Neutron Scattering Investigation of the Chain Trajectory in Thermoreversible Gels†

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ABSTRACT: The chain trajectory in physical gels prepared from isotactic polystyrene (iPS) has been investigated by neutron scattering. The results are solvent dependent. In *cis*-decalin, it is found that the chain possesses a wormlike conformation with a statistical length b of about 80 Å as determined from the q^{-1} behavior observed in the intermediate range. This value is most unusual for this polymer ($b \simeq 20$ Å in the vitreous state). In a blend of *cis*- and *trans*-decalin, whereas the global chain dimensions are about the same (actually 15% lower), the q^{-1} behavior is no longer observed in the intermediate range but rather a q^{-2} behavior is observed. This result is interpreted with a "distorted statistical unit model". All these results are discussed in the light of the current gel structure models. It is, however, stressed again that the gel state seems to be the third state for this kind of polymer.

Introduction

Recent investigations into the thermoreversible gelation of synthetic polymers have unveiled unexpected aspects which have accordingly renewed interest toward these systems.[1-3]

In this respect, the gelation of isotactic polystyrene (iPS) turns out to be a remarkable case. Whereas it was originally thought that this phenomenon was the consequence of fringed micellar crystallization under the usual threefold helical form, Girolamo et al.[1] showed by X-rays diffraction on supposedly dried gels that the characteristic reflections of this form were absent. Rather, a reflection at 5.1 Å was observed which was assigned to a new helical form (12_1 helix).[1] Making use of the unlikeliness of scattering cross section between hydrogen and deuterium, recent neutron diffraction experiments,[4] for which the polymer and the solvent were labeled differently, have pointed out that the 5.1-Å reflection arises probably from the solvent only. As a result, both crystallization and the 12-fold helical form had to be disregarded. Instead, a model reminiscent of nematic structure has been proposed.

Morphological studies performed by electron microscopy,[5] although subject to artifacts, suggest that large structures resembling microfibers form the mesh of the physical network rather than chain portions as would be the case in a fringed micelle model.

Investigations of the mechanical properties through the determination of the compression modulus[6] have revealed unusual types of behavior. Particularly, the stress relaxation rate is far higher than that measured for rubberlike materials and the compression modulus as a function of concentration does not obey a power law but exhibits "features" that are currently unexplained.

This short summary outlines the originality of thermoreversible gels from iPS and the numerous questions that are still unanswered.

So far, only the large-scale (morphology) and the short-scale structures have been investigated. It is felt that a study of the chain trajectory is still missing to provide one with a better understanding of the aforementioned peculiarities and to supplement the knowledge of these systems. This is the purpose of this paper, to report on small-angle neutron scattering investigations that precisely give new insight into the domain.

Experimental Section

(1) **Material.** Isotactic polystyrene samples were synthesized according to the Natta method.[7] Deuteriated isotactic polystyrene was obtained by polymerization of perdeuteriated styrene (Service des Molécules Marquées C.E.A.).

Table I

$10^5 M_w$	M_w/M_n	$10^5 M_w$	M_w/M_n
0.65	1.1	1.7	1.12
0.95	1.13	2.5	1.15
1.45	1.12	3	1.2
1.54	1.13	5	1.2

Hydrogenated polystyrene, which was used without molecular weight fractionation, possesses the following characteristics as determined from GPC in THF at 25 °C:[8] $M_w = 3.2 \times 10^5$; $M_w/M_n \simeq 2.8$.

Fractionation of the raw deuteriated isotactic polystyrene was achieved in toluene–ethanol at 50 °C.[8] Very narrow fractions were obtained (Figure 1) whose characteristics are listed in Table I.

cis-Decalin and a mixture of approximately 50% *cis*- and 50% *trans*-decalin (designated as *cis–trans*-decalin) were used as the solvents. For reasons justified below, each solvent contained a subsequent amount of deuteriated but otherwise identical molecules.

All the solvents were of high purity grade and used without further purification. The deuterium-labeled solvents (over 99% deuteriated) were purchased from Janssen Chemicals.

