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Thermoreversible Gelation of Syndiotactic Polystyrene

Many vinyl polymers form thermoreversible gels in dilute and moderately dilute solutions.[1–6] In this type of gelation a fluid solution is converted into a rigid medium of infinite viscosity, and this process can be reversed by changing the temperature. Some type of three-dimensional network structure is formed that does not involve covalent cross-linking. The determination of the gelation mechanisms of vinyl polymers has been complicated by studies in different solvents for a given polymer with different stereostructures. Different mechanisms could be operative.[7,8] For example, the fact that the gelation of ethylene copolymers is a consequence of crystallization was established by analyzing the influence of systematic changes in the chain structure.[9] For vinyl polymers, on the other hand, only the extreme stereostructures have been studied in detail so far.

The recent synthesis of highly syndiotactic polystyrene (s-PS) by Ishihara et al.[10] has stimulated interest in its chain structure.[10–15] The highly ordered s-PS chain is found to crystallize in one of two conformations, TT or TTGG. The former is claimed to be the more stable of the two.[14] The gelation of s-PS in $CHCl_3$, CCl_4, and C_6H_6 has recently been noted,[16] and the TTGG conformation was assigned to the chain. It was proposed that the gelation of s-PS is caused by strong polymer–solvent interaction without, however, any specific study.

We report the results of detailed kinetic, thermodynamic, and phase-diagram studies of gels, and related crystalline species of s-PS in several solvents. This work is part of a more extensive study that examines the influence of stereoisomerism of the polystyrene chain on gel formation. The results for isotactic polystyrene, i-PS, and epimerized i-PS of varying tacticities, in a variety of solvents, will be reported shortly.[8]

Experimental Section. s-PS was kindly donated to us by Dr. Ishihara of Idemitsu Kosan Co., Ltd., Japan. This polymer has a M_w of 77 400 and an M_w/M_n of 1.7. Three solvents, *cis*-decalin, *trans*-decalin, and cyclohexanol, used in this work were obtained from the Aldrich Chemical Co. and were of highest grade purity. Melting temperatures of all the species were obtained with a Perkin-Elmer DSC-IIB type differential scanning calorimetry. FTIR spectra were recorded at room temperature on a Nicolet 5DBX FT spectrometer, which was capable of performing solvent subtraction. An absorbance subtraction routine was performed following the methods suggested by Painter et al. for i-PS.[17] WAXS experiments were performed with a Philips XIG 3100 diffractometer.

Results. Kinetics studies in the form of time–temperature plots for the formation of s-PS gels, and related species, were performed in the three solvents listed. When a homogeneous solution of the polymer is cooled, crystals first precipitate, followed by the formation of gel at slightly longer times. Visual methods were used to detect these species. We shall refer to this initial species as precipitated crystals and those formed at concentrations so dilute as not to form gels at any temperature as solution crystals. A typical kinetic plot is given in Figure 1 for s-PS in *trans*-decalin for the indicated polymer volume fraction, v_2. In this example, at $v_2 = 0.004$ only solution crystals form, while at $v_2 = 0.095$ both precipitates and gels form. This very unique kinetic plot is found not only with s-PS but also with isotactic and epimerized polystyrenes in a variety of solvents.[7,8] The only difference is that for the other polymers precipitate formation is not a precursor to gel formation.

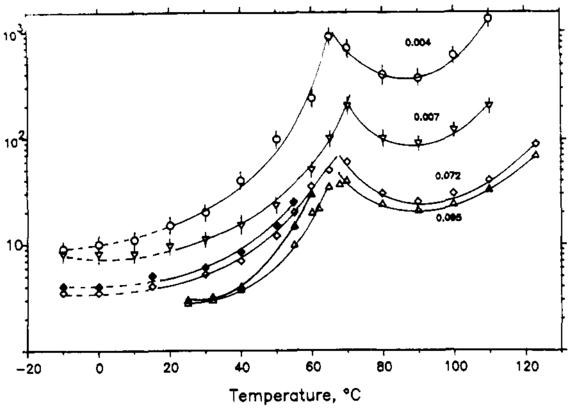

Figure 1. Time–temperature plots of the formation of s-PS gels (filled symbols), solution crystals (open symbols with bar), and precipitates (open symbols) in *trans*-decalin. Species formed inside the estimated binodial are connected by the dashed line; those formed outside are connected by the solid line.

