On the Molecular Structure of Isotactic Polystyrene Physical Gels As Revealed by Differential Scanning Calorimetry and Neutron Diffraction

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ABSTRACT: Through the use of differential scanning calorimetry (DSC), the heat of fusion of the solvent in the gel is investigated as a function of polymer concentration. From this type of experiment, a parameter $\bar{\alpha}$, which stands for the number of solvent molecules adsorbed per monomer unit, can be determined. The knowledge of this parameter enables one to strongly support the existence of solvated structures responsible for the occurrence of physical cross-links. In addition, $\bar{\alpha}$ allows one to coherently explain why the original gel structure is stable in some solvents but transforms into the 3_1 helical form prior to gel melting in some others. By neutron diffraction, three points are dealt with: it is shown (i) that the gel diffraction pattern resembles that of a liquid, (ii) that liquid decalin and the gel have virtually the same diffraction pattern with a pronounced reflection at 0.53 nm, and (iii) that there is no sign of any 0.53-nm reflection when only the polymer is deuterium labeled, which means that the 0.53-nm Bragg spacing does not characterize the chains. All these results are discussed and a molecular model for the gel is proposed. This model assumes that the chains are bridged together by the solvent molecules (ladder-like model). Although the chains certainly possess a rodlike conformation, they do not adopt a well-defined helical structure. It is then concluded that, while the 12_1 helix may exist in the gel, this form is far from being the main structure.

Introduction

The pioneering work of Lemstra and Challa[1] has revealed that moderately concentrated solutions of isotactic polystyrene (iPS) in specific solvents can be turned into a physical gel instead of allowing the growth of chain-folded crystals. At the time it was thought that physical gelation led only to a new morphology.[1] However, Girolamo et al.[2] showed that, unexpectedly, the gel diffraction pattern does not display any of the reflections due to the 3_1 helix which constitutes the usual polystyrene crystals. Despite the paucity of the X-ray diffraction data, there is definitely a more pronounced reflection at 0.51 nm, which has been immediately assigned to a new helical form. This form was first thought to arise from stereoregular defects[2] or from head-to-head or tail-to-tail arrangements. Such a view was soon disregarded,[3] and it was suggested that a 12_1 helix with a sixfold screw symmetry (made of dimer elements) could account for the 0.51-nm reflection. Some evidence exists for stretched and dried gels under the form of layer lines at 3.06 nm,[4] which are apparently in agreement with this helical structure. Yet, the origin of the 0.51-nm reflection and correspondingly the existence of a dimer are still puzzling. In addition intensities calculated on the basis of an oriented and cylindrically averaged 12_1 helix are far from matching the experimental one.

Without calling into question the existence of a 12_1 helix, Sundararajan et al.[5] have suggested that the resulting crystal structure is solvated and can only exist due to solvation. Recent findings that show different stabilities of the original gel structure with the solvent support such a concept.[6]

Clearly, a better knowledge of the molecular structure is of importance and, accordingly, deserves further experimental investigation to throw some light on these points.

The purpose of this paper is to report on results gathered by two independent techniques: DSC and neutron diffraction. These techniques were used to examine whether the solvation concept was well-grounded. Some neutron diffraction results obtained while this problem was investigated have led us to reconsider the interpretation of the 0.51-nm reflection as well.

By DSC, the heat of fusion of the solvent in the gel has been investigated as a function of polymer concentration. From this, as detailed in the Theoretical Section, one can determine a parameter $\bar{\alpha}$ that is the number of solvent molecules per monomer unit. This parameter is a measure of the degree of chain solvation in the gel, the knowledge of which can be useful to explain both the variation of the gel melting point and the stability or unstability of the original gel structure with the solvent.

After a short theoretical section devoted to the potential advantages of neutron diffraction, when solvated compounds are dealt with, results gained from this technique will be detailed (a part of which has already been published elsewhere[7]). They particularly show that (i) the gel diffraction pattern resembles that of a liquid, (ii) liquid *cis*-decalin and the gel have the same diffraction pattern with a pronounced reflection at 0.53–0.54 nm, and (iii) by deuterium labeling, which enables one to only "visualize" the signal arising from the polymer, the 0.53-nm reflection is absent, which means that the presence of a 12_1 helical form is highly questionable (as a result, throughout the text, quotation marks will be used when referring to this structure).

Theoretical Section

Heat of Fusion of the Solvent in a Polymer–Solvent Mixture. The variation of the solvent heat of fusion ΔH with polymer concentration can provide valuable information about the amount of solvent molecules adsorbed on the polymer chain at the melting temperature of the solvent T_{ms}. Such a method has been sucessfully applied to hydrosoluble molecules.[8]

The knowledge of the level of solvent adsorption is of great interest concerning physical gels, for which the structure responsible for the physical cross-links is thought to be solvated.[5-7] In this section, the equation relating ΔH to the average number of adsorbed solvent molecules per monomer unit $\bar{\alpha}$ and the polymer concentration x_p is derived.

The value of ΔH determined at T_{ms} for a given concentration is both a function of the proportion of free solvent x_{fs} and the heat of fusion of the pure solvent ΔH_0 through the simple relation

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$$\Delta H = \Delta H_0 x_{fs} \quad (1)$$

The proportion of free solvent x_{fs} is

$$x_{fs} = \frac{N_{fs} m_s}{N_p(m_p + \bar{\alpha} m_s) + N_{fs} m_s} \quad (2)$$

where N_{fs} and N_p are the number of free solvent molecules and monomer units, respectively, and m_s and m_p are the molecular weights of a solvent molecule and a monomer unit, respectively.