(2) Gel Preparation. To determine the single chain trajectory by neutron scattering, only the coherent signal arising from the deuteriated species must be detectable. Accordingly, the coherent signal of the protonated chains must be as close to zero as possible. To achieve such a goal, a mixture of protonated and deuteriated solvent that possesses the same scattering cross section as polystyrene must be used. The percent x_D (in volume/volume) of deuteriated solvent in the mixture is derived[9] from

$$a_{iPS}d_{iPS}/M_{iPS} = x_D(a_{SD}d_{SD}/M_{SD}) + (1 - x_D)(a_{SH}d_{SH}/M_{SH}) \quad (1)$$

where d, M, and a are the density, the molecular weight (monomer molecular weight for the polymer), and the coherent scattering length respectively, the subscript standing for the polymer (iPS), the deuteriated solvent (SD), and the hydrogenated solvent (SH).

For the system iPS–decalin, relation 1 gives $x_D = 0.195$. Figure 2, which portrays the intensity scattered by a gel containing protonated chains only and prepared from a 20–80 mixture of deuteriated–protonated solvent, confirms that the signal is mainly incoherent. Only an upturn at the smallest angles reveals residual coherent scattering which is difficult to eliminate on account of the large structures present in the gel.[5]

The gels were produced from homogeneous solutions prepared near the solvent boiling point then quenched at the desired temperature. A special mold of the type drawn in Figure 3 was used to produce slabs of 1-mm thickness. Eventually, disk-shaped samples of 15-mm diameter suitable for the neutron experiments were cut off from these slabs. Several temperatures of quench were considered: 0 and −30 °C with *cis*-decalin and −20 °C with *cis–trans*-decalin. These temperatures were obtained in a cryostat thermostatically controlled within ±0.1 °C.

To avoid any aging problems, the gels were kept at the quenching temperature for 20 min. These preparation times are

† This work has been performed at the Institute Laue-Langevin, Grenoble, France.

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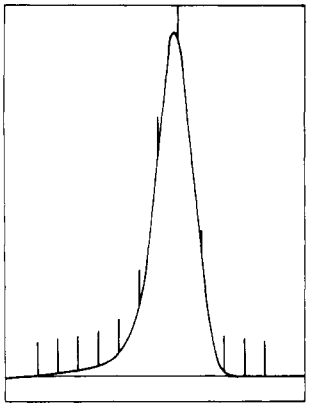

Figure 1. Typical GPC chromatogram of an iPS deuteriated fraction ($M_w = 6 \times 10^4$).

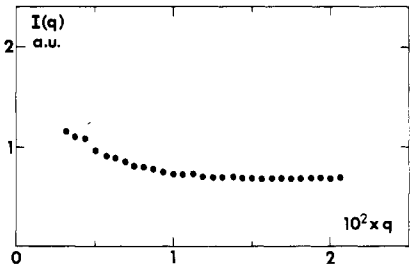

Figure 2. Intensity scattered by a gel containing protonated chains in a 20–80 blend of deuteriated + hydrogenated *cis*-decalin. $I(q)$ is in arbitrary units and q in Å^{-1}.

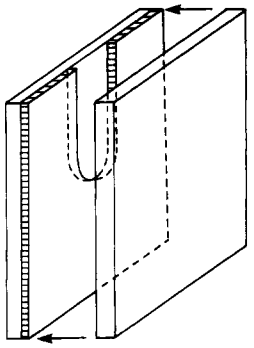

Figure 3. Sketch of the mold used to prepare the gel samples. The mold is made out of aluminum except the edge-hatched part (1-mm spacer) which is made of Teflon. From the tongue-shaped slab of gel, disk-shaped samples can be cut off.

based on recent measurements of the compression modulus as a function of quenching temperature.[10]

(3) Neutron Scattering. (a) Setup. The experiments were performed at the high-flux reactor located at the Institute Laue-Langevin (ILL Grenoble, France) on D11 and D17 small-angle cameras. The transfer momentum $q = 4\pi/\lambda(\sin\theta/2)$ (λ = neutron wavelength and θ the scattering angle) were in the range

$$5 \times 10^{-3} \leq q\ (\text{Å}^{-1}) \leq 1.5 \times 10^{-2} \quad \text{for D11 } (\lambda = 10\ \text{Å})$$

$$10^{-2} \leq q\ (\text{Å}^{-1}) \leq 1.3 \times 10^{-1} \quad \text{for D17 } (\lambda = 12\ \text{Å})$$

A mechanical wavelength selector was used on both apparatus providing a wavelength distribution characterized by $\Delta\lambda/\lambda \simeq 9\%$.

