1) The q^{-1} behaviour is virtually absent at room temperature. Only a small upturn beyond $q^*\simeq0.09$ Å^{-1} is visible. This probably means that rod-like portions are shorter in *trans*-decalin than they are in *cis*-decalin. If one assumes that the ratio of statistical lengths in either *trans*- or *cis*-decalin is similar to the ratio $q^*_{\text{cdec}}/q^*_{\text{tdec}}$ then this would give an estimated value of $b_{\text{tdec}}\simeq5$–6 nm.

The behaviour in *trans*-decalin should be compared with that obtained for a 15% gel in a mixture of decalin isomers[6]. While the chain global dimension was not found to differ markedly from that in pure *cis*-decalin (only 15% lower), no q^{-1} behaviour could be observed[6]. It was concluded that one was dealing with poorly stabilized helices that did not resemble long, straight rod-like portions but were rather like broken rod-like portions. The same thing probably holds here, too, which implies, within the frame of helix solvation, that *trans*-decalin does not stabilize the helical form as efficiently as *cis*-decalin.

It is to be noted that the discrepancy between either isomer of decalin is an argument in favour of solvation. Indeed, any 'anhydrous' crystalline structure is not expected to be sensitive to isomeric effects since the values of the Flory interaction parameters, χ, are virtually identical for *cis*- or *trans*-decalin[17].

(2) At 66 and 95°C the chain statistics do not seem to be markedly different. No q^{-1} behaviour can be clearly seen at 66°C or at 95°C but rather a q^{-2} behaviour. This would suggest that chain rigidity vanishes at a lower temperature than it does in *cis*-decalin. However, it seems that the chain global dimensions are quite large compared to the values known for iPS in the unperturbed state ($b\simeq2$ nm) for which experimental determinations of R_g (in nm) are given by[18,19]:

$$R_g\simeq0.03\,M^{0.5} \tag{5}$$

If one assumes that the q^{-2} behaviour reflects Gaussian statistics with a small statistical segment then $q^2I(q)$ reads using the Debye approximation:

$$q^2I(q)=KM_wC_D\,2/R_g^2 \tag{6}$$

From absolute calibration R_g can be estimated from the plateau obtained in the Kratky plot which eventually

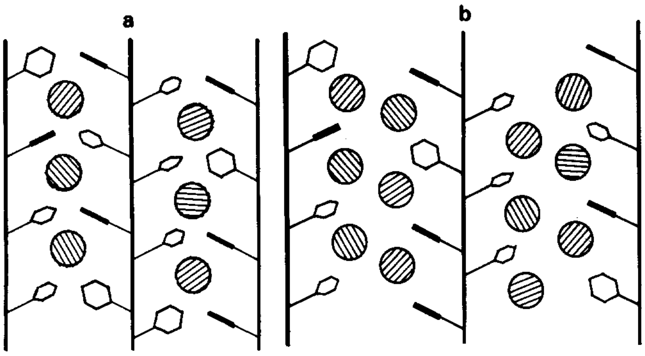

Figure 6 Schematic representation of the ladder-like model[4] (a) and the modified ladder-like model (b). Hatched circles denote solvent molecules; the hatching is randomly oriented to indicate the absence of orientation of the solvent molecules

gives:

$M_w = 2.54 \times 10^5$ $R_g = 28$ nm instead of 15.1 nm from (5)
$M_w = 6 \times 10^4$ $R_g = 13.8$ nm instead of 7.4 nm from (5)

These are quite large discrepancies which may be difficult to account for by thermal expansion (as a matter of course one finds a negative expansion coefficient for atactic polystyrene[20]).

Further, at 95°C the behaviour in either decalin is different. One would have expected to observe good-solvent behaviour ($I(q) \propto q^{-5/3}$)[13,14] in both solvents at this temperature since the systems are supposed to be some 80°C above the θ temperature[17]. While the behaviour in *cis*-decalin gives an exponent close to the theoretical value (1.5 against 1.66) the discrepancy is quite significant in *trans*-decalin (2 against 1.66). One may then wonder whether the q^{-2} behaviour in *trans*-decalin results from Gaussian statistics or from another conformation (embryos of crystals?). Clearly, these systems merit a more detailed study in this temperature range.

