It should be kept in mind that a hexagonal array made of up-and-down chains implies both parallel and antiparallel interactions between neighbors. The approach used here for the modeling analysis rests on the assumption that up-and-down chains are localized at random in the crystal. This is in agreement with the symmetry exhibited by the single-crystal electron diffraction pattern. Although adjacent reentry of an individual molecule will generate an alternating antiparallel row of about 10 stems, the existence of such short-range arrangements should not modify substantially the statistical model.

An orthorhombic lattice (with triclinic symmetry) would arise, on the other hand, if a long-range regular arrangement of up-and-down chains were adopted. However, no signs of symmetry other than hexagonal were detected in the electron diffraction patterns.

The triangular crystalline habit displayed by this polymer is a feature which has allowed us to decide between $p31m$ and $p3m1$ packing models. A similar reasoning could be applied to poly(glycyl-β-alanyl-β-alanine), a polymer crystallizing in triangular lamellae highly resemblant to those described here. It is not, however, the case for other polymers with polyglycine II structure. Thus, nylon 2/6, nylon 1-3, and polyglycine itself crystallize as hexagons so that no clear conclusions about chain conformation can be drawn from the crystal habit in these cases.

The results of our modeling analysis confirm the 3-fold helical conformation for the poly(glycyl-β-alanine) chain. The prediction that the glycyl residue is arranged as in polyglycine II and that a gauche conformation is imposed on the methylene pair of the β-alanyl unit is also corroborated. A planar group $p31m$ is proposed for the packing of the 3-fold helices. The three 2-fold axes normal to the helix which are required by the group symmetry are created by superimposing two lattices made of helices pointing to opposite directions (Figure 7c). This is in fact a pseudocrystal having, on the average, the symmetry of space group $P3_121$.

Model building has been carried out assuming right-handed helices, but a left-handed model should be equally valid as no asymmetric carbon exists in the molecule. However, the helix sense must be kept the same within a given crystallite in order to enable the formation of all hydrogen bonds.

Finally we would like to remark that the building procedure mainly relies on stereochemical and symmetry considerations and only a qualitative evaluation of diagrams has been taken into account. No refinement against diffraction data was undertaken. Nevertheless, conclusions drawn from this study suffice to justify the adequacy of the proposed model.

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Isotactic Polystyrene Phase Diagrams and Physical Gelation

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ABSTRACT: A partial phase diagram was determined for fully isotactic polystyrene of molecular weight 160 000 in nitrobenzene, iPS/NB. Three distinct ways were found in which phase separation occurred; each mode of phase separation was accompanied by a unique gelation process. In region I iPS crystallized from solution, in region II super-cooled iPS solutions underwent a liquid-phase separation followed by iPS crystallization, and in region III the solvent, NB, froze. In both regions I and II gels formed only after phase separation. In region III a gel would form if NB was allowed to thaw. Hence, gels could be formed in three distinct ways. All the modes of gelation resulted in supermolecular structures which were determined by the kineics of phase separation. Subsets of the three mechanism were found operative with other solvents for iPS.

Introduction

Although the gelation of isotactic polystyrene (iPS) solutions has been studied for a long time,[1] little, if any work has been done to determine the phase diagrams of these solutions. This is surprising because a variety of gelation mechanisms have been put forth, all of which are related to different types of phase separation. Hence, knowledge of the phase diagram would help to elucidate the various

mechanisms that have been proposed. These mechanisms include fringed micellar crystallization,[2] liquid–liquid phase separation,[3] and even a stable thermodynamic phase for the gel.[4]

The gelation of other semicrystalline polymers has been studied and mechanisms proposed for the observed phenomena. The gelation of poly(4-methyl-1-pentene) by linking of growing spherulites[5] has been described.

