Thermoreversible Gelation of Isotactic Polystyrene: Thermodynamics and Phase Diagrams

Jean-Michel Guenet* and Gregory B. McKenna†

Institut Charles Sadron, CNRS Université Louis Pasteur, 6 rue Boussingault, 67083 Strasbourg Cedex, France. *Received June 8, 1987; Revised Manuscript Received October 28, 1987*

ABSTRACT: The thermodynamics of thermoreversible gelation of isotactic polystyrene in *cis*-decalin, *trans*-decalin, and 1-chlorodecane was investigated by using differential scanning calorimetry. The gel formation and the gel melting were studied as a function of various parameters such as the cooling or heating rate and the polymer molecular weight. The temperature–concentration phase diagrams were established from both cooling and heating experiments. It is found that the shape of the phase diagram is the same in heating or in cooling, but that for *cis*-decalin differs from the one for *trans*-decalin. The phase diagrams correspond to various types of compound: congruently melting compound in *cis*-decalin and compound characterized by a singular point in *trans*-decalin. In addition, it is shown from optical microscopy experiments and X-ray diffraction experiments that the threefold helical form reappears beyond 50% polymer concentration in *trans*-decalin but does not in *cis*-decalin.

Introduction

Among the numerous thermoreversible synthetic polymer gels that are of current interest, those prepared from isotactic polystyrene exhibit some uncommon and unexpected types of behavior. Two aspects that are still under discussion are particularly worth mentioning.

The physical cross-links do not originate from the growth of crystals made up of 3_1 helices as is usually the case for solution or bulk-crystallized samples. On this point, there is no disagreement. Yet, according to Keller et al.,[1] gelation does arise from crystallization but under a new helical form (12_1 helix). This statement is based on the observation by X-ray diffraction on partially dried and stretched gels of a reflection at 0.51 nm that is attributed to diffraction from the 006 plane. This accordingly requires that the new form possess a sixfold symmetry. On highly stretched and solvent-extracted gels, reflections under the form of layer lines at 3.06 nm are observed that are in agreement with the pitch of the 12_1 helix.[2] However, the main criticism that can be raised against these experiments is that they are representative of the dried and stretched state but not of the nascent state. Making use of the differences in the coherent cross sections of hydrogen and deuterium, some neutron diffraction experiments were carried out on nascent gels.[3] If the polymer is deuteriated and the solvent hdyrogenated, the diffraction pattern is mainly representative of the polymer. Under these experimental conditions, it has been found[3] that the 0.51-nm reflection is absent in isotactic polystyrene/decalin gels. Accordingly, the 0.51-nm reflection is in fact probably due to the solvent. These experiments have led to the reconsideration of the existence of the 12_1 helix and also of the occurrence of crystallization. Instead, a structure reminiscent of nematiclike polymers, where the solvent would "mediate" the chain–chain interaction, has been proposed.[3]

Furthermore, the mechanical properties, i.e., the isochronal compression modulus, do not follow the norm.[4] The variation of the modulus as a function of polymer concentration does not display a power law behavior as usually observed in gels such as PVC. Rather, it varies with concentration in a way that is not smooth but exhibits "features" that are currently unexplained.

These aspects of gel behavior underline the need for a deeper understanding of these gels. The purpose of this paper is to report on thermodynamic investigations that have permitted us to establish the temperature–concentration phase diagram in *cis*-decalin and *trans*-decalin.

Experimental Section

Materials. Three samples of isotactic polystyrene (iPS) synthesized by using the Natta method[5] were used in this study (FK1, FK2, and F10). After extraction of the atactic component by the method described by Utiyama,[6] the samples FK2 and F10 were obtained from fractionation of different batches by using toluene–ethanol at 50 °C. Molecular weights and molecular weight distributions were determined from gel permeation chromatography in tetrahydrofuran at 25 °C with columns calibrated by means of atactic polystyrene standards.[7] The results are

FK1	$M_w = 3.2 \times 10^5$	$M_w/M_n \simeq 2.8$
FK2	$M_w = 7 \times 10^4$	$M_w/M_n \simeq 2.1$
F10	$M_w = 4.5 \times 10^4$	$M_w/M_n \simeq 1.4$

^{13}C NMR experiments carried out in chlorobenzene at 50 °C[7] have shown the degree of stereoregularity of these samples to be over 97% isotactic.

Three solvents from Janssen Chemicals, of high purity grade, were used without further purification: *cis*-decalin (over 99% cis), *trans*-decalin (over 99% trans), and 1-chlorodecane.

