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Thermodynamic Aspects and Morphology of Physical Gels from Isotactic Polystyrene

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ABSTRACT: The purpose of this paper is to contribute to the understanding of physical gelation by presenting some results gathered on isotactic polystyrene gels. The investigations have been carried out through the use of a series of solvents displaying a Θ-domain and therefore a miscibility gap. Gels have been obtained by quenching well below Θ. In particular, two phenomena have been evidenced: (i) a reversible turbid–clear transition seemingly linked to a phase separation different from that giving rise to the gel (as a consequence, if a gel stands below this transition at room temperature it will be turbid); (ii) a conformational transformation of the network from the 12_1 into 3_1 helical form. Only gels produced from decalin do not display such a transformation. As a result, the 12_1 form is stable in decalin and metastable in the other solvents used in this study. Besides, by using an extraction method with a good solvent (toluene) we have been able to recover the crystalline structures under the threefold helical form. Owing to this technique, the morphology of the gels has been determined. We particularly show that the network ensuring the gel character of the system is actually made up with fiberlike structures (or threads) of 100–200-Å diameter and 0.3–0.5-μm length. All these results are discussed, and the origins of gel transparency or turbidity are commented on, in light of recently proposed concepts such as "crystal solvation".

Introduction

Physical gelation of synthetic polymers has steadily received a revival of interest for the past few years,[1-8] although the phenomenon is known for long.[9] Recent investigations in the field have been centered on three main issues: (i) the crystal structure and morphology,[1,3,8] (ii) the mechanism of gel formation,[1,4,6,10] and (iii) the relation between structure and thermal history.[4-7]

Contributions to these issues have been obtained while investigating gels formed with isotactic polystyrene (iPS). Worth mentioning is the discovery of a new chain conformation and the partial determination of the resulting crystal structure.[3,8] This newly found conformation is a 12_1 helix giving a nearly extended chain as opposed to the 3_1 helix observed upon crystallization either from the bulk or from dilute solutions. Owing to the paucity of X-ray pattern, the crystalline structure containing 12_1 helices is not yet fully elucidated.[3,8] In particular, the recently proposed solvated structure,[8,11] although consistent with both the "openness" of the 12_1 helix and with the fact that in spite of comparable energies[12] only the 3_1 helix is observed under usual crystallization conditions, requires further experimental backup. Nevertheless, this introduces the concept of crystal solvation in physical gels, which is otherwise known concerning hardly crystallizable polymers such as PPO and sPMMA.[13,14]

Similarly, the mechanism of gel formation is not entirely comprehended. Challa and co-workers,[2,15] who pioneered the investigations on iPS gels, have noticed that gelation only occurs when the polymer solution is quenched to lower temperatures than those usually considered for growing chain-folded crystals. More detailed experiments carried out in decalin[3] revealed that the upper limiting temperature below which gelation takes place happens to be near 20 °C. This value turns out to be close to the Θ temperature of atactic polystyrene in decalin (18 °C in *trans*-decalin). Although solution properties and particularly polymer–solvent may slightly differ with stereoregularity, Θ-values determined with atactic polystyrene are valuable for the knowledge of solvent quality when dealing with isotactic polystyrene. On this basis, Wellinghoff et al.[6] have shown by using a variety of Θ-solvents that gelation occurs provided that the solution is quenched below the Θ-temperature. They concluded that physical gelation of stereoregular polymers arises from a phase separation prior to crystallization. A similar conclusion had already been reached by Feke and Prins,[10] who had investigated agarose gels formed in water. Seemingly, physical gelation which can be observed in water and organic solvents for natural and synthetic polymers could thus arise from a quite general mechanism.

As a contribution to a better understanding of iPS gels, this paper deals with experimental results that touch upon the three distinct issues mentioned above:

(a) It describes a transition not previously noticed mainly because it is only enhanced and therefore detectable when the gels are cooled down well below the Θ-temperature. This transition manifests itself in the appearance of turbidity and is reversible. It is apparently related to an additional phase separation different from that giving birth to the gel in the first place.

(b) It establishes, mainly through differential thermal analysis, the existence of a conformational transformation from the 12_1 to the 3_1 helical form which occurs at temperatures lower than the gel melting when still under the 12_1 form and is irreversible.

(c) It describes a novel procedure which enables one to selectively dissolve the gel portions under the 12_1 helical form and to preserve the material under the 3_1 helical form. Furthermore, this technique is of great use in determining the morphology of gels obtained from a variety of solvents and submitted to different thermal histories.

The three points under investigation are to some extent interrelated. For example, the 12_1–3_1 transformation alters both the visual aspect of the gel and its behavior toward dissolution. In addition, these effects show themselves to different degrees depending on the solvent and the thermal treatment. As will be shown in this paper, these phenomena which in some solvents can overlap are, however, clearly and individually pointed out through a comparative analysis of gels produced from different solvents.

Experimental Section

(1) Materials. A sample of isotactic polystyrene (designated here as iPS1) synthesized in our laboratory has been used throughout this investigation. Its characteristics after extraction of the atactic content have been determined by GPC and are as follows:[16] $M_w = 3.4 \times 10^5$ and $M_w/M_n = 2.8$.

Six solvents of high-purity grade have been employed and were selected on the basis of their known Θ-temperature for atactic polystyrene as well as their refractive index that has to differ from

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that of iPS so as to enable turbidimetry and phase contrast microscopy observations to be achieved. The solvents thus chosen are *trans*- and *cis*-decalin ($\Theta \simeq$ 18–20 °C and $\Theta \simeq$ 12 °C, respectively), diethyl malonate ($\Theta \simeq$ 36 °C), and a series of chlorinated solvents with increasing Θ-temperatures [1-chlorodecane ($\Theta \simeq$ 7–13 °C), 1-chloroundecane ($\Theta \simeq$ 33 °C), and 1-chlorododecane ($\Theta \simeq$ 52 °C)].

(2) Gel Preparation. All gels were obtained from carefully prepared and moderately concentrated solutions (5–15%). The iPS sample was in particular brought to the vitreous state by a rapid quench after complete melting to below T_g. This thermal treatment ensures that the polymer is rid of any remnants of crystals that might act as germs in the solution and therefore introduce parasitic effects.