N_{fs} can be related to the total number of solvent molecules N_s through the relation

$$N_{fs} = N_s - \bar{\alpha} N_p \quad (3)$$

In order to bring the calculation to completion, x_p has to be written

$$x_p = \frac{N_p m_p}{N_p m_p + N_s m_s} \quad (4)$$

The combination of eq 2, 3, and 4 gives the following expression for x_{fs}:

$$x_{fs} = 1 - x_p(1 + \bar{\alpha} m_s / m_p) \quad (5)$$

Finally, eq 1 can be written

$$\Delta H = \Delta H_0[1 - x_p(1 + \bar{\alpha} m_s / m_p)] \quad (6)$$

From eq 6, it is concluded that ΔH should be a linear function of x_p provided that $\bar{\alpha}$ is independent of polymer concentration. Alternatively, when the variation is found to be linear, the value of $\bar{\alpha}$ is also a characteristic of the state of adsorption in dilute solution. Such a consequence has been applied elsewhere.[9]

The easiest way of determining $\bar{\alpha}$ consists of extrapolating at $\Delta H = 0$, which gives a value of polymer concentration x_p^0. Then $\bar{\alpha}$ reads

$$\bar{\alpha} = \frac{1 - x_p^0}{x_p^0} m_p / m_s \quad (7)$$

Neutron Diffraction. Neutron diffraction possesses two specific characteristics that are intrinsically different from those of X-ray diffraction:

i. Since neutrons only interact with nuclei, atoms can be regarded as point scatterers. As a result, the neutron scattering factor f_N is a constant with diffraction angle.[10] Conversely, the electronic scattering factor f_{XR} displays a fall-off with diffraction angle. This can be a drawback for X-rays when dealing with poorly crystalline or liquid systems, which results in a loss of resolution.[10]

ii. The use of labeled molecules allows one to selectively "visualize" the components of a blend through an appropriate choice of protonated and deuterated species without significant alteration of the physical properties.[11]

The use of the neutronic contrast between hydrogen and deuterium has been so far the only prerogative of copolymers at small angles (Guinier regime). In the diffraction domain, to our knowledge, it has been mainly employed with mineral compounds such as ThH_2 (and ThD_2)[12] or SiH (and SiD).[13] Concerning polymer–solvent complexes, this method has potential advantages over X-rays, for which no contrast variation can be brought about without deeply altering the physical properties.

In this section the theoretical intensity diffracted by a system containing two types of molecules A and B randomly oriented will be derived, where B will represent the polymer. The amplitude is

$$A(\mathbf{q}) = \sum_i^{N_s} A_i(\mathbf{q}) \exp(i\mathbf{q}\mathbf{r}_{is}) + \sum_j^{N_p} B_j(\mathbf{q}) \exp(i\mathbf{q}\mathbf{r}_{jp}) \quad (8)$$

where $q = 4\pi/\lambda \sin(\theta/2)$ (λ is the neutron wavelength and θ is the diffraction angle), and subscripts s and p refer to solvent and polymer, respectively. In expression 8 $A_i(q)$ and $B_j(q)$ read

$$A_i(\mathbf{q}) = \sum_\alpha^n a_\alpha \exp(i\mathbf{q}\rho_\alpha)$$

$$B_j(\mathbf{q}) = \sum_\beta^m b_\beta \exp(i\mathbf{q}\rho_\beta) \quad (9)$$

where a_α is the scattering length of atom α in the molecule of type A and ρ_α is the distance of this atom to the center of mass of the molecule.

When the molecules or the polymer are made up with carbon and hydrogen (or deuterium), (9) yields

$$A_i(\mathbf{q}) = a_H \sum_H^{n_H} \exp(i\mathbf{q}\rho_H) + a_C \sum_C^{n_C} \exp(i\mathbf{q}\rho_C) \quad (10)$$

The complex conjugated amplitude of relation 8 reads

$$A^*(\mathbf{q}) = \sum_t^{N_s} A^*_t(\mathbf{q}) \exp(i\mathbf{q}\mathbf{r}_{st}) + \sum_v^{N_p} B^*_v(\mathbf{q}) \exp(i\mathbf{q}\mathbf{r}_{pv}) \quad (11)$$

From now on, two situations concerning the nature of the blend need be envisaged:

i. When the blend is homogeneous, the intensity reads

$$I(q) = \langle AA^* \rangle = \bar{A}_s^2(q) S_s^{coh}(q) + \bar{A}_p^2(q) S_p^{coh}(q) + 2\bar{A}_s(q)\bar{A}_p(q) S_{sp}^{coh}(q) + S_s^{inc} + S_p^{inc} \quad (12)$$

where, depending on the subscript (s is solvent and p is polymer), $A(q)$ is the structure factor of the molecule or the monomer, $S^{coh}(q)$ the coherent scattering, and S^{inc} the incoherent scattering.

This equation, which contains a cross term $S_{sp}^{coh}(q)$, demonstrates why the use of protonated or deuterated samples does not give the same diffraction pattern. This is the case of ThH_2 and ThD_2.[12] Concerning solvated crystals, the same result should be observed by using either deuterated or protonated solvent for instance.

A special case corresponds to $A(q) = 0$. This is the case of decalin at $q = 0$. Calculations show that as long as a high resolution is not required (say distances comparable to the molecule size), $A(q)$ for protonated decalin is negligible compared to $A(q)$ for deuterated decalin. Thus, with the use of a sample containing deuterated polystyrene with protonated decalin, the diffraction pattern should be representative of only the polymer. In addition, due to the cross term, the use of deuterated solvent suffices to reveal a reflection arising from the polymer even if the polymer is hydrogenated.

ii. When the mixture is inhomogeneous for distances larger than the neutrons wavelength, the diffracted intensity reduces to

$$I(q) = \langle AA^* \rangle = \bar{A}_s^2(q) S_s^{coh}(q) + \bar{A}_p^2(q) S_p^{coh}(q) + S_s^{inc} + S_p^{inc} \quad (13)$$

As the cross term has vanished, the diffraction pattern for unsolvated systems should not differ whether protonated or deuterated solvent is used.

Experimental Section

Materials. Two samples of isotactic polystyrene prepared in our laboratory have been selected for this study, namely, a hydrogenated sample designated as iPSH with $M_w = 3.4 \times 10^5$ and $M_w/M_n = 2.8$ and a deuterated fraction designated as iPSD, with

$M_w = 2.5 \times 10^5$ and $M_w/M_n = 1.15$.

These samples are highly stereoregular, the isotacticity being larger than 97%.[14]

Four protonated solvents of high-purity grade have been used (Θ point of aPS in these solvents are in parentheses): *cis*-decalin (12 °C), *trans*-decalin (18 °C), 1-chlorodecane (7 °C), and 1-chlorododecane (52 °C). Perdeuterated *cis*-decalin has been purchased from Spectrométrie Spin et Techniques (Paris) and is over 99% deuterium labeled.

