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Structures in Isotactic Polystyrene Solutions near the Physical Gelation Threshold

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ABSTRACT: This paper reports on thermal, morphological, and structural investigations of isotactic polystyrene (iPS) solutions in either *cis*-decalin or *trans*-decalin near the physical gelation threshold. In iPS/*cis*-decalin solutions there is an intermediate state between the gel state and the crystalline state. It is shown that there exists a temperature domain, above the gelation threshold (typically 20–30 °C), where giant spherulites can be grown that, however, possess nearly the same melting point as the gel. Despite the high macroscopic organization, X-rays and neutron diffraction experiments reveal a poor molecular order rather reminiscent or smectic arrangements. No reflection at 0.51 nm, characteristic of the 12_1 helix, is seen, which leads one to dismiss the presence of this helical form both in these structures and in the gel. In addition, the large distances observed by the diffraction techniques (2.47, 1.7, and 1.1 nm) provide further support to the intercalate (or polymer–solvent) compound. In iPS/*trans*-decalin solutions there is no intermediate state between the gel state and the crystalline state. This study again emphasizes the difference of the isomers of decalin toward iPS gelation.

Introduction

The mechanism of isotactic polystyrene (iPS) physical gelation and the resulting molecular structure of the gel are currently being investigated and are still under discussion. In fact, what seemed over a decade ago a mere crystallization phenomenon[1] has turned out to be more subtle.

To begin with, Keller and co-workers[2] showed the absence of the characteristic reflections of the 3_1 helix (the usual helical form in iPS crystals) in a partially dried and stretched gel. Instead a 0.51-nm reflection was found which was later assigned to a new helical form,[3,4] namely, the 12_1 helix possessing a sixfold symmetry. To account for the stability of this form, Sundararajan et al.[5,6] put forward the notion of solvation. On the basis of neutron diffraction experiments together with the deuterium-labeling method, Guenet[7] showed that in the nascent state the 0.51-nm reflection does not characterize the polymer. Rather, the 0.51-nm reflection corresponds closely to the first maximum in the diffraction pattern of liquid *cis*-decalin. Simple geometrical considerations led Guenet to propose a model[7] where the chains take on a near-3_1 helical form that are solvated (polymer–solvent compound or intercalate), thus retaining the idea of solvation proposed by Sundararajan.[5,6]

To test this point, Perez et al.[8] carried out a series of NMR experiments. Their results showed the solvent to be virtually as mobile in the gel as in the liquid state. They accordingly concluded that there was no polymer–solvent compound, a statement in contradiction with the temperature–concentration phase diagrams.[9]

Clearly, two points deserve to be further investigated: the very existence of the 12_1 helix and the notion of solvation.

The purpose of this paper is to report on experiments carried out near the gelation threshold. This investigation has allowed us to obtain well-organized structures that otherwise possess the same thermal behavior as the gel. As will be shown, diffraction experiments on these structures allow one to conclusively dismiss the existence of the 12_1 form but also give additional support to the polymer–solvent compound or intercalate model.

Experimental Section

A. Materials. The isotactic samples (either protonated or deuteriated) were synthesized according to Natta's procedure.[10] They are all over 99% isotactic as ascertained from ^{13}C NMR.

The deuteriated samples were obtained from a polydisperse sample fractionated by means of toluene–ethanol as solvent–precipitant. The characteristics were determined from GPC in THF at 25 °C:[11] iPSK (protonated), $M_w = 3.2 \times 10^5$, $M_w/M_n = 2.8$; iPSMD2 (deuteriated), $M_w = 3.6 \times 10^5$, $M_w/M_n = 2.7$; iPSMD3 (deuteriated), $M_w = 9.8 \times 10^4$, $M_w/M_n = 1.19$.

High-purity-grade, protonated *cis*-decalin and *trans*-decalin were purchased from Merck Laboratories. The deuteriated *cis*-decalin was obtained from Janssen. All solvents were used without further purification.

B. Sample Preparation. The gel samples were prepared in test tubes from homogeneous polymer solutions obtained by heating at 175 °C and then quenching at 0 °C. Depending on the technique used, the gels were processed in a different way. For **DSC** experiments and **optical microscopy** investigations, pieces of gels were taken from the test tube and then placed either into a hermetically sealed "volatile sample" pan (DSC) or between two glass slides (microscopy). The DSC pans were heated to 175 °C and then cooled and/or annealed at the desired temperature. The glass slides, hermetically sealed with silicone cement, were heated at 175 °C and then placed into a Mettler hot stage monitored to within 0.1 °C by the FP80 station. For **X-ray diffraction** or **neutron diffraction** investigations the samples were transferred into glass capillaries (1-mm diameter) or amorphous silica tubes (3-mm diameter) that were hermetically sealed. As above, they were molten again by heating to 175 °C and then thermally treated.