The gel samples were held in containers made with two quartz plates (22-mm diameter and 1-mm thickness) spaced 1-mm apart by a ring-shaped piece of glass (15-mm internal diameter). The system was tightly closed so as to prevent solvent evaporation while the data were collected. The experiments were carried out at 20 ± 2 °C.

(b) Signal Processing. As usual, a blank signal, scattered by a gel prepared with hydrogenated chains only, was removed from the total scattered intensity to correct for incoherent scattering. The scattered intensity was also corrected for sample transmission. Finally, the spectra were normalized by an incoherent spectrum scattered by protonated water. The normalized intensity then reads

$$I_N(q) = KC_D M_w S_D(q) \tag{2}$$

where C_D is the concentration of deuteriated material, M_w the deuteriated chains weight-average molecular weight, $S_D(q)$ the scattering function of the same chains, and K a constant which presently reads

$$K = [4\pi\delta N_A(a_D - a_H)^2]/[M_D^2(1 - T)] \tag{3}$$

where δ is the water sample thickness, N_A the Avogadro's number, M_D the monomer molecular weight, T the water transmission, and a_D and a_H the scattering length of the deuteriated chains and of the protonated species, respectively. Such a normalization usually allows calibration within an accuracy of 20–30% to be obtained which is sufficient in the present case.

(c) Analysis. The excess scattered intensity reads in the Zimm approximation[11]

$$I(q) = KC_D M_w[P(q) - 2A_2 C_D P^2(q)] \tag{4}$$

where C_D, M_w, and K have the same meaning as in (2), $P(q)$ is the chain form factor, and A_2 is the second virial coefficient.

Depending on the size R of the chain, two domains of transfer momentum are usually distinguished: (i) In the Guinier domain ($qR < 1$) $I(q)$ reduces to

$$I(q) = KC_D M_w\left(1 - q^2\frac{\langle R\rangle^2}{3}\right)(1 - 2A_2C_D) \tag{5}$$

Usually, the form $I^{-1}(q)$, which is linear over a wider range of scattering vector domain, is preferred:

$$I^{-1}(q) \simeq \left[1/M_w\left(1 + q^2\frac{\langle R\rangle^2}{3}\right)\right] + 2A_2C_D \tag{6}$$

From relation 6, the experimental results give M_w, $\langle R\rangle^2$, and A_2. In this representation, linearity can be experimentally obtained for $qR > 1$. For instance, R_g for a Gaussian chain is measured to within 10% up to $qR \simeq 3$. However, for star-branched polymers or a compact structure the departure from linearity is already seen for $qR < 1$. In this latter case the condition $qR \ll 1$ must be strictly fulfilled.

(ii) In the intermediate domain ($qR > 1$) $I(q)$ reduces to

$$I(q) \simeq q^{-n} \tag{7}$$

where n is an exponent which depends on the chain conformation. In some cases, two regimes with two different exponents can be identified in the intermediate range.[12]

When strong segregation occurs, entailing the formation of clusters wherein the chains have at least one contact with one another, the Zimm approximation is no longer valid. The scattered intensity then reads as in relation 5 except that M_w must be replaced by N_cM_w, N_c being the number of chains in the cluster, and $P(q)$ by $P_c(q)$. $P_c(q)$ stands for the cluster form factor and can be expressed as a function of the single-chain form factor provided that the chain conformation is not perturbed by the clustering:[13]

$$P_c(q) = P(q)/N^2[2P^{n+1}(q) - N_cP^2(q) - 2P(q) + N_c][1 - P(q)]^{-2} \tag{8}$$

It can be easily shown that at larger q, the single chain behavior is retrieved since $P_c(q) \simeq P(q)/N_c$ for $qR > 1$.

Results and Discussion

The results obtained on gels produced from *cis*-decalin are first presented.

Two types of results can be schematically distinguished although they are not basically different as long as the local chain trajectory is involved.