Techniques. A. Differential Scanning Calorimetry (DSC). Melting enthalpies of solvents in the gels were determined by means of a Perkin-Elmer DSCII differential calorimeter equipped with a thermal analysis data station (TADS). Liquid nitrogen was used as refrigerant in order to have access to very fast cooling rates. Approximately 10 mg of wet gel, placed into a "volatile sample" pan hermetically sealed, were scanned at heating rates ranging from 5 to 20 °C/min once the thermal treatment described below was completed.

B. Neutron Diffraction. All the experiments were carried out at the Laboratoire Leon Brillouin (LLB–CEN Saclay) on the high-resolution spectrometer 3T2. The neutron wavelength of $\lambda = 0.1225$ nm is obtained by diffraction of the primary beam onto (335) crystallographic planes of germanium. Intensities are recorded by 0.05-deg steps on a multidetector (further details are available on request).

Preparation of the Samples. A. DSC Experiments. Gels were produced in test tubes beforehand through a rapid quench (just above the solvent freezing point) of polymer solutions prepared at high temperatures (typically a few degrees below the solvent boiling point). The procedures used depended on the solvent and were adopted as follows once the sample had been placed into the DSC furnace at 20 °C:

i. For *cis*- and *trans*-decalin, the samples were heated to 170 °C at 20 °C/min in order to melt the gel and get rid of any type of crystals. Then, they were quenched at −28 °C (*trans*-decalin) or −38 °C (*cis*-decalin) at a cooling rate of 40 °C/min in order to re-form the gel but with a better thermal contact. The samples were allowed to stand at these temperatures for various times (10–30 min) so as to ensure subsequent gelation. Finally, the solvent was crystallized by cooling to −70 °C at a cooling rate of 2.5 °C/min.

ii. For 1-chlorodecane and 1-chlorododecane, the samples were heated to 170 °C at 40 °C/min and then cooled to −28 °C (1-chlorodecane) or −5 °C (1-chlorododecane) at 320 °C/min in order to bypass any crystallization under the threefold helical form prior to gel formation. Then, as previously, the samples were let stand for 10–30 min at the quenching temperature. Crystallization of the solvent was carried out by cooling to −70 °C at a rate of 2.5 °C/min.

Furthermore, samples from 1-chlorododecane were annealed in the DSC pan at 55 °C for 24 h so as to transform the initial gel structure into 3_1 helices (this operation takes place below the original gel melting point). As usual, pans containing the samples were weighed before and after this thermal treatment in order to detect any loss of solvent. Finally, crystallization of the solvent in these annealed samples was achieved as described above.

Generally, for all the polymer–solvent systems, some experiments were also performed on the as-prepared gels from the test tube (no thermal treatment in the DSC before the crystallization of the solvent). A cooling rate of 2.5 °C/min was used as above.

B. Neutron Diffraction Experiments. Thin-wall silica tubes were used as gel containers as required with neutron diffraction (4-mm-o.d.). Approximately 1 g of gel was produced in these tubes by heating at 180 °C until thorough homogenization was achieved and then quenching into ice water. Experiments were only performed with *cis*-decalin (protonated and deuterated) at two concentrations, 20% and 40% (w/w) polymer.

Results and Discussion

Thermal Study of the Solvent. A. DSC Results: Determination of the Amount of "Crystal" Solvation. The solvents employed for this study display almost equivalent thermodynamic properties toward polystyrene. For instance, the Θ point is nearly the same for *cis*- and *trans*-decalin and for 1-chlorodecane. Furthermore, since all the solutions are quenched well below the Θ temperature to produce the gels, gelation takes place by means of a mechanism involving a liquid–liquid phase separation prior to crystallization, as detailed in a previous paper.[6,15]

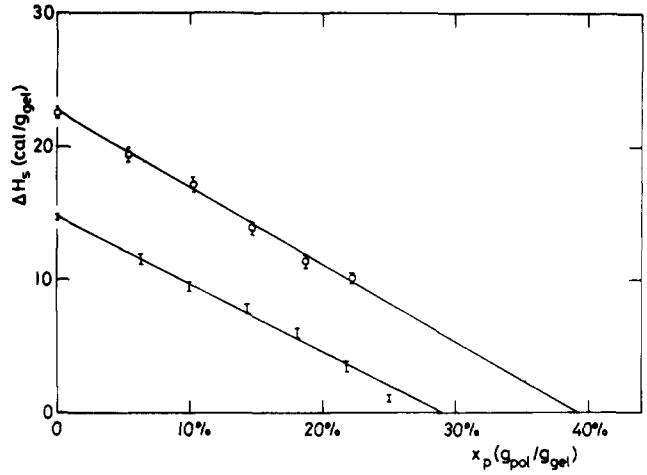

Figure 1. Variation of ΔH_s with x_p for *trans*-decalin (upper curve) and *cis*-decalin (lower curve). Bars represent the experimental dispersion of the data.

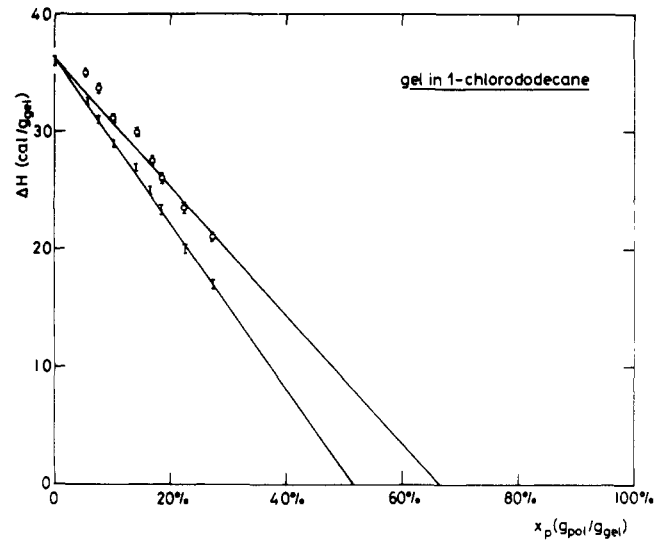

Figure 2. Variation of ΔH with x_p for gels prepared from 1-chlorododecane: nascent gel (lower curve) and gel transformed into the 3_1 helical form by annealing 24 h at 55 °C (upper curve).