C. Techniques. The **DSC** experiments were carried out on a Perkin-Elmer DSC4 apparatus operated by the TADS system (thermal analysis data station). The cold source was provided by a cryostat held at −30 °C. The temperature scale and the measure of energy were calibrated with indium and gallium.

Optical microscopy investigations were achieved by means of a Zeiss photomicroscope II.

X-ray diffraction patterns were obtained on a Philips PW1009 instrument equipped with a Luzzati-Baro camera. Cu Kα radiation with a wavelength of 0.154 nm was used. The intensity was recorded on either a photographic film or a linear detector, the latter being coupled to a computer for data processing.

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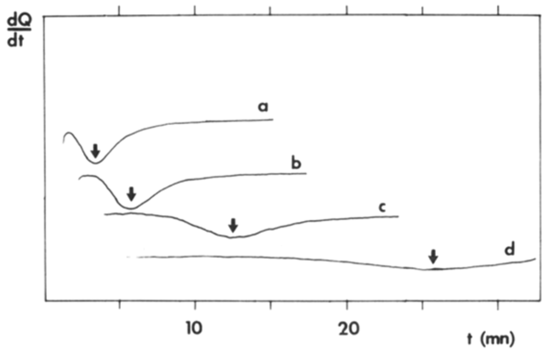

Figure 1. DSC isothermal exotherms obtained at different temperatures for an iPSD/*cis*-decalin solution ($C_{pol} = 30\%$): (a) 18, (b) 19, (c) 20, and (d) 21 °C.

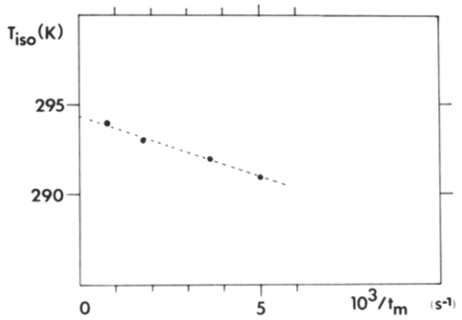

Figure 2. Relation between the annealing temperature (T_{iso}) and the gelation time (t_m). The latter, indicated by an arrow, are taken at the minimum of the exotherm for the system of Figure 1.

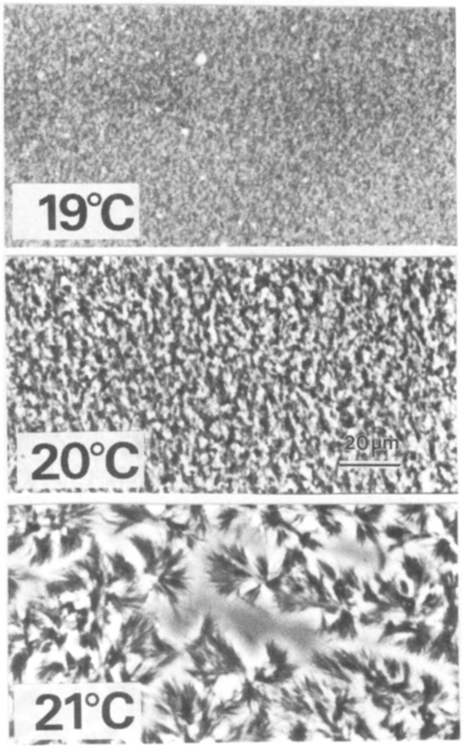

Figure 3. Modification of the texture of a 30%-iPS/*cis*-decalin solution as a function of the annealing temperature (as indicated). The transition from a gel texture (salt and pepper) to another state (spherulites) occurs around 20 °C.

Neutron diffraction experiments were carried out on the G-6-1, a two-axis spectrometer located at the Laboratoire Léon Brillouin (CEA-CNRS). Intensities were recorded on a banana-type detector composed of 400 counting cells, giving an angular resolution of 12′. A wavelength of 0.475 nm produced by a pyrolitic-graphite, vertical-focusing monochromator ($\Delta\lambda/\lambda \simeq 1\%$) was used. A beryllium filter kept at 77 K was also used to eliminate the $\lambda/2$ contribution. Under these conditions the domain of transfer momentum $q = (4\pi/\lambda) \sin(\theta/2)$ ranged from 0.1 to 2.5 Å. The raw data were normalized by a vanadium spectrum to correct for cell efficiency.