(i) Low Concentrated Gels (5%). Here, for gels quenched to 0 °C, isotopic segregation is observed as can be seen in Table II where values of the labeled species molecular weight are gathered. These results may appear

Table II

T, °C	$M_{w,gpc}$	$M_{w,sans}$	A_2, cm^3 g^{-1}	R_g, Å
		5% *cis*-Decalin		
0	0.95×10^5	2.9×10^5	-2.4×10^{-4}	
0	1.5×10^5	7.7×10^5	-0.4×10^{-4}	
0	2.5×10^5	1.1×10^6	-0.3×10^{-4}	
		15% *cis*-Decalin		
0	6.5×10^4	5×10^4	-1.8×10^{-4}	155
-30	6.5×10^4	5×10^4	-1.6×10^{-4}	160
0	1.45×10^5	1.5×10^5	-0.8×10^{-4}	260
-30	1.45×10^5	1.1×10^5	-0.6×10^{-4}	254
0	1.54×10^5	1.4×10^5	-0.6×10^{-4}	265
0	1.7×10^5	1.5×10^5	-0.7×10^{-4}	265
-30	1.7×10^5	1.4×10^5	-0.3×10^{-4}	262
0	2.54×10^5	2.2×10^5	-0.2×10^{-4}	330
-30	2.54×10^5	1.85×10^5	-0.3×10^{-4}	286
		15% *cis-trans*-Decalin		
-20	6.5×10^4	3.2×10^4	-0.4×10^{-4}	130
-20	1.45×10^5	1.1×10^5	-0.4×10^{-4}	228
-20	1.7×10^5	1.2×10^5	-0.6×10^{-4}	238
-20	3×10^5	2.3×10^5	-0.4×10^{-4}	265
-20	5×10^5	4.5×10^5	-0.6×10^{-4}	337

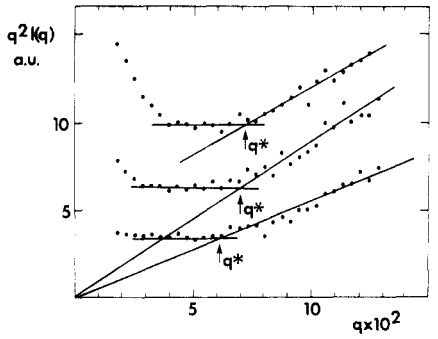

Figure 4. Kratky plot $q^2I(q)$ vs q for a 5% gel in *cis*-decalin. Upper curve $C_D = 1.5\%$; middle curve $C_D = 1\%$; lower curve $C_D = 0.5\%$. $M_{w,iPSD} = 1.5 \times 10^4$.

as surprising since under no circumstances has iPS shown any tendancy to segregate (either in amorphous bulk[14] or in semicrystalline sample[15]). However, it is known that a quench to this temperature inevitably involves a liquid–liquid phase separation.[5] As the molecular weights and molecular weight distributions of the D species differ from that of the H species, the probable mismatch at this concentration of the D and H coexistence curves leads to molecular weight fractionation.

While the values determined for the radius of gyration are useless since they are not representative of the single-chain behavior, worth examining is the intensity scattered in the intermediate range since this latter is less affected by chain clustering as shown by relation 8.

Figure 4 shows the occurrence at the largest q of q^{-1} behavior. At the highest labeled chain concentration this behavior is somewhat obliterated due to the negative virial coefficient effect (see eq 4) but appears quite clearly at the lowest concentrations. From these results, it is concluded that in spite of segregation, the chain possesses a statistical length b far larger than the usual one estimated for polystyrene (usual value $b \simeq 20$ Å).

(ii) Moderately Concentrated Gels (15%). The use of 15% gels allows the segregation problem to be overcome. This is probably so because the coexistence curve mismatch is certainly less important and also because the solution viscosity is higher. As can be seen in Table II, the values of the weight-average molecular weight determined by neutron scattering are in good agreement with those obtained from GPC.