As demonstrated in the same paper,[6] nascent gels formed in these solvents do not contain any detectable amount of crystals constituted of 3_1 helices. The appearance of the threefold helical form is due either to the growth in the dilute phase of chain-folded crystals occurring after subsequent aging or to the transformation of the original gel structure, which only takes place in 1-chlorodecane and 1-chlorododecane after a short annealing below the metastable melting point of the nascent gel.

In view of these gel thermal properties, experiments have been performed both on nascent gels and on transformed gels.

1. Nascent Gels. All the plots of ΔH vs. x_p are linear as illustrated in Figures 1 and 2. Therefore, equations derived in the Theoretical Section can be used to determine $\bar{\alpha}$. This parameter is seen to vary from one solvent to another (see Table I) and spectacularly by a factor of nearly 2 between *cis*-decalin and *trans*-decalin. These results indicate that *cis*-decalin is the most adsorbed solvent, whereas 1-chlorododecane is the least. The most

striking outcome is the increase of the gel melting point (stable or metastable) with the decrease of $\bar{\alpha}$ (see Table I). There are two ways of interpreting such a behavior of the melting point:

a. The helical form supposed to be a "12_1" form in the nascent gel is not solvated; the solvent is only located in the amorphous regions. For such a picture, Flory's equation relating the melting point depression to the total amount of diluent has to be used[16]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u}\frac{V_u}{V_1}(v_1 - \chi_1 v_1^2) \qquad (14)$$

where T_m^0 is the melting point in the absence of diluent (and T_m is the melting point with diluent), v_1 is the volume fraction of the diluent, ΔH_u is the melting enthalpy of 1 mol of chain structural unit, v_u and v_1 are the molar volumes of the polymer and the diluent, respectively, and χ_1 is Flory's interaction parameter.

It is at once obvious that there should not be any observable difference between *cis*-decalin, *trans*-decalin, and 1-chlorodecane, since for these solvents all the thermodynamic parameters of this equation are virtually identical.

b. The structure responsible for the physical cross-links is solvated. Here, the melting point depression should evidently depend on the amount of "cocrystallized" solvent, that is, on $\bar{\alpha}$. Such is the case for the data reported here and particularly without any ambiguity between *cis*- and *trans*-decalin. Accordingly, these experiments provide a further and strong support to the concept of "crystal" solvation, in other words, to the existence of congruently (or incongruently) melting polymer–solvent compounds in the gels of isotactic polystyrene.

One need not emphasize that $\bar{\alpha}$ is not necessarily a measure of the stoichiometry of the polymer–solvent compound. It would be unwise to ignore the presence of "amorphous" regions, whose degree of solvation is expected to be larger and may slightly vary with temperature. Henceforth, the value of $\bar{\alpha}$ represents certainly an overestimate of the actual compound's stoichiometry.

2. Gels Transformed into the 3_1 Helical Form. Gels from 1-chlorodecane and 1-chlorododecane can be readily transformed from the original structure into the three fold helical form by annealing below the gel metastable melting point.[6] There are degrees of metastability in the sense that the transformation takes place within a few minutes in 1-chlorododecane at 55 °C whereas a few hours are needed in 1-chlorodecane at the same temperature. The metastability in the light of solvated structures makes sense and thereby compounds formed in 1-chlorodecane and 1-chlorododecane have to be designated as incongruently melting compounds.

If the transformation is not only conformational but is accompanied by a desolvation process, the value of $\bar{\alpha}$ should be affected. As a matter of fact, crystals builtup with 3_1 helices are known to be nonsolvated ("anhydrous"). It is expected that after gel transformation $\bar{\alpha}$ will have subsequently decreased. Such an assumption is experimentally borne out (see Figure 2). The value of $\bar{\alpha}$ decreases from 0.5 for nascent gels to 0.19 for transformed gels in 1-chlorododecane.

One may nevertheless wonder why $\bar{\alpha}$ does not decrease to zero. As previously, this can be accounted for by the presence of purely amorphous domains that are still swollen by the solvent.

B. Implications of the DSC Findings. The knowledge of $\bar{\alpha}$ may prove to be of interest to cast some light on the reason for the occurrence of the transformation in some solvents and its absence in others. In addition, some anomalies reported on the crystal growth rate of single crystals in dilute solutions of these solvents[1] may receive an explanation.

Table I

solvent	T_{mgel},[a] °C	$\bar{\alpha}_{nas}$[b]	$\bar{\alpha}_{trans}$[c]	ΔH,[d] cal/mol
cis-decalin	37	1.89		2029
trans-decalin	65	1.15		3146
1-chlorodecane	76[e]*	0.69	0.41	5895
1-chlorododecane	92[e]*	0.5	0.19	7362

[a] Determined from DSC experiments at 20 °C/min, by taking the onset of the endotherm. T_{mgel} does not vary significantly with concentration as expected when a liquid–liquid phase separation is involved. [b] $\bar{\alpha}_{nas} = \bar{\alpha}$ for nascent gels. [c] $\bar{\alpha}_{trans} = \bar{\alpha}$ for transformed gels. [d] The melting enthalpy of iPS crystals constituted of 3_1 helices is $\Delta H_m^{iPS} \simeq 2000$ cal/mol.[28] [e] Metastable melting point.

1. Gels. While it was suspected that the degree of "12_1" stability originated from "crystal" solvation, the determination of $\bar{\alpha}$ offers a quantitative basis for discussion. From previous results[6] and those herein, it is shown that the structure is stable (congruently melting) for $\bar{\alpha} > 1$ whereas it is metastable (incongruently melting) for $\bar{\alpha} < 1$.

The case $\bar{\alpha} < 1$ certainly corresponds to an inhomogeneous solvation. Possibly, some monomer units are not solvated at all and thus may act as a nucleus for promoting the growth of 3_1 helices, which, once triggered, entails the expulsion of the solvent. Bearing in mind that this transformation does not occur at a well-defined temperature but seems rather spread over a wide range[6] and that its rate speeds up with increasing temperature, one may safely state that this transformation requires an activation energy (possibly to expel the solvent).