Results and Discussion

A. Determination of the Gelation Threshold. We consider here three criteria for defining the gelation threshold: (1) isothermal annealing, (2) texture modification, and (3) increase of the melting point.

1. Isothermal Annealing. We have investigated an iPS/*cis*-decalin solution ($C_{pol} = 30\%$). The sample, after being placed in a "volatile sample" pan, is heated to 175 °C and then quenched at T_{iso} (annealing temperature) in the DSC. The thermal response is then recorded as a function of time. When the gel forms an exotherm occurs. The time, t_m, at which this occurs (gelation time) is temperature dependent and increases with increasing temperature as expected. Typical DSC traces obtained under these conditions are given in Figure 1. In Figure 2 inverse gelation times are reported as a function of annealing temperature T_{iso}. As can be seen, one finds a relation of the following type:[12]

$$t_m^{-1} = (T_{iso} - T_{gel})/T_{gel} \tag{1}$$

where T_{gel} is the gelation threshold.

From this variation one obtains

$$T_{gel} = 21.2 \pm 0.3\ °\mathrm{C}$$

This value is in good agreement with the value obtained by Guenet and McKenna[9] from DSC experiments carried out at finite cooling rates for the same concentration (T_{gel} = 20 ± 1 °C).

2. Texture. The texture has been examined as a function of annealing temperature. Typical micrographs are given in Figure 3. As can be seen, at 19 °C and below (17 and 18 °C) a "salt and pepper" structure is seen, whereas at 21 °C spherulites are observed. The former texture is probably due to the presence of fiberlike structures that are, in our opinion, characteristic of the gel state as was shown in a previous paper.[13] At 20 °C the texture seems to be intermediate, indicating the gelation threshold may be taken as 20 ± 1 °C, a value still in agreement with the previous one.

3. Melting Point. If we consider that below the gelation threshold we have a gel and above we have spherulitic structures made up of "anhydrous" 3_1 crystals, then the melting point determined at a heating rate of 20 °C/min should change from 55 °C to 120 °C in the case of iPS/*cis*-decalin systems and from 75 °C to 115 °C for iPS/*trans*-decalin systems.[2,9,13]

Whereas this turns out *to be the case for iPS/trans-decalin systems*, the *results are rather unexpected for iPS/cis-decalin solutions*. In fact, in the domain of annealing temperatures located between 20 and 30 °C *the spherolites' melting point is, within a few degrees, the same as the gel's* (see Figure 4) (note that the upper limit, 30 °C, is not well defined and seems to be sensitive to molecular weight). Here we are therefore dealing with a system that, in spite of its spherulitic texture, has probably a molecular structure close to the gel's. Such a system, which is far better organized over large distances, is invaluable for an investigation of the molecular structure since it does not require any drying or stretching process.

Of further interest is the presence of only one melting peak, unlike what was reported for the gels, for which two endotherms were seen.[9] This is so because, here, annealing

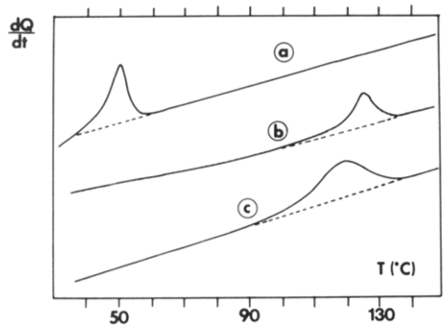

Figure 4. DSC thermograms obtained at 10 °C/min (a) 30% iPS/*cis*-decalin solution annealed at 25 °C for 24 h; (b) the same solution annealed at 60 °C for 24 h; (c) 30% iPS/*trans*-decalin solution annealed at 25 °C for 24 h.

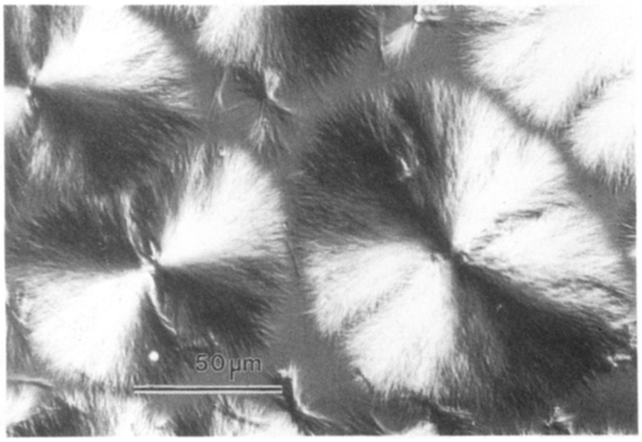

Figure 5. Spherulitic structures (carnation-like structures) obtained from a 30% iPS/*cis*-decalin solution annealed 24 h at 27 °C (nomarsky phase contrast).