In Figure 1, the rates of gel, solution-crystal, and precipitate formation initially increase monotonically with temperature. Eventually, in the vicinity of 60 °C, depending on the concentration, gels do not form even after long time periods. This temperature will be referred to as the critical gelation temperature, T^*. As the temperature is increased further, the rate of crystallization reaches a maximum value and a marked discontinuity is observed at about 70 °C, which results in the formation of a cusp. With a further temperature increase minima are observed at about 90 °C in the rates of both solution-crystal and precipitate formation. With the exception of cyclohexanol, only gels were observed at the low-temperature, left-hand side of the cusp. For high concentrations of cyclohexanol, $v_2 \geq 0.2$, gels were observed on both sides of the cusp.

Gel formation of all polystyrenes that have been studied always occurs in the general vicinity of liquid–liquid phase separation.[7,8] Hence, in analysis of gel formation, it is important to establish the binodial for a given polymer–solvent system. Due to the very rapid crystallization rates, liquid–liquid phase separation could not be directly observed for the s-PS in the solvents studied here. However, on the basis of other studies of i-PS, epimerized PS, and conventional a-PS, the location of the binodial curve does not change by more than 5 °C with variations in the tacticity.[7,8] Therefore, we have estimated the binodial for s-PS in *trans*-decalin to be that directly observed for a-PS in this solvent. This binodial is given in Figure 2. In Figure 1 the dashed portion of the curves indicates gelation and precipitation within the binodial. We note that there is a continuity between the homogeneous and heterogeneous regions.

In Figure 2 a great deal of thermodynamic information is condensed in what can be termed a pseudo phase diagram. In addition to the estimated binodial, T^* is plotted against v_2, as are the temperatures for the formation of precipitates and of solution crystals and their respective melting temperatures, T_m. There are several important features in this plot. Gels can be formed 40–50 °C above the estimated binodial. The melting temperatures of the gels, solution crystals, and precipitates that are formed on the left side of the cusp are comparable with one another. Similarly, the T_m's for the solution crystals and precipitates formed at the right side give a continuous curve. However, the species formed on the right side of the cusp melt 20–30 °C higher than those formed on the left side. These results strongly suggest that the different forms, i.e., precipitates, gels, and solution crystals, have the same T_m

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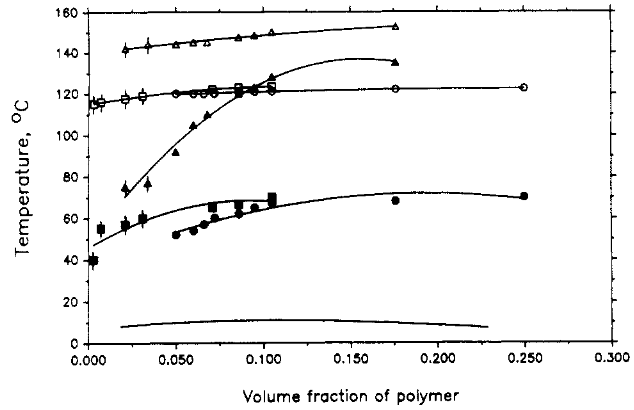

Figure 2. Pseudo phase diagram of s-PS gels, solution crystals, and precipitates in *trans*-decalin: (●,○) T^* and T_m of gels; (■,□) precipitation and melting temperatures for species prepared on the left side of the cusp and (▲,△) prepared on the right side of the cusp; solution crystal formation and the melting temperatures (⧯,⧮) when prepared on the left side of the cusp and (⯅,△) when prepared on the right side of the cusp. The solid curve without symbols represents the estimated binodial curve (see text).

in each temperature region. A similar relation between the different structures was also found in a previous report for linear polyethylene.[9] However, the difference in melting temperatures for the species on either side of the cusp suggests that different structures are formed (cf. seq.). This conclusion is further supported by the fact that the T_m's of dried gels, solution crystals, and precipitates prepared on the left side of the cusp in the decalins are in the range 180–190 °C as compared with 260 °C for the dry species formed on the right side of the cusp.