Conversely, the case $\bar{\alpha} > 1$ corresponds to a situation where all the monomer units are screened by a molecule of solvent, which reduces considerably the probability of having 3_1 nuclei. While there is no reason to disregard the possibility of any structural transformation here, the latter would certainly require a higher activation energy to compensate for the lack of nuclei. This entails an annealing at temperatures higher than the melting temperature of the gel, hence the absence of transformation in this case.

Seemingly, the case $\bar{\alpha} = 1$ happens to be a critical value. In this respect it is interesting to compare the fates of gels produced from *trans*-decalin and those from 1-chlorodecane. Their melting points are relatively close (see Table I) and yet the transformation can be achieved at 55 °C in 1-chlorodecane but is bound to fail in *trans*-decalin. As outlined above, the probable absence of 3_1 nuclei in decalin and thereby the need for a higher activation energy may explain this difference, which would be otherwise puzzling. The knowledge of $\bar{\alpha}$ therefore provides a coherent explanation.

2. Dilute Solutions. It has been stressed in the Theoretical Section that a linear variation of ΔH with polymer concentration means that the value of $\bar{\alpha}$ is independent of the latter parameter. As a result, $\bar{\alpha}$ also describes the state of solvation in dilute solution where microgels can form instead of crystals. This entails, as in the gels, that on average two molecules of *cis*-decalin are adsorbed on a monomer unit and the like.

Values of $\bar{\alpha}$ may help understand and explain why the growth of chain-folded crystals, instead of increasing at higher undercoolings as normally expected, is slower in both decalins.[1] In view of the high degree of solvation, the chain can be regarded as "poisoned". This means that the lifetime of an monomer unit–decalin interaction increases with decreasing temperature to theoretically become in-

finite at the solvent melting point. This poisoning effect is thus capable of hampering crystal growth under the three fold helical form which in principle gives "anhydrous" structures only.

Alternatively, crystal growth is much faster in 1-chlorodecane and 1-chlorododecane without seemingly any decrease when the undercooling increases.[17] This is readily accounted for by the lower degree of chain solvation and correspondingly of chain "poisoning".

In addition, concerning decalins, a transformation observed near 70 °C[18,19] has been assigned to a conformational transformation of the helix–coil type. This means that below this temperature it should be easier to form 3_1 helices and therefore the crystallization rate should increase steadily on lowering the temperature. Such is not the case as mentioned above. Conversely, this transition might be regarded as being a solvation–desolvation transition. The process may be viewed as follows: above a given temperature, although the solvent quality can still be good, the lifetime of a monomer unit–decalin interaction becomes so short that everything happens as if the chain were far less solvated; hence a change of conformation which is not inevitably linked to the disappearance of any type of helix occurs. This would also explain the reason why this transition is visible with atactic polystyrene as well, for which it must be unlikely to find long and regular sequences in such an amount that the conformation would be affected after the transition.

This assumption ought to be experimentally confirmed (maybe by measuring the partial pressure of the solvent as a function of temperature) and is still speculative at the moment.

To conclude, it seems interesting to make a parallel between what takes place in dilute solutions on the one hand and the gel thermal properties on the other hand. When the growth of chain-folded crystals is slow below a given temperature, gels produced from these solvents possess a stable structure that does not transform into the 3_1 form prior to gel melting (the case of decalins). Alternatively, when the growth of 3_1 single crystals is quite rapid, the transformation into the 3_1 form is feasible (the case of 1-chlorodecane and 1-chlorododecane).

Since all these types of behavior turn out to be accounted for through the knowledge of $\bar{\alpha}$, it appears that this constant may become an important thermodynamic parameter to describe the solution properties of slowly crystallizing polymers. In this respect, it is worth dwelling upon the difference between $\bar{\alpha}$ and χ, Flory's interaction parameter. We have shown in a recent paper[9] that for systems wherein χ is nearly the same, $\bar{\alpha}$ can vary by a factor of 2. This can be easily understood since χ is a mean field parameter and accordingly a macroscopic one, whereas $\bar{\alpha}$ is sensitive to the interaction at the molecular level.

Neutron Diffraction. If the structure is solvated, a view strongly supported by the above data, this could be directly demonstrated by neutron diffraction as detailed in the Theoretical Section. As it is claimed that the 0.51-nm reflection arises from a "12_1" helix with a sixfold screw[3] and therefore from the polymer only, this reflection should be chosen for such an investigation. This turns out to be impossible for the unexpected fact that the gel on the one hand and *cis*-decalin on the other hand display exactly the same diffraction pattern. Such a result is illustrated in Figure 3, parts A (40% polymer gel) and B (*cis*-decalin at 20 °C). At this concentration of polymer, all the *cis*-decalin is bound, which means that the gel diffraction pattern is not the result of "islands" of decalin.

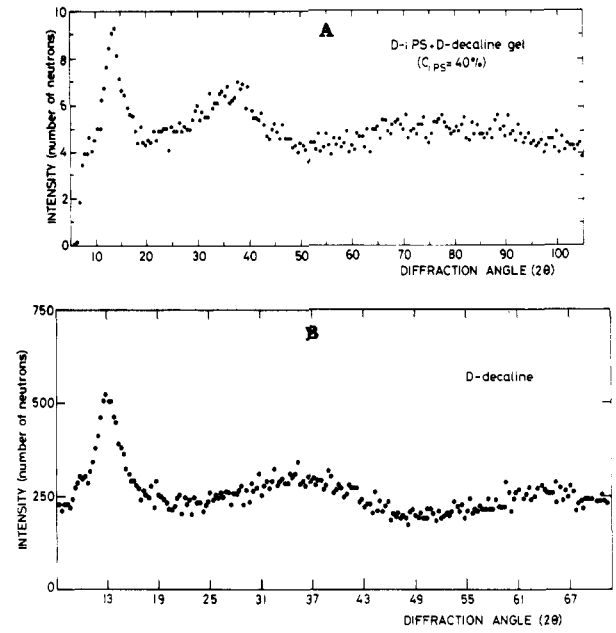

Figure 3. (A) Neutron diffraction pattern of a gel prepared from a 40% polymer solution in *cis*-decalin quenched at 0 °C (both the polymer and the solvent are perdeuterated). (B) Neutron diffraction pattern of liquid *cis*-decalin (perdeuterated). (Note the scale is more expanded in (B).)