Spherulitic crystal growth of iPS has long been known,[2] but little attention has previously been paid to the formation of gels through this mechanism. We will show that for some solvents, such as NB, gelation of iPS by this mechanism is possible but extremely slow. However, for other solvents, such as 1-chlorodecane, the kinetics of gelation by this mechanism are comparable to the more commonly studied gelation occurring at greater supercoolings. Much more attention has been paid to iPS gelation at these greater supercoolings where gelation is almost instantaneous. A variety of semicrystalline polymers can be made to liquid phase separate which results in gel formation. This has been described for poly(4-methyl-1-pentene),[6] for vinyl polymers,[7] and for others. This has also been suggested as the mechanism of gelation of iPS at large supercoolings.[3]

In this paper we will describe our observations of the gelation of iPS in NB (and to a smaller extent in other solvents) as a function of the iPS concentration, the temperature of gelation, and the rate of cooling.[8] In particular, we will describe the sharp and reproducible boundaries separating the various modes of gelation, which we interpret as phase boundaries. We will show the supermolecular structures obtained from each mode of gelation and the similarity of these to the kinetically imposed supermolecular structures obtained from nongeling, but phase-separated, solutions of atactic polystyrene.

Experimental Section

Isotactic polystyrenes of various molecular weights were obtained from Pressure Chemical Co. (Pittsburgh, PA). Weight-average molecular weights were determined for two lots by low-angle light scattering in *cis*-Decalin and found to be 1.6×10^5 and 1.68×10^6. Isotactic content was determined by ^{13}C NMR and found to be at least 95% with an estimated accuracy of ±5%. No atactic component could be detected. Reagent grade NB, or other solvent, was used as received from Aldrich Chemical Co. (Milwaukee, WI). Differential scanning calorimetry (DSC) measurements were done on a Perkin-Elmer DSC Model II. Solutions were prepared by dissolving iPS at 175 °C. Hot solutions were poured into prewarmed glass bottles that were then cooled quickly to the gelation temperature. Gelation was usually accomplished in a temperature-controlled water bath which was regulated to within 0.5 °C. Gels were dried by extraction of NB with liquid carbon dioxide in a high-pressure Soxhlet extractor (J&W Scientific, Cordova, CA). After extraction, carbon dioxide was removed from the gels by taking it above the critical temperature, 40 °C, and bleeding off the pressure. iPS of the molecular weights used had no solubility in carbon dioxide. By carefully extracting the solvent from the gels in the manner described, it was possible to prepare dry gels which had a volume almost the same as the wet gels. This gave us confidence that the large-scale structure, supermolecular structure, in the dry gel was similar to that in the wet gel. Dried gels were characterized by their density, BET surface area, differential scanning calorimetry (DSC), and their supermolecular structure which was determined by scanning electron microscopy (SEM) of broken surfaces of the dried gels.

Discussion of Results

A partial phase diagram for iPS of weight-average molecular weight 1.6×10^5 in nitrobenzene is shown in Figure 1. The phase diagram was determined in the following way. Solutions of iPS at various concentrations were made, and these were then made to phase separate and gel at a variety of controlled temperatures. Their behavior was observed and readily grouped into three categories. In this way the boundaries dividing these regions were ascertained. The behavior in the three regions was as follows.

In region I solutions would appear cloudly after about 3 days. The opacity would slowly increase with time, and after about 2 weeks the solution would gel. The gel point was defined as the ability of the solution to support a steel
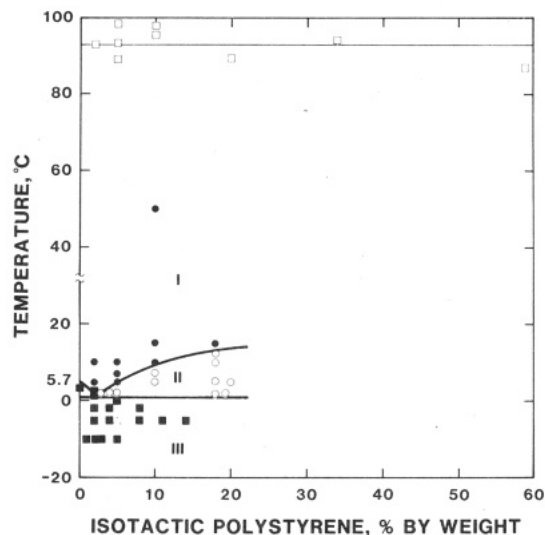