Gel Preparation. The gel samples were prepared in test tubes prior to being placed into the differential scanning calorimetry (DSC) pan. A mixture of solvent and polymer was heated to a temperature close to the solvent boiling point until homogeneous solutions were produced. These solutions were then quenched for a minimum of 20 min into a thermostatically controlled alcohol bath held at the desired temperature. Small samples of approximately 10 mg were cut from the gelled solutions and placed into DSC "volatile samples" pans and thermally processed as described below.

Experimental Setup. The thermal analysis experiments were carried out with a DSCII differential scanning calorimeter from Perkin-Elmer. The cold source was supplied by either a cryostat held at −90 °C or liquid nitrogen. Several heating and cooling cycles ranging from 1.25 to 80 °C/min were used.

The temperature scale as well as the measure of energy were calibrated with indium standards. All the data were processed by means of the Perkin-Elmer TADS system (thermal analysis data station). Both optical microscopy and X-ray diffraction were used to confirm findings made by DSC. Optical microscope pictures were taken on a Zeiss Photomicroscope II, and X-ray diffraction experiments performed on a Philips PW1009 with the Cu Kα radiation ($\lambda = 0.154$ nm) with a Ni filter as monochromator.

Determination of the temperatures at which demixing takes place was achieved by means of a turbidimeter devised by F. Debeauvais from our laboratory. Rates of 10 °C/min were used.

---

† Permanent address: Polymers Division, National Bureau of Standards, Gaithersburg, MD 20899.

0024-9297/88/2221-1752$01.50/0

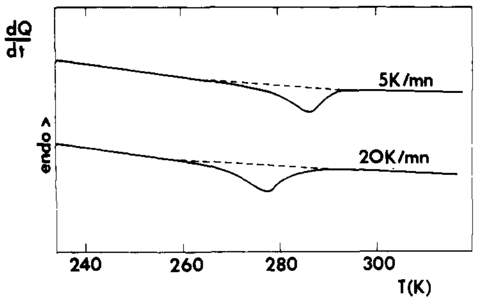

Figure 1. DSC traces obtained upon cooling 30% solutions of isotactic polystyrene in *cis*-decalin at the indicated rates.

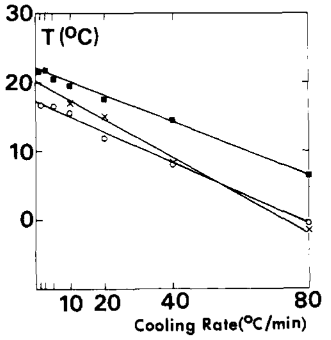

Figure 2. Gel formation onset as a function of the cooling rate: (○) *cis*-decalin; (■) *trans*-decalin; (×) 1-chlorodecane (C_{pol} = 15% w/w).

Results and Discussion

Both gel formation and gel melting were investigated. We first discuss the gel formation and give the phase diagram obtained from cooling experiments. We will subsequently present the phase diagrams obtained on heating the samples.

Gel Formation. Gel formation was studied in *cis*-decalin, *trans*-decalin, and 1-chlorodecane as a function of the cooling rate (from −80 to −1.25 °C/min). The gels, placed in "volatile sample" pans, were heated in the DSC to 170 °C and then cooled at the aforementioned rates to temperatures well below that of gelation. Typical DSC traces obtained under these conditions are drawn in Figure 1. Worth emphasizing here is the reproducibility of this type of experiment. The heating and cooling cycles can be repeated at length without significant alteration of the onset of gel formation or gel formation enthalpy.

Figure 2 depicts a plot of the gel formation onset temperature as a function of the cooling rate at a constant polymer concentration (C_{pol} = 15%). As can be seen, the onset temperature at zero cooling rate depends slightly on the solvent:

cis-decalin $T_{gel} = 17.2 \pm 0.3$ °C

trans-decalin $T_{gel} = 22 \pm 0.3$ °C

1-chlorodecane $T_{gel} = 20 \pm 0.3$ °C

For *cis*- and *trans*-decalin, the difference is similar to that observed for the Θ points as determined with atactic polystyrene ($\Theta \simeq 18$ °C in *trans*-decalin, $\Theta \simeq 12$ °C in *cis*-decalin[8]).

For 1-chlorodecane, gel formation occurs somewhat further from but still in the vicinity of the Θ point ($\Theta \simeq$ 7 °C for atactic polystyrene in this solvent[9]).