The first, narrower, peak corresponds to a Bragg spacing of 0.53–0.54 nm. The slight discrepency observed when compared to X-ray diffraction data may simply arise from the use of deuterated material instead.[11]

The outcome of these diffraction experiments is manifold and far-reaching. First, the gel in the wet and unstretched state possesses essentially the features of a liquid. The analysis in terms of liquid order leads one to reconsider the statement whereby the 0.51-nm reflection is regarded as being due to a "12_1" helix made of dimer elements. For a liquid, the narrow first peak is related to the distance between first neighbors yet not through the usual Bragg's law.[20] Deviations from this law depend on many parameters such as the arrangement of the molecules and their shape. In principle the only way to exactly determine the structure is to calculate the Fourier transform of the experimental intensity over the entire diffraction angle range and use a model. However, the Ehrenfest relation usually holds for a liquid system, *spherically averaged*

$$1.23\lambda = 2d \sin \theta$$

In the present case, the distance d determined through the use of this law gives $d = 0.65$–0.665 *nm*, which happens to be close to the pitch of the 3_1 helix in isotactic polystyrene.

Results reported here may suggest that decalin molecules are trapped by the polymer chains in a state very similar to the liquid, hence the observation of the 0.53-nm reflection in the gel as well (and possibly its appearance as a meridional reflection in stretched gels). Such a picture is coherent with the solvation of the structures of the gel. It is worth mentioning that other examples can be found in the literature, such as the case of poly(γ-methyl L-glutamate) with dimethyl phthalate. For this system, Watanabe et al.[21] have also observed a strong meridional reflection at 0.507 nm, which, according to these authors, comes from solvent incorporation into the α-helical form so as to give a crystalline complex.

However, should the 0.53-nm reflection be only due to decalin molecules, there would not be any trace of order concerning the polymer and particularly the absence of the

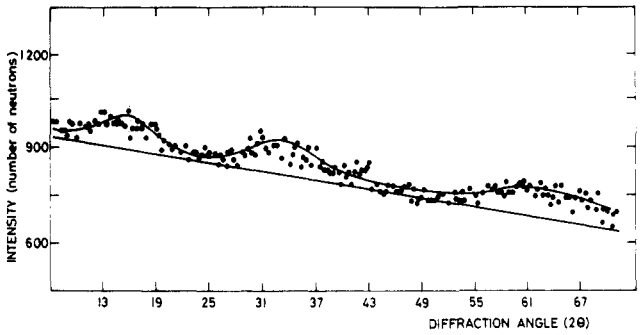

Figure 4. Neutron diffraction pattern of a gel prepared from a 20% polymer solution in *cis*-decalin quenched at 0 °C. Here, only the polymer is perdeuterated, the solvent being protonated.

"12_1" helix. Such a statement can be tested by performing an experiment on a gel sample containing deuterated polystyrene (iPSD) and protonated decalin. Since the scattering length of decalin is close to nought ($\bar{A}_{dec} = 7.6 \times 10^{-14}$ cm), relation 13 shows that diffraction will essentially arise from only the polymer. The results of such an experiment are given in Figure 4. They confirm that the 0.53-nm reflection is absent (or for the sake of cautiousness nearly undetectable). The diffraction pattern only displays oscillations whose exact meaning is difficult to attribute without the use of a model. It seems at any rate premature to venture into any deep modelization with the available data so far.

However, one may wonder whether the system *cis*-decalin–iPS is representative of all the systems promoting physical gelation. This question can be tentatively answered. The value of d, as stressed above, is related to the solvent molar volume. Accordingly, solvents with the same or nearly the same molar volume are supposed to give a diffraction pattern characterized by virtually the same d within a few percent.

Explicit reports of the observation of the 0.51-nm reflection in the literature have been made with systems where the solvent has a molar volume close to that of decalin (144–155 cm^3/mol).[2-5] In addition, Sundararajan et al. report that the value of 0.51 nm is not always found but that they observe a reflection at a value as low as 0.48 nm.[5] In the absence of other reflections, they assign it to the 12_1 helical form.[5] Apparently, this result is found for solvents of lower molar volume. In view of the conclusions developed here, this discrepancy is easily accounted for by the diffraction due to the solvent rather than with a hypothetical distorted unit of the 12_1 helix.

It may be further noted that the 0.507-nm reflection observed by Watanabe et al.[21] and correctly assigned to the solvent confirms the above statement since molar volumes of decalin and dimethyl phthalate differ by only approximately 3%. Incidentally, the same problem may exist in atactic PVC gels formed in dimethyl phthalate where a 0.51-nm meridional reflection has been attributed[22] to the orientation of another form of crystals.

On the whole, it would seem that the 0.51-nm reflection is merely due to the solvent. However, Keller et al.[23] claim that a gel dried by extraction with a more volatile solvent still exhibits this reflection, at least in *trans*-decalin. From their paper it is not clear whether the sample tested by IR to show that there remains less than 0.4% of *trans*-decalin is the same as that investigated by X-ray. If such is the case, it would seem that either the 0.51-nm reflection is genuinely due to a 12_1 helix possessing a sixfold screw symmetry or that 0.4% solvent is still able to produce such a reflection. Clearly, further neutron diffraction experiments are needed to clarify this point.

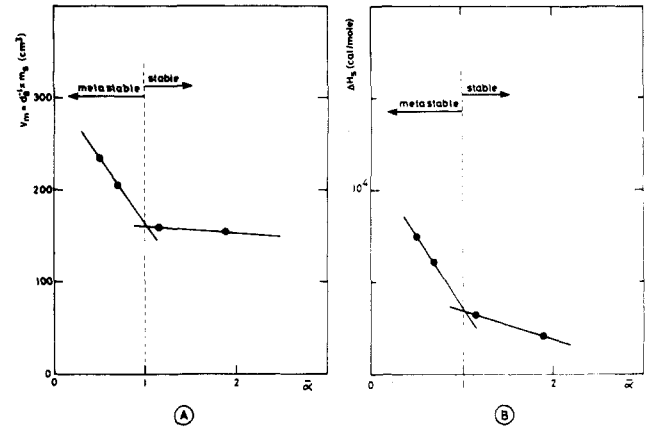

Figure 5. (A) Molar volume of the solvent as a function of the corresponding $\bar{\alpha}$ for iPS. (B) Solvent molar heat of fusion as a function of the corresponding $\bar{\alpha}$ for iPS.