Figure 1. Phase diagram of isotactic polystyrene (weight-average molecular weight 1.6×10^5) in nitrobenzene: fast gelation followed by clouding, O; slow clouding followed by gelation, ●; atactic polystyrene cloud point (molecular weight 1.8×10^6), △; nitrobenzene freezing, ■; gel melting points by DSC, □.
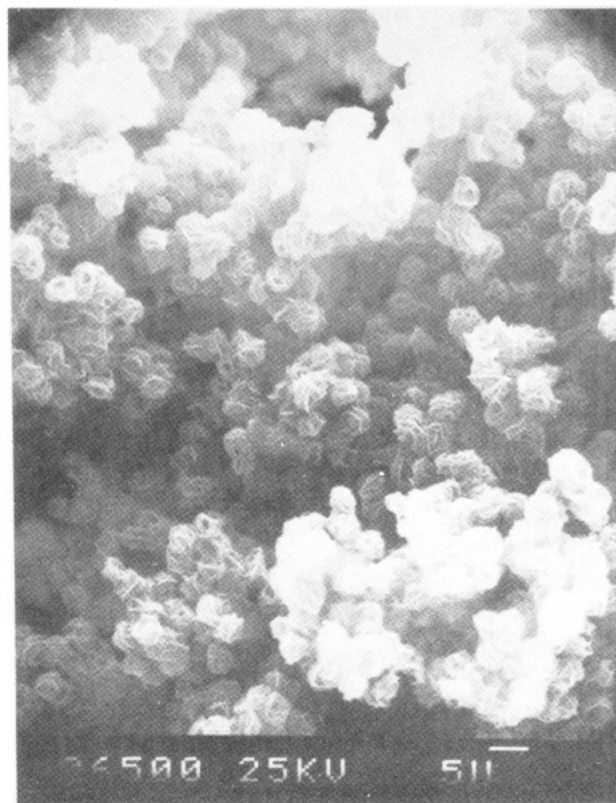

Figure 2. Scanning electron photomicrograph of the supermolecular structure of dried gels formed in region I from a 5% solution. The bar is 5 μm.

ball weighing approximately 3.5 g. Both wet and dry (solvent extracted) gels formed in region I were mechanically weak compared to those formed in region II or III. Scanning electron photomicrographs (SEM) of the dried gels, Figure 2, show that the morphology is composed of porous spheres with a diameter of approximately 4 μm. The connectedness of both the wet and dried gels arise from surface contact between the spheres, which explains the low strength observed. This type of gelation is due to crystal growth from solution as has been observed for other semicrystalline polymers.[5] The crystalline morphology has
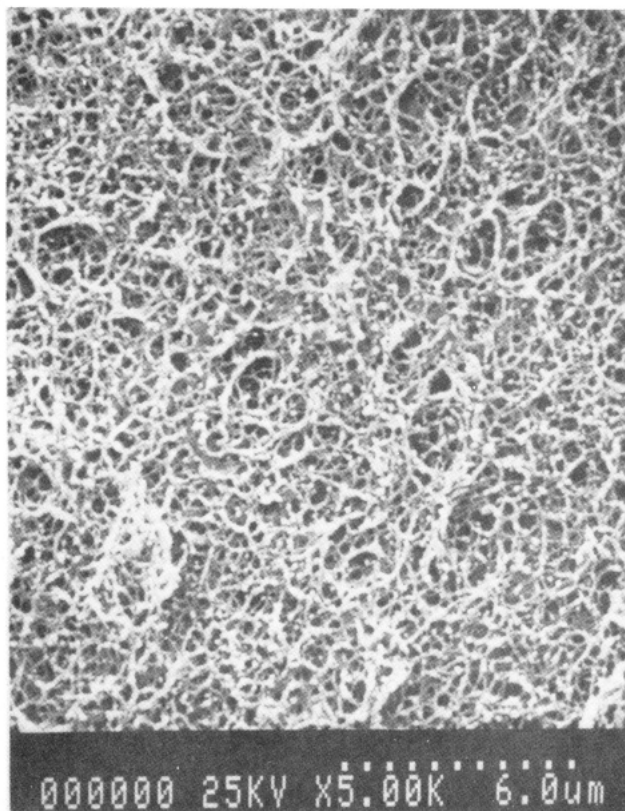
Figure 3. Scanning electron photomicrograph of the supermolecular structure of dried gels formed in region II from a 5% solution. The bar is 6 μm. The BET surface area is 238 m^2/g which corresponds to an average distance between struts of 0.15 μm.