Table I
Diameter of the Carnation-like Structures as a Function of the Annealing Temperature

annealing temp, °C	diameter, µm
21	≃20
23	≃20
25	50–70[a]
27	100–150[a]
30	50–180[a]

[a] Ranges indicate the presence of two populations.

does not take place within a misciblity gap, whereas forming the gel at 0 °C inevitably implies liquid–liquid phase separation to be involved. The latter phenomenon entails the existence of a monotectic transformation and hence the occurrence of a low-temperature endotherm that is invariant with polymer concentration.

B. Morphology above the Gelation Threshold. We have investigated the morphology of the iPS/*cis*-decalin solutions between 23 and 30 °C, a temperature range for which the structures formed melt around 50 °C. Concentrations ranging from 5 to 40% have been investigated.

Spherulites are observed, the size of which (see Figure 5) is strongly temperature dependent within less than 10 °C. Investigations for 30% solutions at different temperatures show variation from 20 up to 180 µm. Results are given in Table I. Two comments can be made from these data:

(i) To our knowledge sizes as large as 180 µm have never been observed, especially at such undercoolings. The maximum diameter reported so far for iPS crystallized from the bulk is ca. 70 µm[14] (iPS diluted in aPS at about the same dilution).

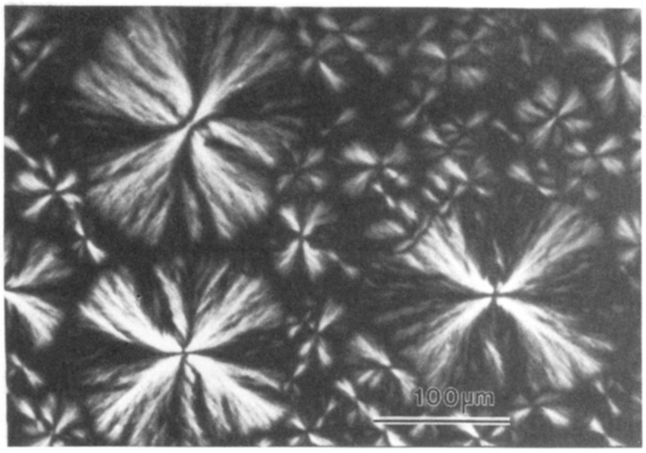

Figure 6. Carnation-like structures grown from a 30% iPS/*cis*-decalin solution at 30 °C. Two populations are seen (nomarsky phase contrast).

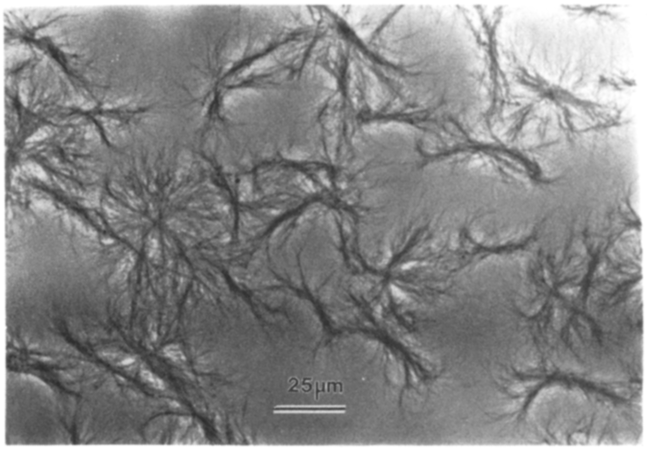

Figure 7. "Hairy" structures obtained at 20 °C in a 5% iPS/*cis*-decalin solution (phase contrast).

(ii) The lower undercooling, the higher the size, yet one observes the appearance of a two-population system above 23 °C. In addition, the discrepancy between the diameter of either type of spherulites increases with decreasing undercooling (see, for instance, Figure 6 for samples annealed at 30 °C). It seems that the transition toward the "anhydrous" crystals made up with 3_1 helices (usual crystalline form of iPS) is not far away.