The gels were formed by quenching the hot solution (typically heated beforehand to dissolve the polymer between 180 and 210 °C depending on the solvent) to temperatures located well below the Θ-point but above the crystallization temperature of the solvent.

(3) Techniques. (a) Turbidimetry. As it is often reported in papers that a gel is either clear or turbid (a somewhat confusing definition), we here define the vocabulary to be used throughout this paper which describes the gel visual aspect with more details: (i) "clear", i.e., transparent, although light is slightly scattered; (ii) "translucent" means that while the gel strongly scatters light, a scale can be read at the back of a test tube of 0.6-cm diameter; (iii) "turbid" means that the same scale has become unobservable, although a beam of light can be partly transmitted; (iv) "opaque" means that no light can pass through the sample.

As to the determination of the transition temperature from the turbid to the clear or translucent state, it has been achieved by means of a turbidimeter equipped with a laser and a solar cell detector (a device imagined and realized by F. Debeauvais from our laboratory).

(b) Thermal Properties. Thermal properties of the gels in the wet state have been determined with a DSCII Perkin-Elmer differential calorimeter equipped with the Thermal Analysis Data System (TADS). Approximately 10 mg of wet gel was placed into a "volatile sample" pan hermetically sealed and scanned at heating rates ranging from 1.25 to 80 °C/min. Heats of fusion were measured through calibration with indium (ΔH = 6.8 cal/g).

(c) Morphology. Optical and electron microscopic observations were performed with a Zeiss Photomicroscope II and a Hitachi HU 11 CS microscope, respectively. For the latter observations, the samples were shadowed with Pt–C and carbon-coated in the usual manner.

Results

Thermodynamic Investigations. As already stressed in the Introduction, different physical phenomena, that sometimes occur simultaneously, govern the optical as well as the thermal properties of iPS gels. An analysis of such systems might have proved difficult had the couples polymer–solvent had exactly the same types of behavior. Fortunately, some systems do not exhibit one phenomenon (for instance no 12_1–3_1 transformation in *trans*- and *cis*-decalin) and/or display another one at a very slow rate (slow chain-folded crystal growth in the dilute phase of *trans*- and *cis*-decalin gels or very slow rate of the 12_1–3_1 transformation in 1-chlorodecane). This therefore enables one to comprehend the more complex systems wherein all effects are observed.

From our experiments, we have come to the conclusion that gels in decalin are the simplest systems. These gels are in particular useful to point out unambiguously the turbid–clear transition which does exist in the other solvents, yet not with the same boldness. Consequently, these gels will be considered as basic systems referred to throughout this paper.

(A) Visual Aspect of the Gels: Evidence of a Reversible Turbid–Clear Transition. Gels in *trans*- or *cis*-decalin are usually prepared by quenching the solution between room temperature and 0 °C. The resulting gels are described as clear.[3] In these gels, irreversible turbidity only sets in over periods of weeks and has been associated with the appearance of chain-folded crystals[3] under the 3_1 helical form. [By irreversible turbidity, it is meant that the turbidity does not vanish until the gel melts.]

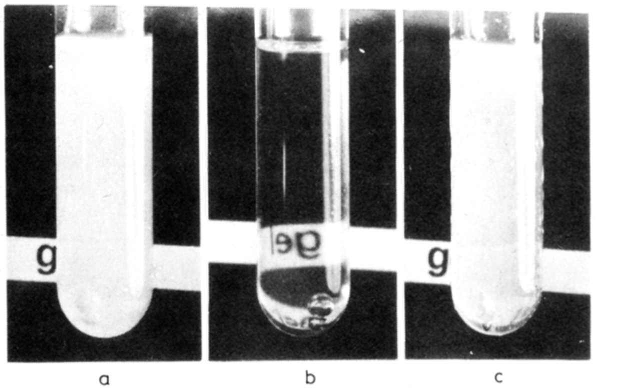

Figure 1. Gel visual aspect of a 5% gel in *trans*-decalin as a function of temperature: (a) turbid gel after quenching the solution at −30 °C (freshly formed gel); (b) gel of (a) heated up to 20 °C; (c) gel of (b) cooled down again to 0 °C.

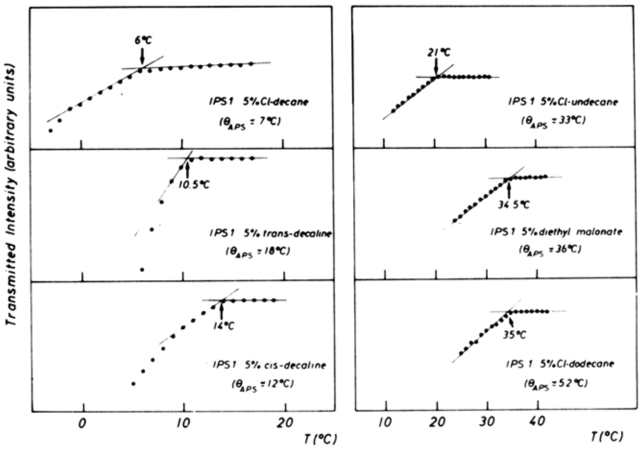

Figure 2. Turbidimetric experiments: transmitted intensity vs. temperature. Heating and cooling rates of about 1 °C/min. Polymer concentration = 5% (w/v). Gels obtained by quenching at −30 °C in *trans*- and *cis*-decalin and 1-chlorodecane, −15 °C in 1-chloroundecane, and 0 °C in 1-chlorododecane and diethyl malonate.

In this section, we report *another type of turbidity* which vanishes or reappears reversibly at a well-defined temperature and well below the gel melting point.

Upon quenching a solution at a temperature between T = +5 and T = −30 °C for *trans*-decalin and T = −40 °C for *cis*-decalin the produced gels are turbid (Figure 1a), this turbidity being enhanced as the quenching temperature is lowered. This transition is reversible with temperature and reproducible. On reheating up to room temperature the gel becomes clear (Figure 1b) and cooling down again entails the reappearance of turbidity (Figure 1c). Turbidimetric experiments show that this transition occurs at 10.5 ± 1 and 14 ± 1 °C in *trans*- and *cis*-decalin, respectively (Figure 2). In these solvents the thermal cycles (heating and cooling between 0 and 25 °C) can be repeated with reproducibility of the location of the transition temperature and without noticeable alteration of the gel visual aspect.