Figure 4. Scanning electron photomicrograph at high magnification of the supermolecular structure of dried gels formed in region II. The bar is 0.05 micrometer (500 Å) which is approximately the diameter of the polymer struts. For comparison, the root-mean-square end-to-end distance of the polymer coils in solution is expected to be a few hundred angstroms.

been reported to be the 3_1 helix.[2]

If the quench is sufficiently fast to avoid crystal growth in region I and the boundary of region II is crossed, then the gelation behavior is dramatically different. Such quenches are easy to accomplish since crystal growth in region I is so slow. In region II clear gels form quickly, within about $^1/_2$ h. The clear gels then slowly cloud with a rate comparable to that in region I. Totally opaque gels result after about 2 weeks. SEM's of the dried gels show that the supermolecular structure is very different from that obtained in region I. The morphology consists of a very open strutlike network, as shown by the SEM photomicrograph in Figure 3. The BET surface area of the dry gel in Figure 3 was 238 m^2/g. The average distance between the struts of the dry gel was determined from the measured surface area to be 0.15 μm.[9] Figure 4 shows an SEM photomicrograph at higher magnification of a dried gel formed in region II. The bar marker in the photomicrograph is 0.05 μm (500 Å), which is approximately the diameter of the struts of iPS. For iPS of molecular weight 1.6×10^5, one would expect the root-mean-square end-to-end distance of the chains in solution to be around a few hundred angstroms. Hence, the strut diameter is only a couple of times the size of an individual coil in solution. This is why the specific surface area of the dry gel is so high.

The boundary between region I an II has a shape consistent with region II being a region of liquid-phase separation with an upper critical solution temperature. This has previously been suggested by Wellinghoff et al.[3] as the mechanism of gelation for iPS and by other authors for different polymers.[6,7] Evidence for this is the fact that atactic polystyrene has cloud points near the same temperature at which iPS gels form. One such cloud point is
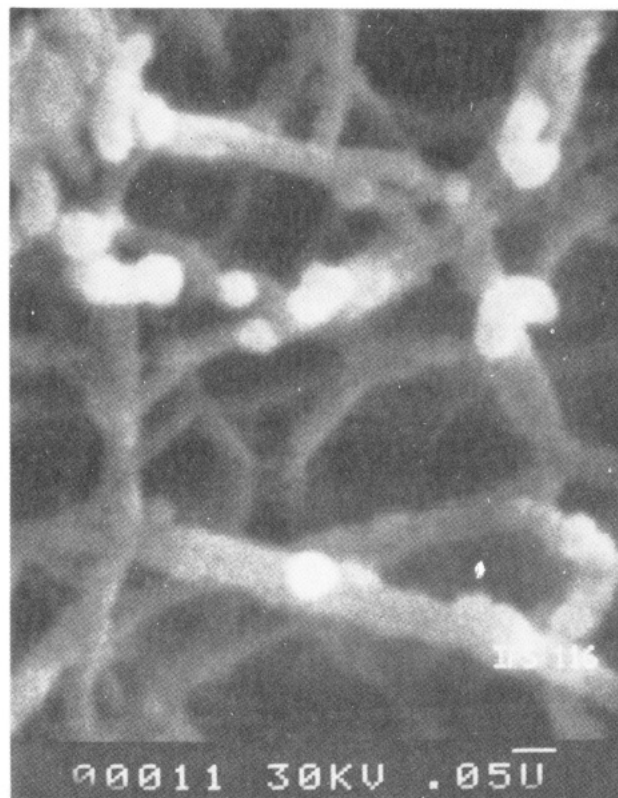
included in Figure 1. The supermolecular morphology of the gels is consistent with a spinodal process, since the resultant phases are bicontinuous.[3] If liquid-phase separation occurred by spinodal decomposition, then the continuous polymer-rich phase would be in poor solvent conditions and the coils would be collapsed. This should be an ideal precursor to crystal growth which would then rigidify or gel the network. Gelation by this mechanism has been reported to result in the formation of some 12_1 helix crystals.[2] Guenet and McKenna[10] have also argued for phase separation of iPS/*cis*-Decalin gels based upon their measurements of the concentration dependence of the compressive modulus.