A similar pseudo phase diagram and related thermodynamic properties of s-PS gels, solution crystals, and precipitates were also observed in *cis*-decalin. However, the diagram for cyclohexanol is different. For example, within the left side of the cusp, the T_m's observed for the gels prepared below 60 °C, for all concentrations, are about 20 °C lower than those observed for the gels prepared above this temperature. The gels formed at the lower temperature give two endotherms, one at about 120 °C and the other at about 135 °C. On the other hand, the T_m's observed for gels prepared at temperatures above 60 °C, but still in the left side of the cusp, give only one melting peak at about 135 °C. This temperature is comparable to those for precipitates and solution crystals prepared on the right side of the cusp. These gave only one melting peak. All the solution crystals and precipitates prepared on either side of the cusp gave the same T_m values. Starting with an independently prepared low melting form, it was shown by kinetic studies that this form initially develops at all temperatures on the left side of the cusp but transforms to the high-temperature form with time. The rate of this transformation is temperature dependent and is very rapid above 60 °C so that only the high-temperature form is observed within the time scale of the experiments.[7,8] The T_m's observed on either side of the cusp for dried species, initially prepared in cyclohexanol, are about 260 °C. This T_m corresponds to that of the bulk-crystallized s-PS. Hence, in contrast to the decalins, where the low-temperature form is preserved on drying, a transformation occurs in cyclohexanol.

The kinetic studies and pseudo phase diagrams were used as a guide to analyze FTIR spectra and wide-angle X-ray patterns to understand the basis for the two different melting forms. A typical set of solvent-subtracted FTIR spectra of s-PS in *trans*-decalin are given in Figure 3. The FTIR spectra of gels and precipitates that were prepared on the left side of the cusp (Figure 3a,b) show significant differences from either the precipitates prepared on the right side (Figure 3c) or the bulk-crystallized samples (Figure 3d). The FTIR spectra of the samples prepared on the left side of the cusp are characterized by bands at 1378, 1353, 1332, 1319, 1276, 1168, 932, and 907 cm^{-1}. Those prepared on the right side of the cusp are characterized by the bands at 1374, 1350, 1336, 1278, 1092, 911, and 905 cm^{-1}. The latter are the same as those observed for the melt-crystallized s-PS. Identical spectra were obtained with samples prepared in *cis*-decalin. Satisfactory solvent-subtraction spectra could not be obtained with cyclohexanol because of the strong interaction between solvent and polymer.

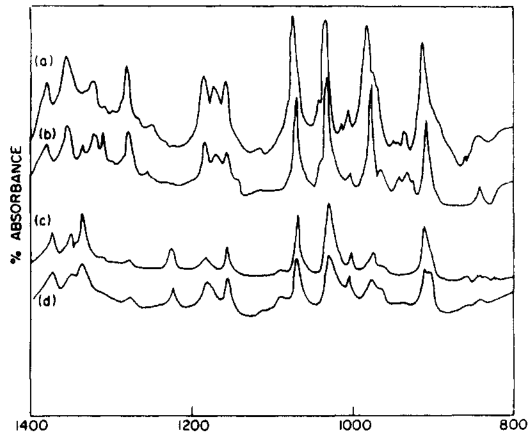

Figure 3. Solvent-subtracted FTIR spectra of s-PS in *trans*-decalin: (a) gel prepared at 35 °C, υ_2 = 0.05; (b) precipitate prepared at 50 °C, υ_2 = 0.045; (c) precipitate prepared at 90 °C, υ_2 = 0.045; (d) bulk-crystallized (T_c = 160 °C) s-PS film.