CONCLUSIONS

The results presented reveal an unexpected aspect of the gel melting process and, by extrapolation, of the gel formation mechanism. Clearly, thermoreversible gelation of iPS, where the solvent plays a major role, is a phenomenon quite distinct from usual crystallization. The role of the solvent has already been emphasized elsewhere using different techniques[4,6,21,22] and is underlined here. The conclusions drawn here lead us however, to modify slightly the ladder-like model proposed by one of us[4] to describe the gel short-range molecular structure (*Figure 6a*). In this model the chain–chain interaction is said to be mediated by the solvent which is accordingly regarded as the rungs of the ladder. This inevitably implies, in our opinion, a zip mechanism similar to a crystallization process, that is, long, straight helices should not exist beforehand but should be created together with the gel. We have found that this is not the case. Rather, it seems that the solvent does not mediate the interaction between chains but simply promotes the formation of helices that associate afterwards at lower temperature. The model in *Figure 6b* appears to be more relevant to describe the actual structure. This modification is not fundamental as far as the static structure is concerned, yet it may be of importance for reconciling n.m.r. findings[5] with other results[4,12,21,22]; since the solvent molecules are not trapped between two chains, as required by the ladder-like model, their mobility is certainly higher in the modified ladder-like model.

To conclude, while the rough molecular structure seems reasonably well elucidated, the fine structure is still to be determined.

REFERENCES

1 Girolamo, M., Keller, A., Miyasaka, K. and Overbergh, N. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 39
2 Atkins, E. D. T., Hill, M. J., Jarvis, D. A., Keller, A., Sarhene, A. and Shapiro, S. J. *Colloid Polym. Sci.* 1984, **262**, 22
3 Sundararajan, P. R., Tyrer, N. and Bluhm, T. *Macromolecules* 1982, **15**, 286
4 Guenet, J. M. *Macromolecules* 1986, **19**, 1960
5 Perez, E., Vanderhart, D. L. and McKenna, G. B. *Macromolecules* 1988, **21**, 2418
6 Guenet, J. M. *Macromolecules* 1987, **20**, 2874
7 Sadler, D. M. and Keller, A. *Macromolecules* 1977, **10**, 1128
8 Sadler, D. M., Spells, S. J. and Guenet, J. M. *Polymer* 1990, **31**, 195
9 Yoshisaki, T. and Yamakawa, H. *Macromolecules* 1980, **13**, 1518
10 Rawiso, M., Duplessix, R. and Picot, C. *Macromolecules* 1987, **20**, 630
11 Des Cloizeaux, J. *Macromolecules* 1973, **6**, 403
12 Klein, M., Mathis, A., Menelle, A. and Guenet, J. M. *Macromolecules* 1990, **23**, 4591
13 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, 1953
14 Cotton, J. P., Decker, D., Farnaix, B., Jannink, G., Ober, R. and Picot, C. *Phys. Rev. Lett.* 1974, **32**, 1170
15 Reiss, C. *J. Chim. Phys.* 1966, **10**, 1209
16 Reiss, C. *J. Chim. Phys.* 1966, **10**, 1307
17 Berry, G. C. *J. Chem. Phys.* 1966, **44**, 4450
18 Krigbaum, W. R., Carpenter, D. K. and Newman, S. *J. Phys. Chem.* 1958, **62**, 1586
19 Guenet, J. M., Picot, C. and Benoit, H. *Macromolecules* 1979, **12**, 86
20 Saeki, S., Kuwahara, N. and Kaneko, M. *Macromolecules* 1976, **9**, 101
21 Guenet, J. M. and McKenna, G. B. *Macromolecules* 1988, **21**, 1752
22 Klein, M., Brûlet, A. and Guenet, J. M. *Macromolecules* 1990, **23**, 540