In region III of the phase diagram nitrobenzene freezes. As solvent freezes, iPS is excluded from the growing solvent crystals and therefore becomes concentrated at the grain boundaries of the solvent crystals. If the solvent is allowed to thaw, then a cloudy gel results. The characteristic supermolecular structure of the dry gels is shown in the SEM photomicrograph of Figure 5. However, as discussed below, this morphology depends upon the quench rate through region I and/or region II.

The boundaries between the three regions were very sharp and reproducible if the quench was fast compared to the kinetics of phase separation. Gelation temperatures were controlled to within 0.5 °C, and any data point in the phase diagram of Figure 1 could be reproduced within this accuracy. This is evidence that the boundaries are true phase boundaries. The upper boundary of the phase diagram was determined by DSC melting points of the gels. Some representative DSC results are shown in Figure 6. The clear gels formed in region II have a small melting endotherm at about 60 °C. All cloudy gels, regardless of the region in which they were formed, have a large melting
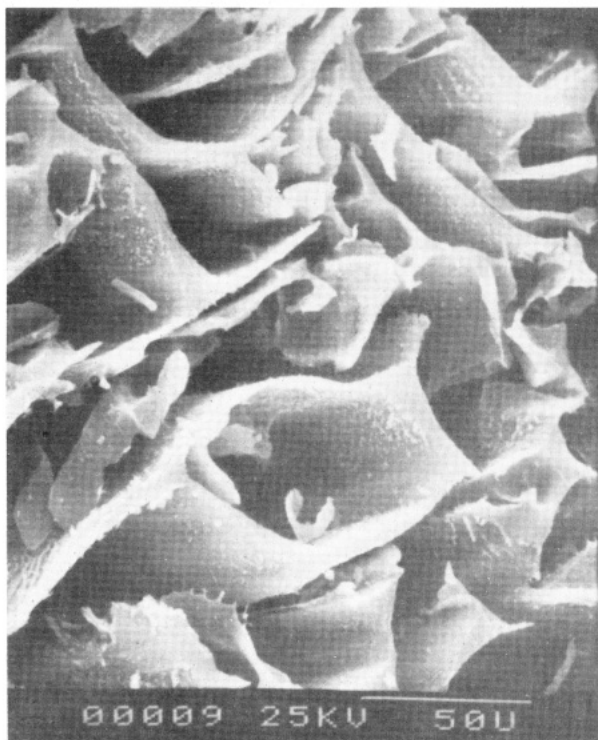
Figure 5. Scanning electron photomicrograph of the supermolecular structure of dried gels formed in region III from a 5% solution. The bar is 50 μm.
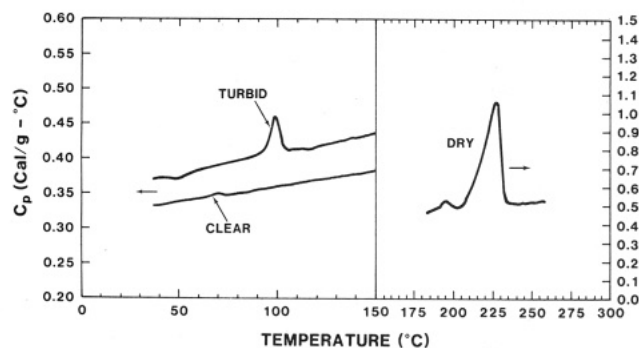

Figure 6. Representative DSC endotherms for the melting of either clear or turbid 5% gels (left) and for dry gels or dry starting polymer powder (right). Turbid gels formed in any of the three regions display the same endotherm.

endotherm at about 93 °C. No differences could be found between the melting endotherm of cloudy gels formed in the different regions. In all cases, the DSC melting endotherms corresponded to gel melting points (i.e. the gel would no longer support a steel ball). In addition, for cloudy gels, the DSC melting endotherm also occurred at the same temperature at which the gels became clear. The dry gels exhibited DSC melting points identical with the starting polymer powder. A representative example is also shown in Figure 6. The melting endotherms are quite sharp and peak at about 225 °C. Measurement of the area under the melting endotherm and comparison to that predicted for fully crystalline iPS[11] indicated that the percent crystallinity in both dry gels and starting polymer powder is about 40%.