The same type of transition is observed for the other solvents, although this time it should rather be designated as turbid–translucent transition. [The fact that in these solvents one is dealing with translucent instead of transparent gels once above the transition is most probably due

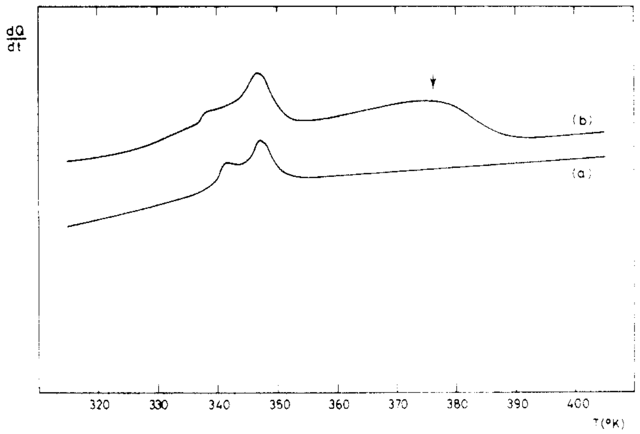

Figure 3. DSC thermograms, heating rate 20 °C/min. Gel in *trans*-decalin (C = 5%) produced from a quench at -20 °C: (a) freshly formed gel; (b) after annealing at 18 °C for 4 weeks. Gels annealed at 56 °C for a week give a thermogram similar to (a).

to the larger difference of refractive index with polystyrene.] If the determination of the transition is difficult visually, turbidimetry enables one to clearly evidence the occurrence of the transition as well as its location (Figure 2). While in 1-chlorodecane the heating and cooling cycles around the transition can be repeated as in decalin, it is not so with 1-chloroundecane, 1-chlorododecane, and diethyl malonate. As will be shown in the following, either the rapid growth of chain-folded crystals or the 12_1–3_1 transformation leading both to the irreversible turbidity aforementioned jam turbidimetric measurements when those are carried out repeatedly on the same sample especially at a very slow heating rate. Solely experiments accomplished on freshly prepared gels are reproducible and enable one to measure the transition temperature.

From these experiments (Figure 2), we therefore conclude that this type of transition affecting the gel visual aspect exists whatever the solvent, provided the solution has been rapidly cooled down well below Θ.

(B) 12_1–3_1 Transformation. Calorimetric analysis of physical gels is a convenient tool to point out the existence and the relative proportion of the two crystalline components, i.e., 12_1 helix and 3_1 helix, since the former melts at temperatures much lower than the latter (typically 40–80 °C lower, depending on the solvent).

Characterization of the gels formed in decalin again reveals a simple thermal behavior whereas in the other solvents the behavior can be very complex depending on the thermal history, the heating rate, etc. Analysis of the calorimetric data shows that in these solvents a conformational transformation from the 12_1 to the 3_1 helical form takes place within the network at temperatures well below the melting temperature of the 12_1 crystals.

In order to demonstrate the validity of this statement, experimental results are first given for *trans*- and *cis*-decalin gels wherein the 12_1–3_1 transformation *is absent* and compared to those gathered on 1-chlorodecane, 1-chloroundecane, 1-chlorododecane, and diethyl malonate wherein the 12_1–3_1 transformation *does occur*.

(a) Gels from *trans*- and *cis*-Decalin. Experiments carried out at various heating rates (10–80 °C/min) only reveal a low-melting endotherm (70 °C in *trans*-decalin and 40 °C in *cis*-decalin) which corresponds to the melting of the gel[3] (see Figure 3 for example). Determination of the heat of fusion (endotherm area) shows that ΔH_{gel} is constant with the heating rate within the experimental uncertainties as expected with a stable system (see Table I). Furthermore, aging the gel for a week at 56 °C (5% iPS in *trans*-decalin) does not alter the DSC traces.

Table I
Melting Enthalpies (ΔH_{gel}) Obtained from the Area of the Low-Melting Endotherm (Gels in the Wet State)[a]

solvent	concn, % (w/v)	heating rate, °C/min 10	20	40	80
diethyl malonate	10	<0.05	0.1	0.28	
	15	<0.1	0.23	0.52	
1-chlorodecane	5	<0.05	0.13	0.27	0.48
	15	<0.1	0.25	0.94	1.37
1-chlorododecane	5	<0.1	0.13	0.25	0.79
	10	<0.1	0.12	0.47	0.67
trans-decalin	5	0.28	0.32	0.35	0.37

[a] Values are given in cal/g; calibration with indium.

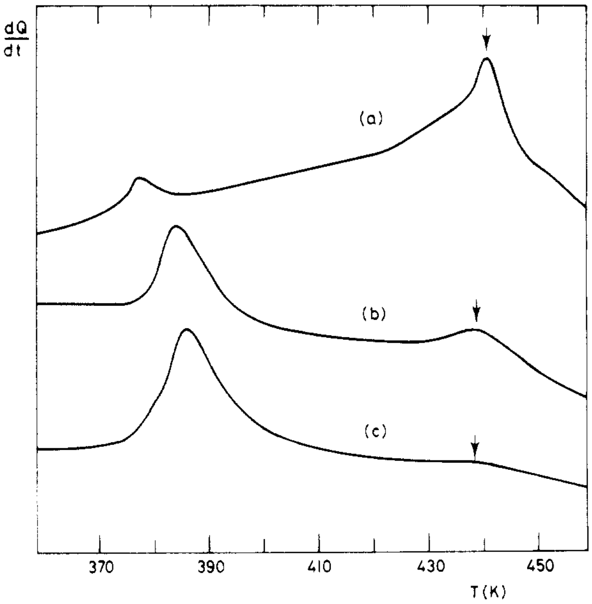

Figure 4. DSC thermogram. Gel in 1-chlorododecane (C = 5%) obtained by a quench at -5 °C. Variation of the intensities of the low- and the high-melting endotherm with heating rate: (a) 20 °C/min; (b) 40 °C/min; (c) 80 °C/min.

The appearance of a high-melting endotherm only occurs over periods of weeks (Figure 3) as already shown in ref 3 and corresponds to the presence of chain-folded crystals containing the threefold helical form within the dilute phase. (This point will be proven directly in the section devoted to morphology.)

From this evidence, we conclude that the 12_1 helix once formed is *stable* in decalin gels.