Table I
Bragg Spacings (Å) for Dried Gels, Precipitates, and Solution Crystals of s-PS[a,b]

1[c]	2[d]	3[e]	4[f]	5[g]	6[h]	7[i]
13.9 (m)						13.9 (m)
			12.0 (m)	12.0 (m)	12.0 (m)	
			8.8 (s)	8.8 (s)	8.9 (s)	
8.4 (m)						8.4 (m)
7.5 (s)	7.5 (s)	7.5 (s)				7.5 (vs)
6.4 (s)	6.5 (m)	6.5 (m)				
5.7 (vw)	5.6 (m)	5.6 (w)				5.6 (w)
			5.4 (s)	5.4 (vs)	5.4 (s)	
4.7 (s)	4.6 (vs)	4.7 (w)	4.6 (s)	4.6 (s)	4.6 (s)	4.6 (s)
4.3 (w)	4.3 (vs)					4.3 (s)
3.7 (w)			3.8 (s)	3.8 (s)		3.7 (w)
2.5 (w)	2.4 (w)					2.5 (w)

[a] vs = very strong, s = strong, m = medium, w = weak, vw = very weak. [b] WAXS results identical with those given in column 7 were obtained for dry gels, solution crystals, and precipitates of s-PS/cyclohexanol prepared on the right side of the cusp. [c] s-PS film melt crystallized at T_c = 160 °C. [d] Precipitate (υ_2 = 0.045) at 90 °C (right side of cusp) in *trans*-decalin. [e] Solution crystal (υ_2 = 0.016) in *trans*-decalin at 93 °C (right side of cusp). [f] Gel at 30 °C (left side of cusp) in *trans*-decalin (υ_2 = 0.045). [g] Gel in *cis*-decalin at 32 °C (left side of cusp) (υ_2 = 0.05). [h] Solution crystal in *cis*-decalin (υ_2 = 0.016) at 43 °C (left side of cusp). [i] s-PS/cyclohexanol gels (60 °C, υ_2 = 0.11), solution crystals (48 °C, υ_2 = 0.025), and precipitates (80 °C, υ_2 = 0.09) prepared on left side of the cusp.

The characteristic Bragg spacings obtained for gels, precipitates, and solution crystals, dried from each of the solvents studied, are listed in Table I. The spacings observed after crystallization from the pure melt are given in the first column and serve as a reference for the other results. We shall term this the normal structure as it corresponds to the high-melting form. We note that the Bragg spacings found for either solution crystals, precipitates, or gels are always the same. What distinguishes the results from one another is the solvent used and the point in Figure 1 from which the sample is prepared. The spacings for the species prepared on the right side of the cusp for the decalins (columns 2 and 3) are in very good agreement with the bulk-crystallized reference. However, the dried species prepared on the left side of the cusp from the decalins (columns 4–6) are uniquely characterized by strong and medium spacings at 12.0, 8.8, and 5.4 Å. These spacings are absent from the species prepared on the right side of the cusp and the reference. Clearly a different crystal structure is formed by crystallization from the decalins on the left side of the cusp irrespective of the particular species formed. The spacings obtained for cyclohexanol are given in the last column of the table, and all the species give the same results irrespective of on which side of the cusp they are formed. We have previously pointed out from DSC studies that the lower melting form prepared from cyclohexanol on the left side of the cusp (less than 60 °C) is rapidly transformed upon drying.

Discussion. The DSC, FTIR, and WAXS studies show that irrespective of whether solution crystals, precipitates, or gels are formed the same chain conformation, crystal structure, and thermodynamic stability are observed. However, with the decalins there is a distinct difference in these structural and thermodynamic properties, depending on whether the samples are prepared on the right or left side of the cusp in Figure 1. One of two crystal structures can be formed, depending on the temperature and concentration for crystallization (precipitation). A polymorph, whose melting temperature is about 30 °C lower than the more stable form, is developed in the left side of the cusp. WAXS results reported by Vittoria et al.[12] for nonstretched s-PS glass cast films treated with dichloromethane agree well with those observed here for the low-melting polymorph. Reynolds et al.[13] reported significantly different FTIR results between an extruded fiber and solution-cast film of s-PS in chloroform in the 500–1400-cm^{-1} region. Although our FTIR experiments were limited to the 800–1400-cm^{-1} region, they agree well with those in the 800–1400-cm^{-1} region. Kobayashi et al.[16] reported FTIR spectra for s-PS gels prepared in $CHCl_3$. Their results are identical with those reported here for all three species that form on the left side of the cusp. The results reported here make clear that the formation of a lower melting polymorph relative to the high-melting form is crucially dependent on the initial polymer concentration and temperature. In the solvents studied so far the low-temperature polymorph of s-PS always accompanies gelation. However, this result may not be general, as evidenced by the results with i-PS.[7] This crystalline form is not unique to gels, as it is also found in precipitates and solution crystals. Depending on the specific solvent, the rate of transformation to the more stable form can be very rapid.