A study at constant annealing temperature (25 °C) but different concentrations was also carried out. We observed a maximum diameter for the spherulites at $C_{\text{pol}} = 30\%$ (35 µm for $C_{\text{pol}} = 20\%$, 70 µm for $C_{\text{pol}} = 30\%$, and <20 µm for $C_{\text{pol}} = 40\%$). Curiously, this concentration happens to be the stoichiometric composition of the compound forming the gel junctions.[9]

Also worth mentioning are the structures obtained at lower concentrations (see Figure 7, where $C_{\text{pol}} = 5\%$ and $T_{\text{iso}} = 20$ °C) that do not resemble spherulites but seem to be "hairy" assemblies of either lamellae (axialites?) or fibers.

Another point of interest concerns the use of a high molecular weight ($M_w > 10^6$) and highly polydisperse sample (deuteriated material prior to fractionation). From this sample it has been impossible to grow these larger spherulites. Instead, a kind of coarse "salt and pepper" structure is seen together with long threads, the latter being probably fibers (see Figure 8).

Finally, the morphology in *trans*-decalin solutions at the same annealing temperatures consists of small spherulites (diameter < 1 µm). Unlike *cis*-decalin solutions, no

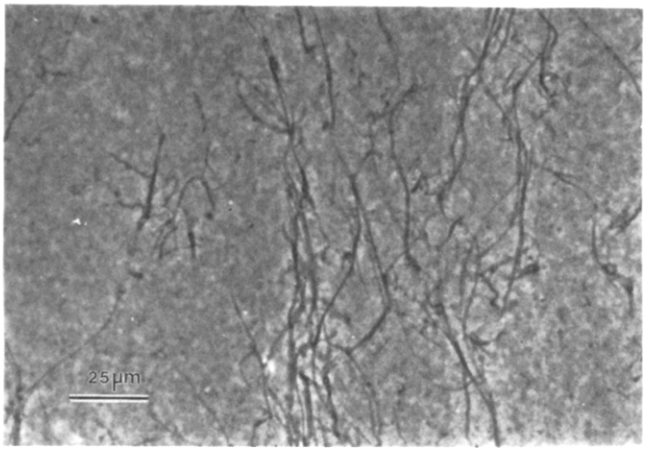

Figure 8. Morphology of a 30% iPS/*cis*-decalin solution of unfractionated material as observed by means of phase contrast.

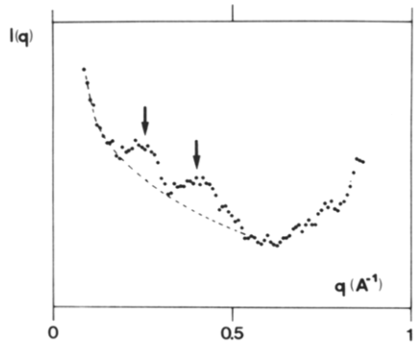

Figure 9. X-ray diffraction pattern recorded on the position-sensitive counter, $I(q)$ vs q. Arrows indicate the positions of the maxima.

special features are observed on varying either the annealing temperature or the polymer concentration.

These results again emphasize the difference existing between these isomers as to their properties toward gelation of iPS.

For the sake of clarity, we shall designate the spherulites formed in *cis*-decalin as carnation-like structures and use the term spherulites for those formed in *trans*-decalin.

C. X-ray and Neutron Diffraction Investigations. 1. X-ray Diffraction. All samples were investigated without undergoing any drying or stretching process.

As expected, investigations on iPS/*trans*-decalin samples (without drying) annealed above 22 °C show the characteristic reflection of the "anhydrous" crystals made up of 3_1 helices. The following crystallographic planes can be assigned to these reflections: 110, 300, 211, 410.[15] The 220 plane, being located close to the maximum of the solvent halo, cannot be unmistakably identified.

As to iPS/*cis*-decalin samples, a typical diffraction pattern obtained on the position-sensitive counter is given in Figure 9. Only two reflections can be observed, which give the following distances using Bragg's law: 2.45 ± 0.1 and 1.56 ± 0.1 nm. Apart from the solvent halo, no peak can be detected at larger angles. Three comments are worth making:

(i) Surprisingly, despite the high macroscopic order (spherulites), these reflections are rather broad and weak. They are not typical of crystalline order but rather of liquid crystalline systems. We may have here a kind of smecticlike arrangement. This type of situation is also encountered with liquid crystalline polymers containing mesogenic segments.[16]