(b) Gels from the Other Solvents. Unlike decalin, DSC thermograms gained from these gels, in particular at a heating rate of 20 °C/min (usual rate for a thermal behavior investigation), point out to the presence of both helical structures through the low- and high-melting endotherms (see Figure 4) whereas toluene extraction indicates that only the 12_1 helical form is present in the freshly formed gels. The relative proportions vary significantly with the heating rate and the thermal treatment. Generally speaking, the following results are obtained:

(i) With fresh gels, the high-melting endotherm vanishes when the heating rate is increased (see Figure 4). Experiments of Figure 4 show that the 3_1 form is actually absent in nascent gels at room temperature; this form appears only when submitting the sample to a thermal treatment in the DSC.

(ii) On the other hand, the disappearance of the low-melting endotherm when scanning at very slow heating rates (see Figure 5) and correspondingly the strong dependence of the gel heat of fusion (low-melting area endotherm) when decreasing the heating rate (see Table I)

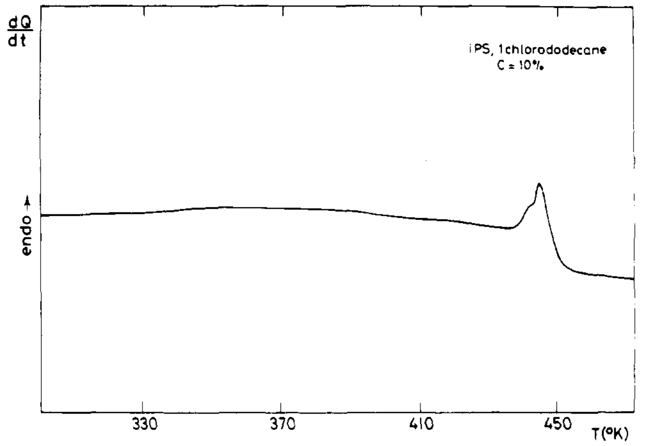

Figure 5. DSC thermogram, heating rate 1.25 °C/min. $C = 10\%$; gels obtained in 1-chlorododecane by quenching at −5 °C.

show that the 3_1 form grows at the expense of the 12_1 form.

(iii) In the same line as (i) prominent high-melting endotherm along with the absence of the low-melting endotherm for gels aged well below the melting of the 12_1 species as determined with high heating rates (20 to 80 °C/min) (see Figure 6). Correspondingly, one observes the rising of opaqueness in these annealed gels.

These results altogether suggest that the 12_1 helical form is *metastable* in these solvents and thus can transform below its metastable melting point into the 3_1 helical form as unquestionably witnessed by Figure 6.

It is, however, worth emphasizing that not only the transformation of the network into the 3_1 helix but also the growth of chain-folded crystals takes place. Figure 6 indeed displays an endotherm always composed of two peaks attesting the presence of two crystalline species under the 3_1 helical conformation, since the second peak does not originate from a recrystallization effect (compare Figures 5 and 6 where different heating rates have been used and where no change in peak proportion can be evidenced which differentiates the effect from fusion–recrystallization[17]). The growth of chain-folded crystals comes either from crystallization within the dilute phase prior to 12_1 species melting or from recrystallization of the chains of the molten network on scanned gels or, as on aged gels, from nucleation on sites created after the 12_1–3_1 transformation. All these points will be illustrated by the morphological investigations.

As anticipated with metastable states, their lifetime must depend on the temperature and the solvent. From our experiments, we have come to the following degrees of metastability (from the "stablest" to the least stable): 1-chlorodecane, 1-chlorododecane, 1-chloroundecane, and diethyl malonate.

(C) Toluene Extraction. Another method of assessing the occurrence of the 12_1–3_1 transformation relies upon the difference of solubility that each helical structure can display when submitting the gel to an excess of good solvent (necessarily miscible to the gel solvent). As a matter of fact, either the openness of the 12_1 helix or its possible solvation renders it more liable to be dissolved by a good diluent contrarily to the 3_1 helix. On the same line, by carefully choosing a good solvent wherein isotactic polystyrene can crystallize under the 3_1 helical conformation but at a very slow rate, one should be able to both preserve the existing 3_1 species and prevent the chains of the dissolved network from recrystallization into chain-folded crystals.