Actually, Figure 1 represents two phase diagrams, one approximates true equilibrium between iPS solution and iPS crystals and the other represents liquid-phase separation of the super-cooled liquid. Hence, the phases that are drawn together in Figure 1 for simplicity cannot in fact

exist together. To indicate this, we have separated the two phase diagrams on the temperature axis. This must be so if one considers the phase rule. For a two-component system at a given temperature and pressure, only two phases can simultaneously exist. If polystyrene crystals are produced in region I, then at equilibrium pure crystals exist in equilibrium with an iPS solution (ideally). This solution could not undergo a further phase separation since then too many phases would exist. Hence, phase separation in region II (be it liquid-phase separation or any other type) can only occur in the super-cooled liquid in which crystal growth in region I does not occur. If the quench through region I is sufficiently slow so that crystal growth does occur, then region II gelation does not occur. The same can be said of region III gelation. If the quench through region I is sufficiently slow, then region III gelation does not occur. If the quench is adjusted, one can also obtain region II gelation even though the quench ultimately ends in region III.

These experimental observations all point to the fact that the gels are kinetically imposed structures. This must be so because if one quenches slowly in an attempt to approach equilibrium, then one always gets iPS crystal growth in region I. At equilibrium, the gelation occurring in region II, which is usually studied,[1-4] would never occur. Although iPS gels are referred to an "thermally reversible", it is clear that they are not reversible exactly in the normal sense. For example, gels formed in regions II and III can be formed at nominally 0 °C, but they must be heated to over 93 °C in order to melt them. In contrast to this are the gels formed in region I, whose formation temperature could be made to occur arbitrarily close to their melting temperature. The gel formed at 50 °C in Figure 1 melts at the same temperature as region II gels (above 93 °C). The same would hold true of gels formed in this region at even higher temperatures.

Further evidence that the gel structure is kinetically imposed comes from the similarity of the supermolecular structure to that obtained from phase-separated solutions of atactic (noncrystalline and nongeling) polystyrene. For example, if a solution of atactic polystyrene is quenched so that liquid phase separation occurs and is then quickly frozen, the solvent can be removed by freeze-drying (sublimation under vacuum), leaving behind the polystyrene in a morphological form imposed by the liquid-phase separation.[12] Figure 7 shows a scanning electron photomicrograph (SEM) of polystyrene ($M_n = 1.8 \times 10^6$) which was first dissolved in cyclohexane, quenched through the binodal, frozen, and then freeze-dried. The supermolecular morphology is identical with that obtained in isotactic polystyrene gels formed in region II. Similarly, Figure 8 shows an SEM of polystyrene ($M_n = 1.8 \times 10^6$) which was first dissolved in benzene, frozen, and then freeze-dried. In this case, no region of liquid phase separation is accessible. The supermolecular morphology is determined now by solvent freezing. The morphology is identical with that obtained in isotactic polystyrene gels formed in region III. Hence, gels formed in regions II and III have analogous phase separation phenomena occurring with atactic polystyrene with the appropriate solvents. Only gelation in region I, which relies exclusively on polystyrene crystal growth, has no analogy with atactic polystyrene. Gels have also been made in NB with iPS of molecular weight 1.68×10^6. Clear, region II gels could be quickly formed at 2 °C. These gels would remain clear for many months, however, before slowly turning cloudy. Similarly, region I gels would take many months to form because of the much slower crystallization kinetics of the