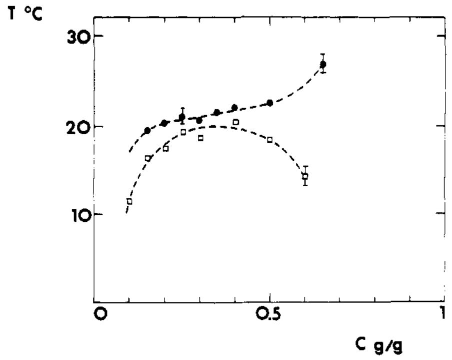

Figure 3. Onset temperature of gel formation as a function of polymer concentration: (□) *cis*-decalin; (●) *trans*-decalin. The results are obtained from DSC experiments carried out at −5 °C/min.

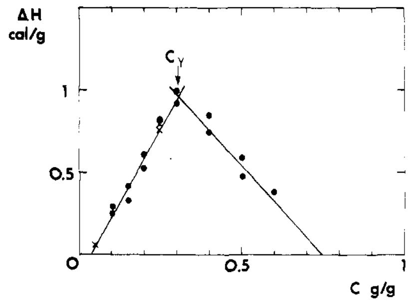

Figure 4. Gel formation enthalpy (per gram of gel) in *cis*-decalin/iPS system as a function of polymer concentration: (●) FK2; (×) FK1.

The occurrence of gelation apparently does not require a liquid–liquid phase separation since turbidity measurements locate the miscibility gap a few degrees below the gelation temperature. For instance, we obtained the following values for the onset of turbidity in FK2-*trans*-decalin solutions quenched rapidly to 50 °C and then slowly cooled at 10 °C/min T_{tur} = 12.6 °C for 15% and T_{tur} = 11 °C for 25%. Correspondingly, gelation temperatures are molecular weight independent.

As already emphasized by Girolamo et al.,[1] Wellinghoff et al.,[10] and Guenet et al.,[11] in some solvents there is a marked competition between gelation and crystallization under the threefold helical form. Such is the case in 1-chlorodecane solutions for which the growth of "3_1 crystals" manifests itself at low cooling rates under the form of an exotherm located at higher temperatures. Therefore, we did not attempt to establish phase diagrams for the iPS/1-chlorodecane gels.

For *cis*- and *trans*-decalin, the study was subsequently extended to other polymer concentrations. In Figure 3 are plotted the onset temperatures of gel formation as a function of polymer concentration. It can be seen that in *cis*-decalin the onset temperature goes through a maximum, whereas in *trans*-decalin, with the exception of a shoulder at $C_{pol} \simeq 0.4$, it increases continuously. Here, worth emphasizing is that for the iPS/*cis*-decalin gels, the gel formation phase diagram must not be confused with a coexistence curve although it exhibits a nearly identical shape.

The enthalpies involved in gel formation (gel formation enthalpy) are plotted as a function of concentration for *cis*-decalin (Figure 4) and *trans*-decalin (Figure 5). Note that gel formation enthalpies are given per gram of gel. The values measured at −20 and −5 °C/min are systematically given for the FK2 fraction. No tendency to obtain values higher at −5 °C/min than at −20 °C/min was observed, indicating little if any kinetic effect on the measured gel formation enthalpy. At higher concentrations, possible kinetic effects were assessed by using samples prepared from fraction F10. Here no marked discrepancies were observed either.

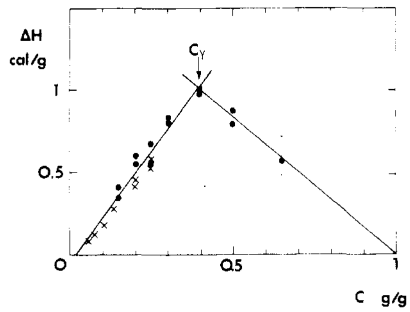

Figure 5. Gel formation enthalpy (per gram of gel) in *trans*-decalin/iPS system as a function of polymer concentration: (●) FK2; (×) FK.

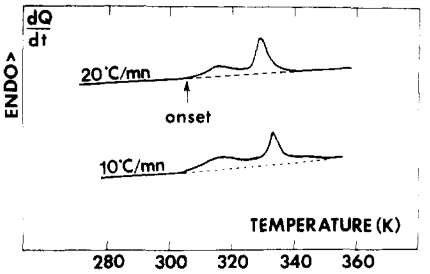

Figure 6. Typical endotherms recorded on heating a *cis*-decalin/iPS gel formed at 0 °C for 30 min; C_{pol} = 20%; heating rate 20 °C/min.