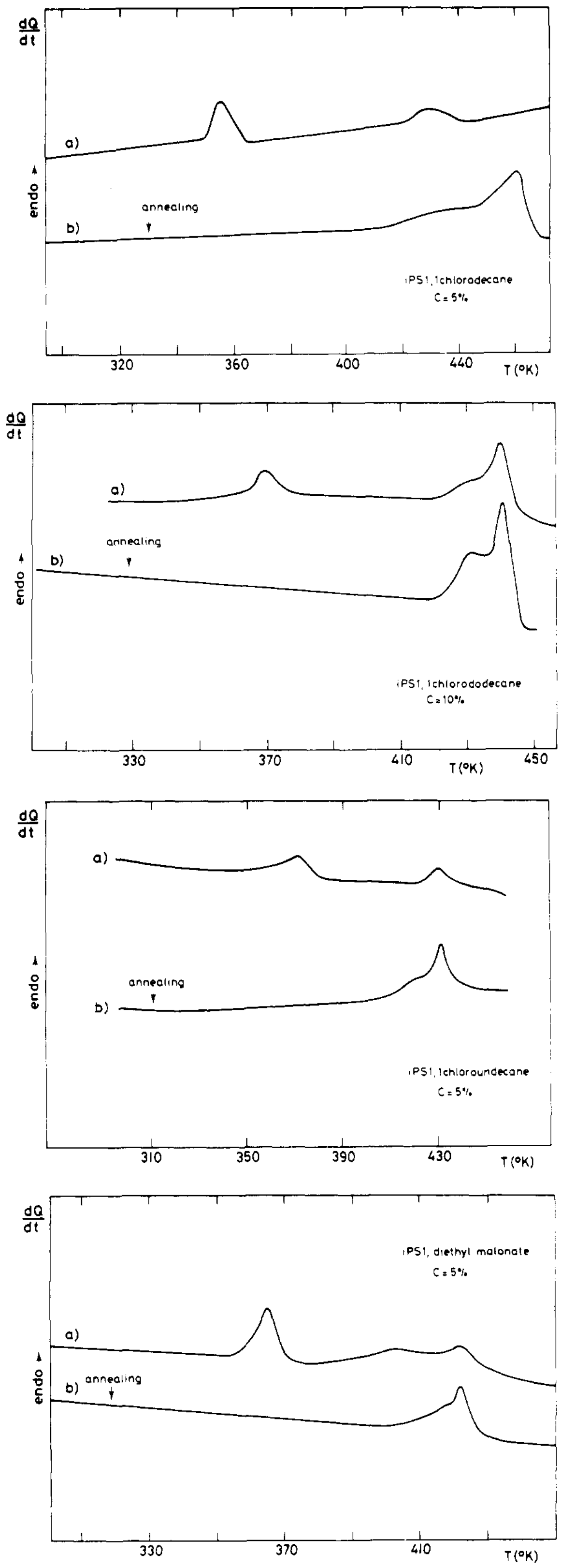

Figure 6. DSC thermograms of gels prepared in various solvents: (a) freshly formed gels; (b) after annealing well below the low-melting endotherm (arrow) (in 1-chlorodecane annealed 3 h at 55 °C, in 1-chlorododecane annealed 15 min at 56 °C, in 1-chloroundecane annealed 15 min at 40 °C, and in diethyl malonate annealed 5 min at 45 °C). Heating rate 20 °C/min.

Talen and Challa[18] reported that, although *toluene* is a very good solvent for isotactic polystyrene, chain-folded crystals under the threefold helical form grow at a very slow rate (at least 1 day to observe a significant manifestation of their presence). As toluene is totally miscible with the solvents employed for this study, it meets the above specifications at room temperature.

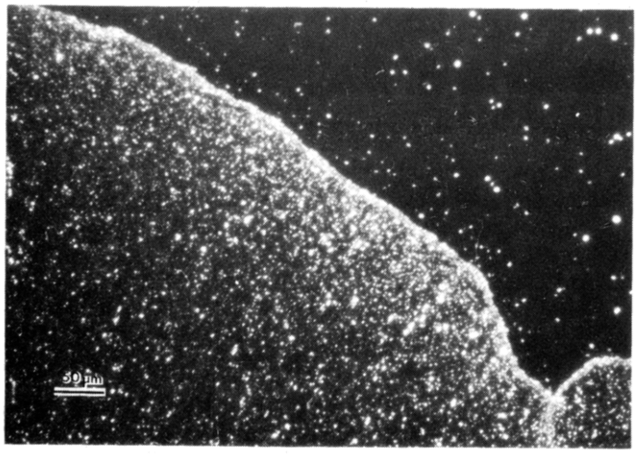

Figure 7. Optical microscopy picture (between crossed-polarizers). Gel 5% in 1-chlorodecane prepared between glass slides (quenching temperature −18 °C) annealed 24 h at 30 °C.

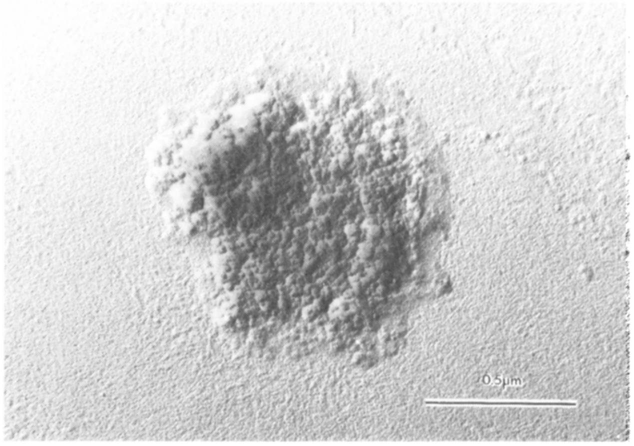

Figure 8. Single crystal obtained from toluene extraction of a 5% gel in 1-chloroundecane (quenching temperature −15 °C) annealed 6 days at 20 °C.

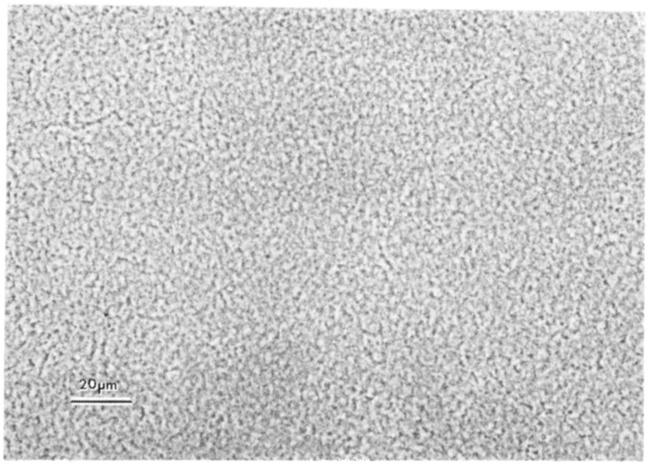

Figure 9. Phase-contrast microscopy. Gel from diethyl malonate prepared between glass slides ($C = 10\%$, quenching temperature 0 °C). Observation of the "salt and pepper" structure after 12_1–3_1 transformation more pronounced than under the 12_1 form.

On this basis, three types of phenomenological experiments have been carried out:

(i) Just after gelation has set in, *all the gels* are thoroughly dissolved by an excess of toluene at room temperature without noticeable difficulty. Any trace of chain-folded crystals is absent as ascertained by optical microscopy observations. This experiment allows us to show that the high-melting endotherm systematically recorded in gels of 1-chlorodecane, 1-chloroundecane, 1-chlordodecane, and diethyl malonate does not arise from 3_1 crystals that might have grown before or while the gel was forming. This experiment shows the absence of the 3_1 form in fresh gels and thus only the presence of the 12_1 form.

(ii) After aging the gels at room temperature, they are still dissolved by an excess of toluene. Yet, the resulting solution contains chain-folded crystals (cloudy solution and observation by optical microscopy).

(iii) After annealing at higher temperatures so as to achieve the 12_1–3_1 transformation, the gels are *no longer soluble* in toluene which confirms that the 12_1 helix has transformed into 3_1 helix. Only a kind of "weathering" can be noticed, giving rise to particles of various sizes (this effect may come from the inhomogeneity of the sample).