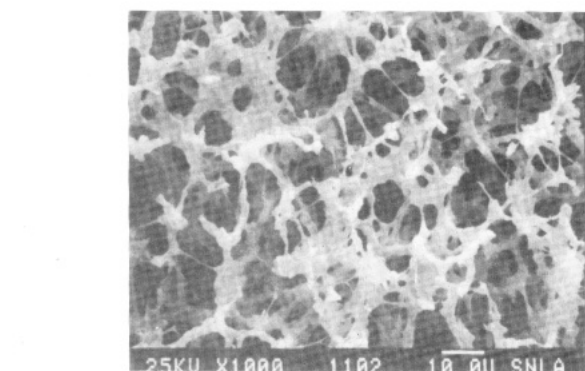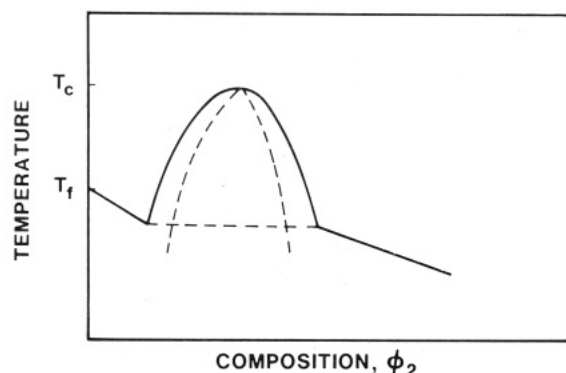## POLYSTYRENE/CYCLOHEXANE

POLYSTYRENE/BENZENE

Figure 7. Schematic of the phase diagram for atactic polystyrene ($M_n = 1.8 \times 10^6$)/cyclohexane solutions and the resulting polystyrene morphology after quenching through the binodal, freezing, and freeze-drying the cyclohexane off.
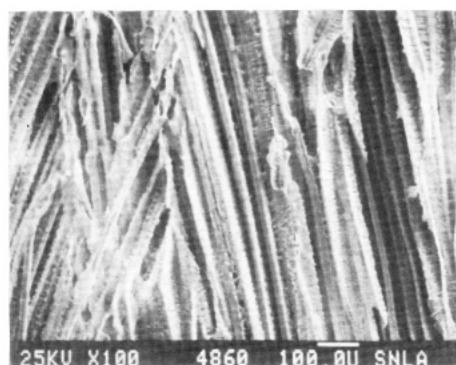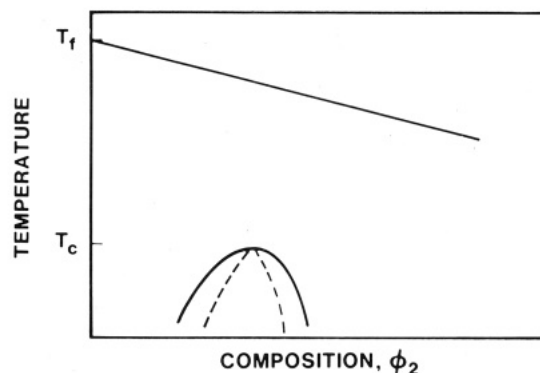
Figure 8. Schematic of the phase diagram for atactic polystyrene ($M_n = 1.8 \times 10^6$)/benzene solutions and the resulting polystyrene morphology after quenching and freezing the benzene and then freeze-drying the benzene off.

higher molecular weight iPS.

Other iPS solvents show similar behavior, although we have not investigated any others as thoroughly as NB. Gels made with 1-chlorodecane show all three types of gelation. Figure 9 shows the supermolecular structure of dried 1-chlorodecane gels formed in regions I and II. They are essentially the same as NB gels formed in the respective regions. In the case of 1-chlorodecane, however, the kinetics are more nearly the same in regions I and II. The transistion between regions I and II occurs at between 20 and 25 °C for an iPS concentration of 10% (manufacturer estimated $M = 1.33 \times 10^5$). Table I summarizes observations on a number of iPS solvents. Two of the solvents display region I gelation of iPS but at very slow time scales. Some of the solvents (acetophenone, benzonitrile, o-dichlorobenzene, 1-bromonaphthalene, 1-chloronaphthalene, 1,3-dibromobenzene, and toluene) have been previously identified as room-temperature solvents,[3] but this is clearly not the case. The discrepancy is due to the very slow crystallization rates of iPS and possibly because of the very high tacticity of the polymer used in this study or the different molecular weight. A number of the solvents, which form a precipitate or cloudy solution but do not gel iPS at room temperature, can be made to gel iPS if the solution is quenched in liquid nitrogen and then returned to room temperature (region III gelation). This variability is due to the kinetics of crystallization and is not a manifestation of any fundamental difference in the thermodynamics of the phase separation. This is again a demonstration of the kinetic nature of the gelation process. We have not investigated any iPS gels made with the solvents cis- or trans-Decalin, although we would like to apply our extraction technique to these gels. They have been investigated extensively by Guenet[13,14] and may in-