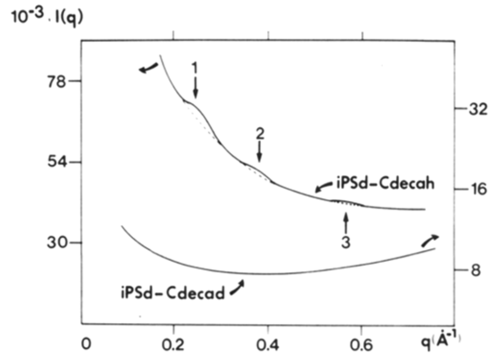

Figure 10. Neutron diffraction pattern, $I(q)$ vs. q, for 30% iPS/*cis*-decalin solutions annealed at 28 °C for 48 h: upper curve, iPSMD2/protonated *cis*-decalin (iPSD+CdecaH); lower curve, iPSMD2/deuteriated *cis*-decalin (iPSD+CdecaD). Arrows indicate the position of the different peaks: (1) 2.47, (2) 1.7, and (3) 1.1 nm.

(ii) If the distances are characteristic of chain spacing, then they imply the existence of intercalates.

(iii) Since the polymer and the solvent have roughly the same diffraction power toward X-rays, there is no way to find out whether the 0.51-nm reflection characteristic of the 12_1-helical form is present or not. To answer this point, neutron diffraction together with the deuterium-labeling method must be used to enhance iPS's diffraction power to the detriment of the solvent's. This method also allows one to avoid sample stretching.

Before presenting the neutron diffraction results, we note that "anhydrous" 3_1 crystals are observed in *cis*-decalin solutions annealed at 60 °C, as expected.

2. Neutron Diffraction. The neutron diffraction investigation was carried out on two types of samples: (i) the polymer and the solvent are both deuteriated (iPSD+CdecaD); (ii) the polymer is deuteriated and the solvent is protonated (iPSD+CdecaH).

Plots of the diffracted intensity vs the transfer momentum q for both types of samples are reported in Figure 10 for a 30% iPS/*cis*-decalin sample. For the iPSD+CdecaH sample the diffraction pattern is composed of two well-defined maxima at 2.47 ± 0.1 and 1.7 ± 0.1 nm, distances that are in good agreement with those determined by X-ray diffraction. Besides, there is apparently a reflection at 1.1 ± 0.1 nm, rather weak, which had not been detected by X-ray diffraction.

For the iPSD+CdecaD sample *all these reflections are absent* (Figure 10). This shows that these reflections correspond to the chain spacing and not to a helical order along the chain (a reflection would be expected from a 12_1 helix at 1.4 nm, which is associated with its pitch). This result also demonstrates that we are dealing with a polymer–solvent intercalate.

The diffracted intensity reads

$$I(q) = a_p^2 S_p(q) + a_s^2 S_s(q) + a_p a_s S_{sp}(q) \qquad (2)$$

in which $S(q)$ and a stand for the scattering function and the coherent scattering amplitude, respectively. Subscripts stand for the polymer (p), the solvent (s), and the cross terms (sp).

If the system is solvated (intercalates), then the cross term cannot be ignored. In addition, in the case considered here, the distances involved (>1 nm) allow us to use the incompressibility hypothesis,[17] which eventually leads one to

$$I(q) = (a_p - a_s)^2 S(q) \qquad (3)$$

where $S(q)$ is the scattering function of the system. It is

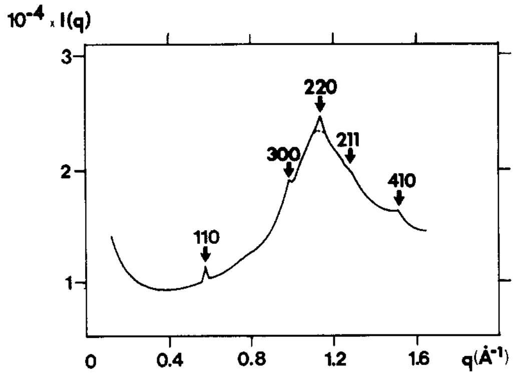

Figure 11. Neutron diffraction pattern, $I(q)$ vs q, for a 30% iPSMD3/*cis*-decalin solution annealed at 30 °C for 24 h. Arrows indicate the positions of the different reflections arising from the 3_1 crystals with the corresponding crystallographic plane.