A typical Kratky plot of the results gained in the intermediate range is drawn in Figure 5. Two regimes can

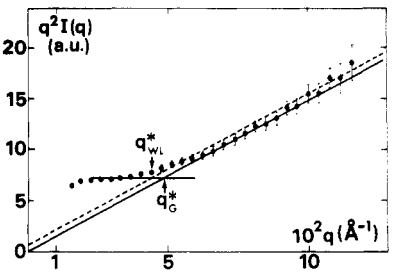

Figure 5. Kratky plot, $q^2I(q)$ vs q, for a 15% gel in *cis*-decalin. $C_D = 1\%$; $M_w = 2.5 \times 10^5$. q^*_{WL} and q^*_G stand for wormlike and Debye chains.

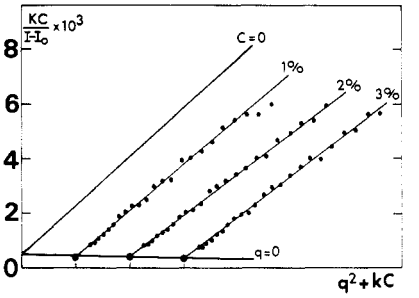

Figure 6. Typical Zimm plot for a 15% gel in *cis*-decalin, $M_w = 2.5 \times 10^5$. Concentrations of deuteriated material as indicated.

be unambiguously evidenced: for $q < q^*$, although very narrow, a domain wherein $I(q)$ behaves as q^{-2} and for $q > q^*$ a domain where $I(q)$ varies as q^{-1}. Such a plot corresponds exactly to what is theoretically expected for a wormlike chain or a Debye chain with a long statistical unit. Theoretical expressions for the form factor $P(q)$ of a wormlike chain were derived by Kratky et al.[16] and more recently by Des Cloizeaux.[17] It is demonstrated in the limit of very long chains that two regimes are expected in the intermediate range:

$$\text{regime 1} \qquad P_1(q) \simeq 6/q^2a^2 \tag{9}$$

$$\text{regime 2} \qquad P_2(q) \simeq \pi/qa + \tfrac{2}{3} \tag{10}$$

where a represents the persistence length. If q^* is defined as being the intersect in the Kratky representation between the asymptotes of $q^2P_1(q)$ and $q_2P_2(q)$, then q^* straightforwardly reads

$$q^* = 16/3\pi a \simeq 1.7/a \tag{11}$$

(note that Heine et al. obtained $q^*a \simeq 1.6$).

From this relation and the value of q^*_w in Figure 5, a persistance length of $a \simeq 40$ Å is found for the chains in iPS thermoreversible gels.

If a Debye chain with a statistical unit b is considered, one ends up with

$$\text{regime 1} \qquad P_1(q) \simeq 12/q^2b^2 \tag{12}$$

$$\text{regime 2} \qquad P_2(q) \simeq \pi/qb \tag{13}$$

q^* then reads

$$q^* = 12/\pi b \tag{14}$$

From q^*_G in Figure 5, $b \simeq 80$ Å.

Before going further into the discussion about the magnitude and the observation of such a persistence length, it is of importance to discover what the chain global behavior is as determined from the Guinier range.

A typical Zimm plot is given in Figure 6. As can be seen both from this figure and from Table II the virial coefficient are slightly negative, a normal situation since gel formation has involved a liquid–liquid phase separation.

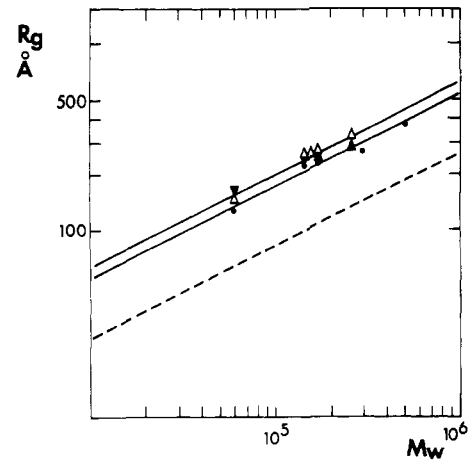

Figure 7. Double-logarithmic scale representation of R_g vs M_w. (△) 15% gels in *cis*-decalin quenched to 0 °C; (▲) 15% gels in *cis*-decalin quenched to −30 °C; (●) 15% gels in *cis–trans*-decalin quenched to −20 °C. The dotted line stands for the unperturbed values of iPS at 25 °C as reported in ref 14 and 18.