Table I
Summary of Observations on the Gelation Behavior of Isotactic Polystyrene ($M = 1.6 \times 10^5$) in Various Solvents at a Concentration of 5%

solvent	gelatn temp	qualitative kinetics	type of gelatn
toluene		insoluble	
carbon disulfide		insoluble	
o-dichloro-benzene	room[a]	solution clouds slowly no gel within 1 year	
1,3-dibromo-benzene	room	solution clouds slowly gels within 1 year	I
1-chloronaph-thalene	room	solution clouds slowly no gel within 1 year	
benzonitrile	room	a gel formed within 3 months	I
1-bromonaph-thalene	room	solution clouds slowly no gel within 1 year	
1-methylnaph-thalene	room	soluble	
acetophenone	room	precipitate formed no gel within 1 year	

[a] Room temperature was approximately 23 °C.

volve additional phenomena.

Summary

In general isotactic polystyrene gels can be formed by three distinct mechanisms. All three mechanisms have been demonstrated in the solvents nitrobenzene and 1-chlorodecane, while subsets of the three mechanisms have been demonstrated in a number of other solvents. The boundaries between the three regions are very sharp and reproducible, which is indicative of phase boundaries. In region I, gels are formed by the growth of iPS crystals and
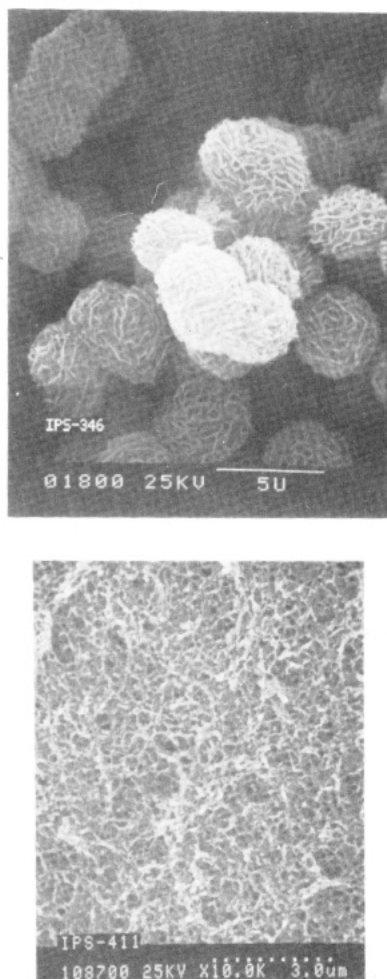
Figure 9. Scanning electron photomicrographs of the supermolecular structures of dried iPS gels formed in 1-chlorodecane (manufacturer estimated $M_w = 1.33 \times 10^5$): top is a region I gel formed at 30 °C from a 10% solution and bottom is a region II gel formed at 0 °C from a 6.7% solution.

their subsequent interlocking. In region III, gel formation is preceeded by solvent freezing which concentrates the polymer solution at the solvent grain boundaries. Region II gelation has been the most studied type of gelation but at the same time remains the most controversial.

We have shown that region II gelation can only occur if crystal growth in region I is avoided by a relatively quick super-cooling. This has been explained by using thermo-dynamic arguments concerning the number of simultaneous equilibrium phases possible. It was argued that in this region liquid-phase separation of the super-cooled liquid occurs. This was supported by the following experimental observations: (1) Atactic polystyrene has cloud points in the same temperature region. (2) Phase separation in the region occurs only in the absence of crystal growth in region I. (3) The shape of the boundary is what is expected for liquid-phase separation of a polymer solution. (4) The morphology of dried gels formed in region II is identical with that obtained in atactic polystyrene solutions that have been liquid phase separated, frozen, and finally freeze-dried. A possible mechanism of gelation in region II is liquid-phase separation followed by crystal growth in the concentrated and interconnected phase. Crystal growth in that phase would be promoted by coil collapse in the poor solvent conditions.

Registry No. iPS, 25086-18-4; NB, 98-95-3.

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