To definitely settle the matter, it would be of interest to evidence the 0.51-nm reflection with a gel wherein the solvent has a smaller molar volume to avoid any ambiguity ($V_m \simeq 100$ cm^3/mol, for instance). So far, no explicit reports on the observation of this reflection with such solvents have been done.

It is however necessary to emphasize that the existence of the 3.06-nm reflection is consistent with a 12_1 helical form and cannot be assigned to the solvent. This would mean that the 12_1 helix has in fact a twelvefold screw symmetry. As the 3.06-nm reflection is only seen in gels once they have been stretched, it may be suggested that this 12_1 helix, which is in fact the conformation with minimum energy of an extended chain, only arises from the stretching process and that it does not form during gelation. The fact that gelation leads to a rather high degree of solvation may prevent the chain from crystallizing under the usual 3_1 form. Then, stretching while slowly drying might promote the formation of the 12_1 helix.

Correlation between Neutron Diffraction Results and DSC Data. As underlined above, neutron diffraction results suggest that the molar volume of the solvent can be an essential parameter. In particular, the fact that the 0.53-nm reflection is observed both in *cis*-decalin and in the gel, and seems to be only attributable to the solvent, indicates that the solvent possesses the same order when located in the gel. This could mean that the polymer adopts such a conformation that the liquid order of *cis*-decalin be unperturbed.

It is of interest on this basis to plot the solvent molar volume as a function of the parameter $\bar{\alpha}$. Such a plot (Figure 5A) gives evidence of two regimes. Admittedly, the results are still scarce so that the relevancy of such a plot as well as its nonfortuity remain to be confirmed. Yet, the change of regime occurs at $\bar{\alpha} \simeq 1$ which correlates with the fact that below $\bar{\alpha} = 1$ the gel melting point is metastable while it is stable above. Seemingly, there exists a critical size for the solvent. This size effect may be viewed as follows: as long as the solvent molecule can enter a "cavity" characteristic of the polymer conformation without deeply perturbing it, the gel exhibits a stable melting point. Once the solvent molecules possess a size larger than this critical size, they cannot enter this "cavity"; hence a lower degree of solvation may be possible and metastability of the original gel structure appears.

From the first peak at 0.53 nm in *cis*-decalin, one ends up with 0.65–0.665 nm. This could suggest that the "cavity" is the result of benzene rings spaced by this distance, which would imply that the chain conformation is in fact not far away from a 3_1 helical form in nascent gels.

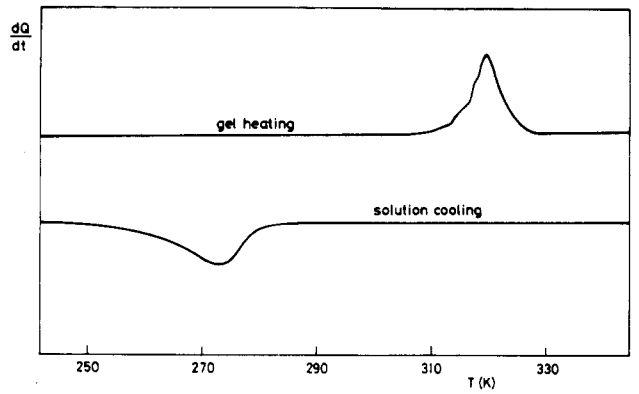

Figure 6. DSC traces illustrating the existence of an exotherm of gel formation and an endotherm of gel fusion (10% iPS in *cis*-decalin).

Similarly, when a comparison is made between the 3_1 crystals melting enthalpy (2000 cal/mol) and the solvent heat of fusion (2029 cal/mol) of *cis*-decalin, there is again a match. As previously, a plot of the heat of fusion of the solvent vs. $\bar{\alpha}$ exhibits two regimes with a critical value at $\bar{\alpha} \simeq 1$ (Figure 5B). Similar conclusions have been drawn by Delmas et al.[24] on the formation of physical gels from poly(4-methyl-1-pentene).

Concluding Remarks

It has been suggested, to originally account for gelation of atactic polymers,[15] that the polymer-rich phase created by the liquid–liquid phase separation lies below its glass transition temperature T_g. This would ensure the existence of a network without the need for crystallization. Experimental determinations of T_g by DSC for highly concentrated solutions of aPS (59% (w/w)) in decalin show that $T_g < 0$ °C. Unless the polymer-rich phase turned out to be very concentrated, which seems at any rate unlikely, the network would not persist at temperatures as high as 60 °C, for instance.

Two experimental facts differentiate the gel structure from an amorphous one:

i. There does exist a melting endotherm that cannot be confused with any stress relaxation since an exotherm of formation is also visible (Figure 6). Consequently, both the gel formation and the gel fusion proceed from a thermodynamic transition of the first order.

ii. The solvent melting point measured in the gel as a function of polymer concentration does not markedly vary, especially when the comparison is made with a totally amorphous system (Figure 7).

Another interesting feature concerns the very low melting enthalpy of the gel, which would make sense in the case of a poorly crystallized system but carries another meaning for a system wherein crystallization is virtually absent.

Once the gel characteristics are encompassed and regarded with a new look, one realizes that they are amazingly reminiscent of those of liquid crystals and more specifically of nematic liquid crystals: the liquid order,[25] the first-order transition on melting,[26] and the low-melting enthalpy.[27] In this respect the gel melting ought to be an "anisotropic structure–isotropic liquid" transition. Obviously gels are not true liquid crystals since they do not flow.