However, as stressed above, no isotopic seggregation is evidenced (see Table II).

The variation of R_g with molecular weight is given in Figure 7 (explicit values of R_g may be found in Table II). Two main conclusions emerge:

(i) The exponent n of the relation $R_g \simeq M^n$ is close to $n \simeq 0.5 \pm 0.05$, a value consistent with the above result.

(ii) The values of R_g are approximately twice as large as those found for iPS in the unperturbed state either from dilute solutions[18] or in the bulk amorphous state[14] but are independent of whether the gels have been produced at 0 or −30 °C.

As already seen, relation 14 gives a value for the statistical unit of about 80 Å. Another way of estimating b consists of using the criterion of Rawiso et al.[19] which considers that the q^{-1} behavior is reached when $qb \simeq 7$. This provides one with $b \simeq 100$ Å.

By taking $b \simeq 20$ Å for the statistical length in the unperturbed state[19] and assuming that the number of statistical elements per chain is directly proportional to $1/b$, the ratio $\rho = R_{g,gel}/R_{g,unpertubed}$ should equal 2–2.24. This result is in good agreement with the experimental values of $\rho \simeq 2.4$.

Worth dwelling upon is the magnitude of the statistical length which was not known to exist for this polymer. Rodlike chain portions of about the same size can only be found in the crystalline state. However, in this state, the chain does not remain Gaussian. Chain folding which propagates along an (*hk*0) crystallographic plane in the course of crystallization gives birth to a thin sheet structure. (Amusingly, the thin-sheet form factor behaves just as the reverse of the wormlike chain form factor,[20] that is q^{-1} at the smallest angles and q^{-2} at the highest ones.)

Concerning the vitreous state, the observation of the q^{-1} behavior is, under usual conditions, unattainable on account of the rather large chain cross section of polystyrene.[19] As a matter of fact, for threadlike systems with finite radial dimension, $P(q)$ reads[19]

$$P(q) \simeq (\pi/qb) \exp(-q^2\langle z^2\rangle/2) \qquad (15)$$

where $\langle z^2\rangle$ is the mean-square radial radius of gyration. If b is far larger than the thread diameter, then the exponential term reduces to unity in the range $1/b > q > 1/\langle z^2\rangle^{1/2}$. The statistical length of polystyrene, which amounts to $b \simeq 20$ Å in the vitreous state, is of the same order of magnitude as the thread diameter (≃8 Å).[19] As a result, $P(q)$ behaves as q^{-2} throughout the intermediate range. Only the use of backbone-labeled chains, which artificially reduces the thread diameter, allows the wormlike chain behavior to be observed as recently reported by Rawiso et al.[19] Owing to the large value of b in iPS physical gels, no special labeling need be brought about.

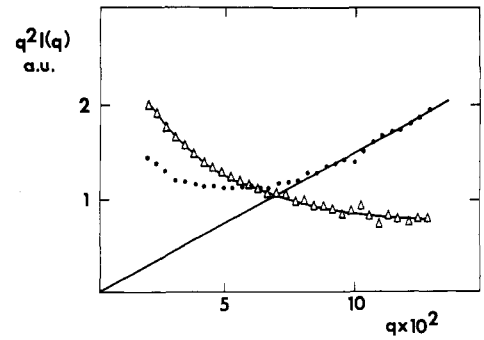

Figure 8. Kratky plot $q^2I(q)$ vs q for 5% gels and $C_D = 1\%$, in *cis*-decalin (●) and in *cis–trans*-decalin (△). In both cases, $M_w = 1.5 \times 10^5$.

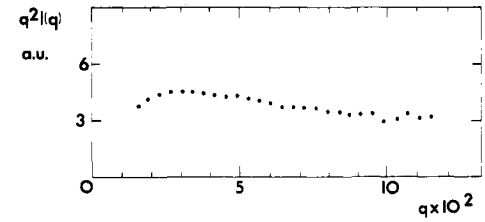

Figure 9. Kratky plot $q^2I(q)$ vs q for a 15% gel in *cis–trans*-decalin. $C_D = 3\%$; $M_w = 1.7 \times 10^5$.