The thermoreversible gelation of s-PS is due to a crystallization process, as evidenced by the identity of the FTIR and WAXS results of the gels as compared with those of solution crystals. The concurrence of gel melting with a melting endotherm supports this conclusion. Gelation can take place about 40 °C above the binodial, and there is no difference in the thermodynamic properties of the gels prepared inside or outside the binodial. Therefore, gelation due to liquid–liquid phase separation is not an acceptable mechanism for this polymer–solvent system.

The kinetics observed on the right side of the cusp, where the high-melting polymorph is always formed, are those expected for the crystallization of polymer–diluent mixtures. This type of kinetic behavior has been described previously by Boon and Azcue for the crystallization of i-PS-diluent mixtures.[18] At high-crystallization temperatures, nucleation processes dominate and the crystallization rate is slow. However, as the undercooling is increased, the nucleation rate increases and is reflected in turn in the crystallization rate. As the glass temperature is approached, however, the transport term in the crystallization rate dominates and the temperature becomes retarded once again. The minimum in the rate results from the competition between the nucleation and transport processes. Both the melting and glass temperatures are affected by dilution, and the crystallization rate is altered accordingly.[18] In the vicinity of the temperature of the cusp, the time required for crystallization of the more stable polymorph increases very rapidly. Consequently, the crystallization of this polymorph ceases. The lower melting form then appears, for apparently kinetic reasons, as the temperature is lowered. A very definite discontinuity in the crystallization rate develops with the change in crystal structure. To the left side of the cusp temperature, either solution crystals or precipitates form initially. However, when for a given concentration the crystallization temperature approaches T^*, gelation occurs.

We conclude that the crystallization of s-PS from solution is similar to that of i-PS[7,8] and follows a very unique type of kinetics. The lower melting polymorph is always formed on the left side of the cusp, and its observation in gels is a natural consequence of crystallization kinetics.

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References and Notes

(1) Lemstra, P. J.; Challa, G. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1809.
(2) Atkins, E. D. T.; Isaac, D. H.; Keller, A.; Miyasaka, K. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 211.
(3) Tanigami, T.; Suzuki, H.; Yamaura, K.; Matsuzawa, S. *Macromolecules* **1985**, *18*, 2595.
(4) Berghams, H.; Donkers, A.; Frenay, L.; Stoks, W.; De Schryver, F. E.; Moldenaers, P.; Menis, J. *Polymer* **1987**, *28*, 97.
(5) Francois, J.; Gan, J. Y. S.; Guenet, J. M. *Macromolecules* **1986**, *19*, 2755.
(6) Nunes, S. P.; Wolf, B. A. *Macromolecules* **1987**, *29*, 1952.
(7) Prasad, A. Ph.D. Dissertation, The Florida State University, 1989.
(8) Prasad, A.; Mandelkern, L., to be submitted for publication.
(9) Domszy, R.; Alamo, R.; Mandelkern, L. *Macromolecules* **1986**, *19*, 310.
(10) Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356.
(11) Kobayashi, M.; Nakaoki, T.; Uoi, M. *Polym. Prepr. Jpn.* **1989**, *37*, 1187 and 1189.
(12) Vittoria, V.; de Candia, F.; Iannelli, P.; Immirzi, A. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 765.
(13) Reynolds, N. M.; Savage, J. D.; Hsu, S. L. *Macromolecules* **1989**, *22*, 2869.
(14) Doherty, D. C.; Hopfinger, A. J. *Macromolecules* **1989**, *22*, 2472.
(15) Guerra, G.; Vitagliano, V. M.; DeRosa, C.; Petraccone, V.; Corradini, P. *Macromolecules* **1990**, *232*, 1539.
(16) Kobayashi, M.; Nakaoki, T.; Ishihara, N. *Macromolecules* **1990**, *23*, 78.
(17) Painter, P. C.; Kessler, R. E.; Snyder, R. W. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 723.
(18) Boon, J.; Azcue, J. M. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 885.
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