In addition to the confirmation of the occurrence of the 12_1–3_1 transformation, the toluene-extraction method offers further advantages such as the recovering of the chain-folded crystals grown from the dilute phase. As a result, the extracted species can be studied by microscopy and thus their morphologies can be determined.

Morphology. The toluene-extraction technique described above proved to be of great help for investigating the various morphologies in the gel through electron microscopy. Within this framework, detailed observations have been achieved on 3_1-chain-folded crystals as entities independent of the network, on this network itself once transformed into the stable threefold helical form and on more complex morphologies where the transformed network nucleates the growth of 3_1 crystals.

(1) Nascent Gel. Observations of nascent gels between glass slides by means of phase contrast microscopy reveals a very faint "salt and pepper" structure. Since the toluene-extracted freshly formed gels give perfectly clear and homogeneous solutions, the observed structure does not arise from the clustering of tiny chain-folded crystals. This therefore suggests that this structure is the network itself.

(2) Aged Gels: Appearance of Chain-Folded Crystals. When the gels are aged for a given time (a few minutes to a few weeks depending on the solvent) at temperatures where the 12_1–3_1 transformation does not occur, one observes the formation and growth of chain-folded crystals within the dilute phase. Between crossed-polarizers these crystals show up as birefringent units and are present both in the gel and in the liquid extruded from the gel (see Figure 7) during sample preparation.

The solvent-extraction procedure enables after recovering the crystal suspension by centrifugation to isolate these crystals from the network wherein they were embedded and thereby to examine them by electron microscopy. As apparent from Figure 8 they are ill-formed, rounded platelets. Their average size is about 0.7–1 μm whatever the gelification solvent used.

(3) Transformed Gels. Observations of a transformed gel by the phase-contrast method reveals as previously a "salt and pepper" structure, yet the contrast is greatly improved after transformation (see Figure 9) without noticeable alteration of the general aspect seen with non-transformed gels (i.e., under the 12_1 form). Between crossed-polarizers, a transformed gel has become birefringent (Figure 10) (note that as opposed to what is observed in Figure 7 the solution in contact does not contain any chain-folded crystals).

While after 12_1–3_1 transformation, gels are insoluble in toluene, they, however, disaggregate into "clumps" of various sizes. Thanks to this disaggregation, it has been possible to obtain thin enough gel particles to be observed by electron microscopy. The morphology is of fiberlike

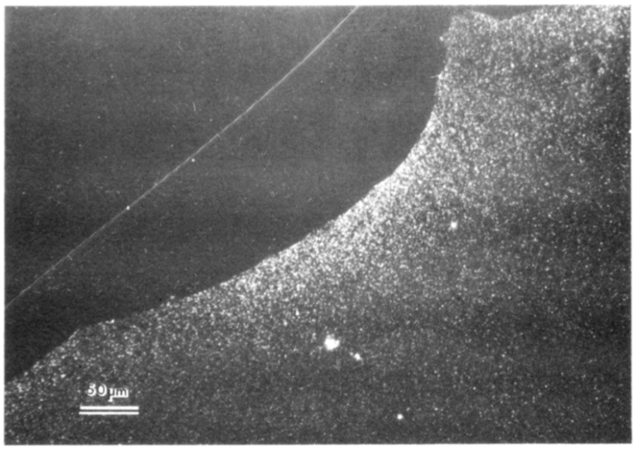

Figure 10. Optical microscopy between crossed-polarizers. Gel from diethyl malonate (quenched at 0 °C, $C = 10\%$). Annealed 5 min at 40 °C between glass slides so as to achieve the 12_1–3_1 transformation (note in the upper part the solvent released after transformation).

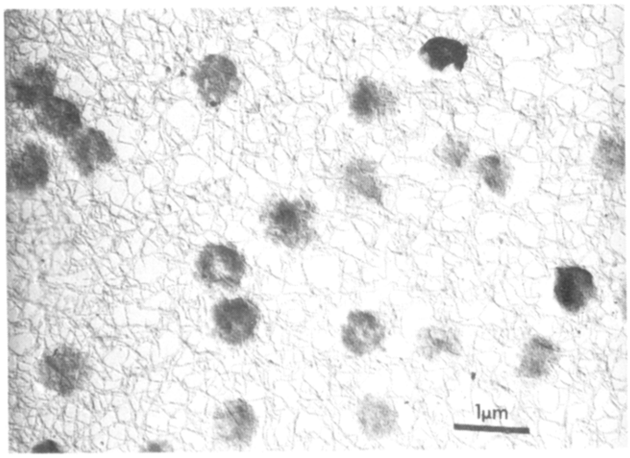

Figure 11. Electron microscopy picture of a thin gel particle obtained from a 7% gel in 1-chlorododecane (quenching temperature −5 °C, aged a week at 20 °C) after 12_1–3_1 transformation achieved at 72 °C and toluene extraction (Pt/C shadowed and C coated). Single crystals $\simeq$ 0.7 µm and threads of ~200–400-Å diameter.

nature, the fibers or threads having a diameter of approximately 200–400 Å and a mean length between contact points of the same order of magnitude than the 3_1 crystals size (Figure 11). It is quite likely that this fiberlike structure is also present in the nontransformed gels (in the 12_1 form) and may well be responsible for the "salt and pepper" structure discovered by phase contrast.

(4) Nucleation of Single Crystals from the Partially Transformed Gel: Case of Diethyl Malonate. Gels from diethyl malonate annealed at room temperature dissolve readily in toluene. While extracted crystals from the other solvents do not exhibit particular features, those obtained from diethyl malonate are far more fascinating. Three types of structures can be distinguished (Figure 12): (i) chain-folded crystals under the threefold helical form of 0.6 µm in size similar to those observed previously (Figure 12a), (ii) fiberlike or threads entities similar to those observed in the transformed gels (Figure 12b), and (iii) small shishkebobs (Figure 12c).

Bearing in mind that gels from diethyl malonate are the less stable under the 12_1 helical form, the existence of these morphologies can be consistently accounted for. As previously, the independent chain-folded crystals come from crystallization within the dilute phase before 12_1–3_1 transformation sets in. Similarly, the threads arise from the transformation after the previous growth process has completed. The intermediate situation between these two morphologies leads to the shish kebob structure which arises most probably from partly transformed threads into the 3_1 form that nucleate the overgrowth of folded-chains lamellae. The gels when extracted with toluene were apparently far from being totally transformed into the 3_1 form, hence the possibility of observing the morphologies of Figure 12.