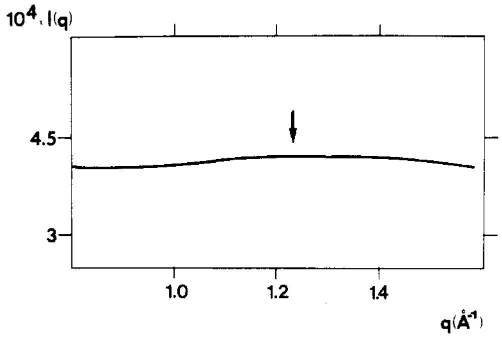

Figure 12. Neutron diffraction pattern, $I(q)$ vs q, for the larger angles for a 30% iPSDM2/*cis*-decalin (iPSD+CdecaH) solution annealed 48 h at 28 °C. The arrow indicates where the reflection corresponding to the 12_1-helical form (0.51 nm) should be observed.

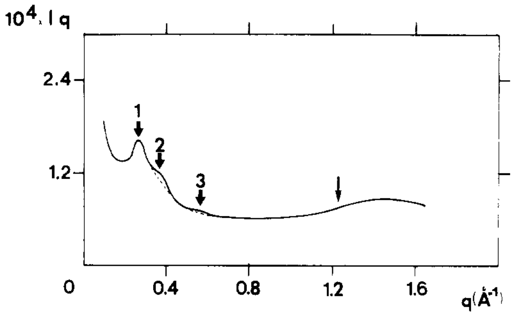

Figure 13. Neutron diffraction pattern, $I(q)$ vs q, for a 30% iPSMD2/*cis*-decalin (iPSD+CdecaH) solution annealed at 28 °C for 48 h and then partially dried. Numbered arrows indicate the positions of the different peaks: (1) 2.47, (2) 1.7, and (3) 1.1 nm. The unlabeled arrow again shows the place where the 0.51-nm reflection corresponding to the 12_1 helix should have been seen.

then clear that for $a_p = a_s$ the diffraction pattern should show no maxima whatsoever, which is the case encountered for the carnation-like structures.

Conversely, if the system is not solvated, then the cross term is negligible provided the crystals are large enough, a condition that is satisfied in the q domain investigated. $I(q)$ then reads

$$I(q) = a_p^2 S_p(q) + a_s^2 S_s(q) \tag{4}$$

As a result, labeling has no effect on the presence or absence of the maxima (diffraction peaks) in the structure factor of the polymer crystalline lattice. Only the magnitude of the maxima can be affected. To illustrate this latter case, we have investigated the same sample (iPSD+CdecaD), but this time "anhydrous" 3_1 crystals have been grown. As can be seen in Figure 11, all the main reflections characterizing this crystalline form are observed according to eq 3 despite the absence of contrast between the polymer and the solvent (note that these reflections are narrow compared to those observed for the carnation-like structures).

Incidentally, one may wonder why reflections are detected by X-rays on an iPSH+CdecaH sample (no labeling) whereas nothing is seen with neutrons on an iPSD+CdecaD sample. The reason lies in the contrast factor K, which is more important for X-rays than for neutrons under these conditions, even in the absence of labeling with heavier atoms.

For neutrons we have

$$K_N = \sigma/4\pi = (A - fB)^2 \text{ b/sr} \tag{5}$$

where A and B are the coherent scattering amplitudes of the polymer and the solvent, respectively, and $f = V_p/V_s$, where V_p and V_s are the molar volumes. $A = A_0\sum\langle\exp(i\mathbf{qr}_j)\rangle$ and $B = B_0\sum\langle\exp(i\mathbf{qr}_k)\rangle$. For distances larger than 1 nm we end up with $A \simeq A_0$ and $B \simeq B_0$. Calculating K_N with a polymer density $d_p = 1.06$ (density of amorphous polystyrene) yields $K_N < 1$ b/sr.

For X-rays the contrast factor K_X reads on assuming incompressibility

$$K_X = (e^4/m^2c^4)(Z_A - fZ_B)^2 \simeq 7.9 \times 10^{-2}(Z_A - fZ_B)^2 \text{ b/sr} \tag{6}$$

where Z_A and Z_B are the number of electrons per monomer and per solvent molecule, respectively, e is the charge of the electron, m is its rest mass, and c is the speed of light in a vacuum. This yields for K_X under these conditions $K_X > 4$ b/sr, a value much larger than the one calculated for K_N (note that if the polymer density is >1.06, which is probably the case, then K_N is smaller while K_X becomes larger).