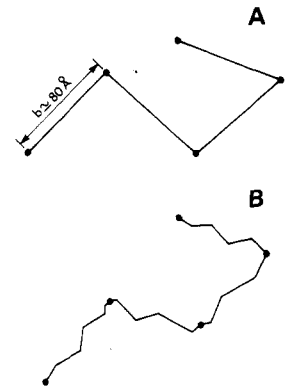

Figure 10. Schematic representation of the chain with a rodlike statistical unit (A) and the chain with a "distorted statistical unit" (B).

To summarize, for the two quenching temperatures considered, the chain trajectory in iPS–*cis*-decalin gels exhibits a globally Gaussian behavior with a statistical length of about 4 times as large as in the unperturbed state.

Allegedly, the same type of result would be expected in the *cis–trans*-decalin gels. Yet data gathered in the intermediate range clearly indicate that the q^{-1} behavior is unexistent (see Figures 8 and 9). Rather, once the seggregation effect for the 5% gel and the virial effect for the 15% gel (note that this is a 3% concentration) are ignored, a q^{-2} behavior is seen all the way.

As to R_g, it can be seen in Figure 7 that this parameter still varies as $M^{0.5}$. Only the prefactor is approximately 15% lower than the one obtained in the previous gels.

Admittedly, the chains in the *cis–trans*-decalin gels are globally Gaussian. The disappearance of the q^{-1} behavior may arise from local pertubations and accordingly may be viewed as follows: instead of being nearly straight, the statistical unit is distorted as schematically represented in Figure 10 (distorted statistical unit model). This model

accounts for both the discrepancy between the R_g values and the loss of the q^{-1} behavior. Another explanation is worth considering: as in crystals, chain folding might be envisaged which would lead to the formation of a "Garland" model.[21] If such were the case, interferences between close enough rod segments would also entail the appearance of a q^{-2} behavior to the detriment of the q^{-1} behavior. However, this model has to be ruled out since such a conformation should rather possess a radius of gyration close to that of the unperturbed state.[21]

Such a result with the "distorted statistical unit model" would imply that the formation process of the chain trajectory at shorter scale is solvent dependent.

Concluding Remarks

Concurrently, two models have been proposed for the gel molecular structure:

(i) The Keller's group model considers that gelation arises from the crystallization of chains under the 12-fold helical form instead of the usual 3-fold helix.[1] A variant version of the model due to Sundararajan et al.[22] consists of solvated 12-fold helices.

(ii) Guenet's model,[4] based on neutron diffraction experiments, is at variance with the previous one since it considers that gelation is not due to crystallization but rather to the formation of a kind of nematic-like structure involving the chains and the solvent (ladderlike model) wherein the chain adopts a conformation not very different from the 3_1 helix. In this model the chain–chain interaction is "mediated" by the solvent.

It seems interesting to discover to what extent the results reported here can give support to one model or the other.

First of all, it seems difficult to support either models from the values of R_g. As a matter of fact, the number of monomers per unit length is virtually the same with a 12_1 form (12 monomers for 30.6 Å) and a nearly 3_1 form (13.9 monomers for 30.6 Å in the case of the 3_1 helix).

The observation of a rodlike statistical element of about 80 Å would be consistent with small crystals consisting of two turns of 12-fold helical form (pitch 30.6 Å). However, the solvent dependence of the short-range structure is difficult to account for at least with "anhydrous" crystals. "Solvated" helices must at least considered.

The ladderlike model, for which parts of different chains are supposed to align, requires the existence of a large statistical length and can accommodate a distorted one. Also, the chain trajectory is reminiscent of polymeric nematic liquid crystals which may indicate an analogy.[23] It is known that gel properties either in *cis*- or *trans*-decalin differ considerably. Accordingly, the solvation with molecules of different conformation (*cis* and *trans*) may introduced a loss of cooperativity along the chain whereas solvation with identical molecules may promote this cooperativity. Such a hypothesis can account for quite naturally the "distorted statistical unit".

To conclude, the results presented here cannot definitely confirm or invalidate either model. Further experimental tests are needed.

At any rate, it can be again stated that the gel state is the "third state" for this kind of polymer since the chain trajectory derived from neutron scattering has never been observed before.

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