A possible structure that takes into account all the aforementioned requirements could resemble a ladder (when two chains are considered), where the role of the rungs would be played by the solvent molecules. While the solvent molecules would show a liquid type order (a distance between first neighbor decalins of 0.665 nm with possibly decalin layers distant of 0.53 nm), the chain, if displaying rodlike portions, would not necessarily be under any well-defined helical form. It may be however suggested that the chains could possess a conformation not unlike the 3_1 helix. In this model, the solvent "mediates" the interaction between chains. Accordingly, the solvent is not only occluded but plays the major role.

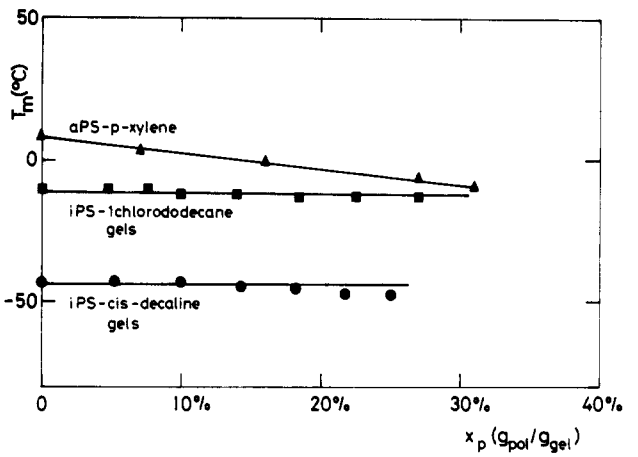

Figure 7. Plot of the solvent melting temperature T_{ms} as a function of polymer concentration: (●) gels in *cis*-decalin, (□) gels in 1-chlorododecane, and (▲) solution of atactic polystyrene in *p*-xylene (from ref 9).

If the above model describes correctly the molecular structure of the gel, the structure would then be the third state for polymers, the two first being the amorphous state and the crystalline state (liquid-crystal polymers being discounted).

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Registry No. iPS, 25086-18-4; iPSD, 102494-77-9; $H_3C(C-H_2)_9Cl$, 1002-69-3; $H_3C(CH_2)_{11}Cl$, 112-52-7; neutron, 12586-31-1; *cis*-decalin, 493-01-6; *trans*-decalin, 493-02-7.

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Modeling of Polymer Epitaxial Crystallization: β-Poly(vinylidene fluoride) on (111) CaF_2

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ABSTRACT: Molecular mechanics interaction energy calculations have been carried out in an effort to model the epitaxial behavior of the β phase of poly(vinylidene fluoride) (β-PVF_2) on the (111) cleavage surface of CaF_2. The Coulombic contribution to the total energy for this system is much higher (about 40%) than for other polymer/substrate systems that have been modeled with the same technique. The lowest energy configuration is one in which the β-PVF_2 chain axis is parallel to and centered over a row of fluoride ions in the substrate surface. In this energy minimum, the β-PVF_2 molecular dipoles are parallel to the surface. However, another low-energy configuration having the β-PVF_2 dipoles perpendicular to the surface exists and has an interaction free energy only 2.7% higher than the lowest energy minimum. The implications that these calculations have on the prospect of forming a piezoelectric film of β-PVF_2 directly via epitaxial crystallization are discussed.

Introduction

Since the first observation by Willems and Fischer,[1,2] many experimental accounts of polymer epitaxial crystallization have appeared in the literature.[3] Less numerous are theoretical or modeling studies that attempt to justify the experimentally observed polymer chain orientations and crystal structures in the epitaxial thin films. Computer modeling of the epitaxial process was first carried out by Hopfinger et al.[4-7] for polyethylene and poly(oxymethylene) on various alkali halide substrates. The molecular mechanics method was used, which involves pairwise summation of all possible polymer atom–substrate ion interactions, using molecular potential functions that represent dispersion-repulsive, Coulombic, and induced dipolar energies. The total interaction energy for a polymer segment frozen into its crystalline conformation was mapped out as a function of the orientational variables of the polymer/substrate system, and minima were located. In accord with experimental results, they found that the energetically preferred chain orientation was ⟨110⟩ on all substrates. They were also able to account for the existence of the metastable monoclinic phase in thin films (<50 Å) of polyethylene on NaCl by considering a "monolayer nucleus" consisting of seven polyethylene chain segments as the depositing species.[7] These early successes established the molecular mechanics approach as a valid predictive tool for polymer epitaxial processes. The molecular mechanics technique has been used subsequently in computer modeling studies of the epitaxial behavior of poly(sulfur nitride) on alkali halides by Mauritz et al.,[8] polyethylene on graphite by Baukema et al.,[9] poly(ethylene oxide) on nylon-6 by Hoyt et al.,[10] and poly(*p*-xylylene) on NaCl and KCl by Isoda[11] and to account for varying nucleation densities of poly(oxymethylene) on alkali halide substrates by Balik et al.[12]

A common characteristic of the modeling studies mentioned above is the relatively small contribution (typically less than 10%) of the Coulombic (polar) term to the total interaction energy at the global minimum for the polymer/substrate system. The dispersion-repulsive term has been found to be the major force controlling the epitaxial behavior of these systems. This is because relatively nonpolar polymers are involved, interacting with nonpolar substrates. Even the ionic alkali halides, whose (001) cleavage planes have often been used as epitaxial substrates, have an electrically neutral surface with a rapidly decaying electric field as distance from the surface increases.

In this paper we model the epitaxial behavior of a polymer/substrate system in which polar interactions play a more important role. For this purpose, the poly(vinylidene fluoride)/CaF_2 system has been chosen. CaF_2 cleaves on its (111) planes to produce a charged surface consisting entirely of F^- ions, unneutralized by surface ions of opposite charge, and has not yet been considered as an epitaxial substrate for polymers. Poly(vinylidene fluoride) (PVF_2) is a polar polymer that has been intensively studied and characterized as a piezoelectric material. This property is dependent on the degree of molecular or dipole orientation. Epitaxial crystallization is a means for producing polymeric thin films having a high degree of chain orientation and therefore represents a potential technique for controlling and modifying the piezoelectric properties of this polymer. In order to obtain a piezoelectric film of PVF_2 epitaxially, the substrate must cause the C–F_2 dipoles to align uniformly normal to the surface. Orientation

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