The neutron investigation has also been extended to larger angles for the iPSD+CdecaH sample in order to settle the question of the 0.51-nm reflection[2-4,7] since *cis*-decalin's diffraction power is significantly attenuated with respect to the polymer's. The 0.51-nm reflection should be seen if 12_1 helices are present, even on nonoriented samples as demonstrated by Sundararajan and Tyrer[6] on solvent-exposed samples. As can be seen in Figure 12 *no reflection can be observed.* We therefore conclude that 12_1 helices are not present in these structures. Extrapolating these conclusions to the gel leads us to dismiss definitively the presence of this form in the nascent state. Here we wish to emphasize that this statement does not concern stretched and dried gels for which Keller et al.[4] report additional reflections (layer lines) at 3.06 nm corresponding to the pitch of the 12_1 helix. Incidentally, the 3.06-nm layer line should give rise to a reflection at 1.4 nm with an unoriented sample which is not seen here either. However, stretching seems to be one of the key processes to make the 12_1 form appear. We have further examined a sample prepared at 28 °C and then partially dried (final concentration ca. 60–70%). As can be seen in Figure 13, we still observe the three aforementioned reflections plus a broad halo at 0.44 nm indicating the presence of amorphous polymer material *but no reflection at 0.51 nm.* It must be emphasized that this reflection was the *strongest one* observed by Keller et al.[2] and should be accordingly seen here.

The first reflection (2.5 nm) seems to be enhanced, something that would be in contradiction with the intercalate hypothesis. In fact, only this reflection is enhanced because the scattering (rod scattering), which is significant in this domain for a 30% solution, has now strongly decreased, more rapidly than the diffraction (see the intensity levels that are normalized by the neutron flux).

To summarize, none of the reflections that led Keller et al. to put forward the 12_1 helix are observed here.

3. On the Molecular Structure. At this stage of the discussion it seems appropriate to attempt to outline a possible crystallographic structure with the data at hand. First of all, we are dealing with a kind of smecticlike arrangement in the sense that we have only order, admittedly poor, in only two dimensions (*a* and *b* axis). No reflections are apparently related to the *c* direction. A monoclinic cell with $a \simeq 2.5$ nm, $b \simeq 1.7$ nm, and $\alpha \sim 100°$ would be well suited to account for the three reflections (100 plane for 2.5 nm, 010 plane for 1.7 nm, and 110 plane for 1.1 nm). However, if the chains take on a near-3_1 helical form, then a centered monoclinic cell might prove to be more appropriate since a chain could then have six first neighboring chains (not exactly at the same distance) instead of eight in the case of a simple monoclinic cell. The latter case would not fit the threefold or near-threefold "symmetry" of the helix. Such a structure would be reminiscent of the one observed for the "anhydrous" 3_1 crystals, the differences being the presence of intercalated solvent and a distortion of the unit cell that otherwise possesses a threefold symmetry.

It is our feeling that if the solvent were perfectly adapted to the 3_1 helix shape, as is the case for PEO-*p*-dibromobenzene compounds,[18,19] then well-organized intercalates would be obtained. Since adequacy between *cis*-decalin's shape and the 3_1 helix's shape is poor, only partially ordered structures are obtained. The adequacy is probably still poorer with *trans*-decalin, which precludes growing carnation-like structures in this solvent.

Concluding Remarks

In this paper we have shown that giant spherulites can be grown from iPS/*cis*-decalin solutions that apparently display the features of highly organized structures but possess, in fact, a poor molecular order. This contrasts with iPS/*trans*-decalin solutions in which small spherulites are obtained that possess the usual crystalline order. The low order in iPS/*cis*-decalin solutions together with the presence of lamellae constituting the spherulites is reminiscent of smecticlike arrangements. It then seems that, depending upon temperature, this type of solution can exhibit three different states: the gel state (nematiclike), giant spherulites (smecticlike), and the crystalline state (crystals). The gel is thus the state of lower molecular order.

Unlike liquid crystalline polymers, the state of lower molecular order is obtained at larger undercooling. This is so because the ultimately stable phase is the crystalline state only. If this state is reached, there is no way, to our present knowledge, to transform it into either of the two other states by subsequent cooling.

That the "smecticlike" phase is absent in iPS/*trans*-decalin solutions again shows that the isomers of decalin have different effects on gelation. This together with the distances observed by diffraction is consistent with the formation of polymer–solvent intercalates. To try to account for the results presented here in terms of classical crystallization will lead one to inconsistent interpretations.

Finally, it would be of interest in light of the results presented here to examine the solvent's mobility in the carnation-like structures.[8] This would help to discover whether NMR is an adequate technique to point out the existence of loosely bound polymer–solvent compounds.

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