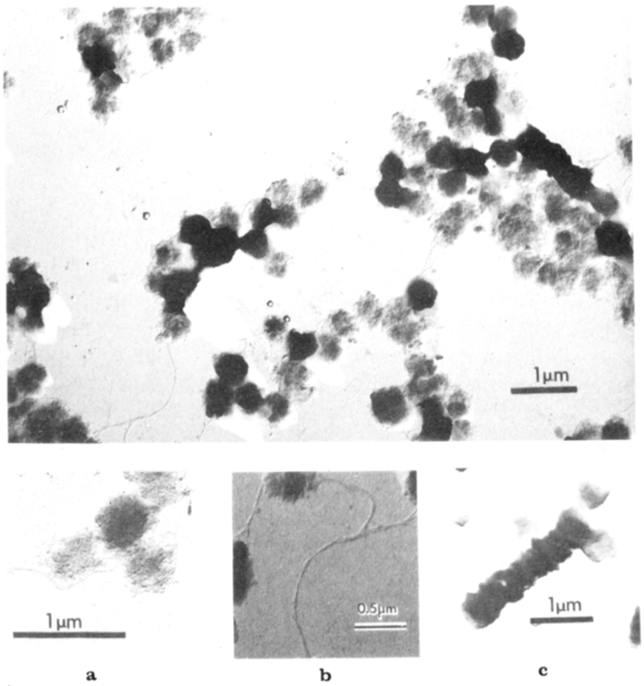

Figure 12. Electron microscopy picture of the material toluene-extracted from a 7% gel in diethyl malonate aged 2 weeks at room temperature. Enlarged portions show (a) flat crystals (chain-folded crystals), (b) threads, and (c) shish kebobs.

Discussion

The various phenomena described above have been purposefully not discussed hitherto since the knowledge of one result (morphology for instance) is mostly required to understand and to explain another one.

In the first place, the origins of the turbid–clear transition as well as the 12_1–3_1 transformation will be examined in the light of the sofar propounded mechanisms and concepts. Then, the network morphology displaying threads will be compared to other morphologies encountered in physical gels produced from other polymers. Finally, the reasons why a gel is clear, translucent, turbid, or opaque will be tentatively given.

(1) Origin of the Turbid–Clear Transition. The procedure used to prepare the gels studied in this paper leads up to the following comments:

(i) As the solutions have been quenched well below Θ, the system has undergone gelation within the miscibility gap.

(ii) Thermodynamic considerations entail that, under such circumstances, phase separation must definitely occur prior to any crystallization process[19] provided the solution has reached the demixtion area unaltered (absence of chain-folded growth, a condition fulfilled in our gels).

As a consequence, gels investigated here have been obtained through the mechanism of phase separation prior to crystallization.

The reversibility of this turbid–clear transition (within 1 °C) and its reproducibility (at least in decalin and 1-chlorodecane) rather suggest that an additional phase separation phenomenon is occurring as opposed to a crystallization. [Concerning *cis*-decalin, the transition occurs slightly above Θ determined for atactic polystyrene. It is however quite possible that the Θ-temperature and correspondingly the position of the cloud-point curve is altered by a few degrees due to higher stereoregularity of isotactic polystyrene.[20]] In addition, DSC experiments do not show any peak at the transition temperature. Inspection of Figure 2 and particularly of the transition temperatures shows a close correlation with the Θ-temperature reported for atactic polystyrene in these solvents. In most cases, they are located below Θ which may thereby relate this transition to the crossing of the cloud-point curve where liquid–liquid phase separation through nucleation and growth occurs. As soon as gelation has set in, the only species that are capable of undergoing phase separation are the chains that failed to incorporate into the network and therefore are independent and mobile (the dilute phase). Morphological evidence demonstrates the existence of such chains through their ability to form chain-folded crystals independent of the network. As a result, a plausible explanation for the turbid–clear transition would be provided by invoking a secondary phase separation taking place within the dilute phase, the primary one being the gel formation itself.

(2) 12_1–3_1 Transformation. Experimental results reported here clearly show that the 12_1 helical form displays a degree of stability which depends upon the solvent and can perturb the measurement of the turbid–clear transition temperature. In decalin, this conformation seems to be completely stabilized (at least the thermal treatment applied did not lead to any 12_1–3_1 transformation), while in the other solvents this helical form is metastable. This means that well below its melting point the 12_1 helix can spontaneously transform into the 3_1 helix.

As phase separation entails the formation of a polymer-rich phase, which forms the network, two situations are conceivable:

(i) After phase separation the system is immediately frozen in. In such a case, molecules of solvent are trapped and confined within the concentrated phase and can thereby participate to the crystalline lattice. As a result, the degree of stability can vary with the solvent but for energetical or steric interactions.

(ii) After phase separation the system is not immediately frozen in so that molecules of solvent can escape from the crystallizing phase leading to a polymer-pure phase. As a consequence, the 12_1 helical form should exhibit the same or nearly the same degree of stability regardless of the solvent.

The results presented in this paper rather meet the conclusions of the first statement (i) and therefrom, if not demonstrating its existence, seem to be consistent with the solvation hypothesis. However, the question still pertains as to know whether the 12_1 helix definitely need be stabilized by solvent molecules so as to exist and to build up crystals or the 12_1 helix incorporates solvent on account of the peculiar gel preparation (should other exist). While our results rather support the solvated structure model (decalin being then one of the best stabilizers), further and direct experimental evidence is required.

At this point, it is worth mentioning that the coexistence of 3_1 and 12_1 helical structures has been reported on various occasions[8,11,12] for gels of iPS which were, however, dried prior to X-ray examination while the present gels are analyzed in their wet state. Under the conditions reported in the literature three types of gels were observed which have either 3_1, 12_1, or a mixture of 3_1 and 12_1 helices. It was further concluded that both species could exist in the nascent gels and that the melting of the 12_1 and crystallization of the 3_1 do not involve the same chain segments.[8] In light of the present results, it would seem that the latter conclusion is not straightforward. For instance, the drying process may well trigger the transformation from 12_1 to 3_1 helix, if the former structure stability depends on the presence of solvent and accordingly on its concentration.

(3) Consequences of iPS Gel Morphology. In papers devoted to the study of iPS gels,[2,3,6] the overall structure has always been described with a fringed-micelle model mainly on account of gel transparency. In such a model, which is reminiscent of the chemical gel structure, cross-links are achieved through tiny crystals of mean size of the order of 100 Å and the average distance between cross-links is of the same order of magnitude. Clearly, the morphologies presented in this paper lead to the dismissal of this model which was already disregarded in bulk-crystallized material.

The fiberlike nature of the network in a physical gel is not something new since similar morphologies have been already discovered in various gels of polymers such as nylon[21] and PLGB.[22] As previously stressed by Tohyama and Miller,[22] such a morphology seems to arise from the consequences of a phase separation maybe through spinodal decomposition, frozen in by crystallization. The results reported here on gels prepared by this mechanism support their conclusions.

Finally, the similitudes of morphologies encountered in so different polymers (iPS is a slow crystallizing polymer unlike nylon and PLGB can form liquid crystalline structures) do suggest a common mechanism of gel formation and therefore a large universality of the phenomenon.

(4) Origins of the Gel Visual Aspect and Its Relation to Morphology. The intensity with which a two-component system and particularly a mixture of polymer–solvent scatters and/or absorbs light depends on the difference in refractive index between both species. Should both indices match, such a system will appear as crystal clear even if large structures are present. For this reason, we shall not be concerned in this discussion with gels produced from a polymer and a solvent of same refractive index.

From our study, we conclude that turbidity or opaqueness originates from three different phenomena, the occurrence of which need not be simultaneous: (i) from the turbid–clear transition if the gel stands at room temperature (reversible turbidity), (ii) from the growth of chain-folded crystals (irreversible turbidity), and (iii) from the 12_1–3_1 transformation of the network (irreversible opaqueness).

It is worth emphasizing that turbidity is often associated with the presence of chain-folded crystals which may happen to be wrong (cf. the turbid–clear transition).

On the other hand for a gel to be clear or translucent, the following conditions are altogether required: (i) to stand above the turbid–clear transition, (ii) absence of chain-folded crystals, and (iii) gel under the 12_1 helical form. If one of these conditions is not fulfilled, the gel will be either turbid or opaque. For example, only gels produced from decalin and 1-chlorodecane can be clear or translucent at room temperature.

Besides, in the light of the fiberlike nature of the gel, transluscence is easily accounted for. It most probably comes both from simple scattering and from multiple scattering by the threads whose dimensions are of the order of light wavelength. Conversely, the fact that gels are clear in decalin deserves to be commented. As the scattering is proportional to Δn^2, gels from decalin scatter and absorb 2.5–3 times less than gels from the other solvents ($\Delta n \simeq 0.11$ in decalin and $\Delta n \simeq 0.16$–0.17 in the other solvents). Scattering from decalin gels, if weak, exists and is offhand comparable to that of agarose gels in water for which experiments have shown it to be consistent with the presence of large structures.[10] From this we conclude that transparency is far from being a well-grounded criterion to anticipate on the gel structure at the molecular level. Only careful light scattering experiments can be decisive.

Conclusion

In this paper, both thermodynamic properties and morphology of iPS gels have been investigated. We have shown that when the gels are prepared through phase separation prior to crystallization, a turbid–clear transition is observed the temperature at which it occurs is linked to the Θ-point. Accordingly, for solvents wherein the transition is well above 20 °C, the gel is turbid at room temperature. This phenomenon, which must not be confused with a crystallization, is thought to arise from a secondary phase separation undergone by the chains that failed to incorporate into the network during gelation.

In addition, we report the observation of a conformational transformation of the network from the 12_1 to the 3_1 helical form. This transformation is pointed out either by using very slow heating rates in DSC experiments or by annealing below the gel melting point (i.e., when still under the 12_1 form). This transition takes place together with the rising of opaqueness.

Finally, morphological investigations reveal that the iPS gels are of fiberlike nature which leads to the dismissal of the fringed-micelle model to describe the structure of such gels.

This study also enables one to discuss and elucidate the various origins of the gel visual aspect.

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Concerning Gelation Effects in Atactic Polystyrene Solutions

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ABSTRACT: Published data on gelation of atactic PS's as a function of $\bar{M}_w$ and concentration, C, in ten organic diluents with solubility parameters, $\delta_s^{1/2}$, from 7.8 to 10 have been reexamined in terms of entanglement effects, influence of $\delta_s^{1/2}$, and comparison with previously unexplored literature results on other PS–diluent systems. Three regions of gel behavior can now be defined: I, low $\bar{M}_w$, low C, no gels; II, intermediate combinations of C and $\bar{M}_w$ which lead to coil overlap, gels; III, high C and $\bar{M}_w$ giving both overlap and entanglements, supergels. T_{gel} (°C) at fixed C and $\bar{M}_w$ is strongly dependent on $\delta_s^{1/2}$, being a minimum when $\delta_s^{1/2} = \delta_p^{1/2}$: It has been demonstrated that $T_{gel} > T_g$ and that T_{gel} should not be identified with T_g except at $C < 50$–100 g/L. The sharp, thermally reversible melting of atactic PS gels at T_{gel} can be considered as a "local melting" of segment–segment contacts first postulated by Lobanov and Frenkel to explain $T > T_g$ relaxations. T_{gel} should be a phenomenon general to all atactic polymers. For PS one can write the numerical identity valid for comparable values of C: T_{gel}, °C ($C \geq 130$ g/L) $\equiv T_f > T_g$ (T_f being the "fusion-flow" temperature of Ueberreiter; $\equiv T_{ll} > T_g$ of Gillham and co-workers). The designation "T_{gel}" appears very appropriate for gelation phenomena of the type being discussed and should be retained.

Introduction

Gelation phenomena in solutions of isotactic PS at concentrations greater than 3–5% have been discussed in detail by Girolamo et al.[1] A number of perplexing results not germane to the present study were reported. However, the closing paragraphs discuss pertinent observations about interactions between isotactic and atactic PS's present in a common solvent. Each polymer species seems aware of and reacts to the presence of the other in a manner not then understood. The authors concluded[1] that these exploratory results are likely to have a bearing on the structure and properties of amorphous PS. This prediction

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