As can be seen from Figures 4 and 5, in both solvents the formation enthalpies first increase linearly to a concentration C_γ and then decrease to zero: at $C_{\mathrm{pol}} \simeq 0.75$ in *cis*-decalin and $C_{\mathrm{pol}} \simeq 1$ in *trans*-decalin. The value of C_γ is solvent dependent: $C_\gamma \simeq 0.3$ in *cis*-decalin and $C_\gamma \simeq 0.4$ in *trans*-decalin. These concentrations are virtually the same as those previously determined from solvent crystallization experiments carried out as a function of polymer concentration.[3]

Results presented in Figures 3–5 are typical when molecular compounds form[12] and have also been found with the gelling system atactic polystyrene/CS_2.[13]

Gel Melting. Phase Diagrams. A methodical investigation of the thermal behavior on heating is usually performed after subsequent treatment in the DSC. In principle, it is recommended that one melt the sample in the DSC pan and then cool it to the desired temperature prior to scanning or thermal treatment. Under these conditions, a somewhat surprising behavior is seen with these gels: whenever a gel has been melted in a hermetically sealed DSC pan and quenched to below the gelation temperature, no melting endotherm is observed on reheating in spite of the fact, described above, that a significant enthalpy of formation is detected.

Such a behavior has already been observed with PVC gels.[14] It is not clear at the moment whether something takes place in the small DSC pan that supresses the melting peak or attenuates it to such an extent that it becomes difficult to detect.

To examine the matter more deeply and try to overcome this problem, we carried out a systematic DSC investigation as a function of the heating rate on a series of gels formed in test tubes, i.e., outside the DSC. This enables one to obtain equilibrium conditions after extrapolation of the results to zero heating rate.

1. iPS/*cis*-Decalin Gels. Typical melting endotherms obtained with *cis*-decalin gels formed at 0 °C are shown in Figure 6. The endotherms are composed of two peaks, independent of the heating rate, the meaning of which will be straightforward in what follows.

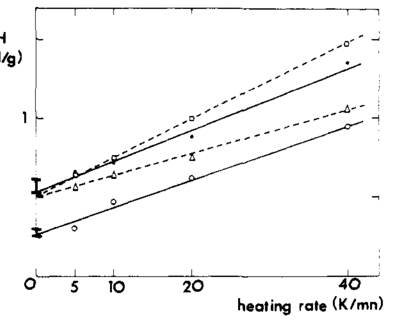

Figure 7. Melting enthalpy (per gram of gel) as a function of the heating rate for *cis*-decalin/iPS gels. Bars at 0 °C/min stand for the values found for the gel formation enthalpies for 10% and 40%, respectively: (□) FK2, 40%; (△) FK1, 40%; (●) FK2, 20%; (○) FK2, 10%.

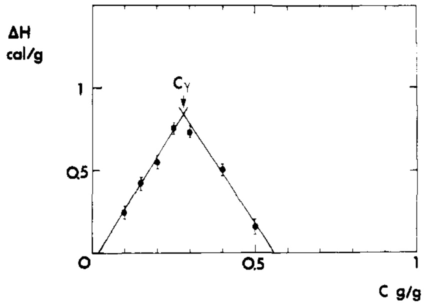

Figure 8. Melting enthalpies (per gram of gel) as determined from extrapolation to zero heating rate as a function of polymer concentration in *cis*-decalin/iPS gels.

The variation of the enthalpy associated with this endotherm as a function of the heating rate is given in Figure 7 for several polymer concentrations (enthalpies are as above given per gram of gel). As apparent from this figure, the enthalpies are heating-rate dependent. Extrapolating to zero heating rate gives finite values that are close to those found for the gel formation. Evidently, part of the measured melting enthalpy has a kinetic origin. For example, whereas the melting enthalpies for the fractions FK1 and FK2 differ considerably at 40 °C/min (1.05 cal/g for the former against 1.5 cal/g for the latter), the extrapolation to 0 °C/min yields virtually the same value. Since the FK1 fraction is of higher M_w, this suggests that the lower the viscosity of the solution resulting from gel melting, the larger the kinetic contribution to the measured enthalpy. This hypothesis receives further support when comparison is made between the slopes of ΔH versus heating rate, which are steeper for 10% and 20% than for 40%.

Gel melting enthalpies, obtained upon heating and extrapolating to 0 °C/min, are given in Figure 8. This figure is similar to Figure 4. Here, $C_\gamma \simeq 0.28$, which is in good agreement with what was found on cooling. Worth noticing, however, is that the melting enthalpy at C_γ is about 15% lower than the enthalpy determined on cooling. This discrepancy may represent the experimental error on the determination of this parameter.

The same procedure of extrapolation is used for the melting temperatures to establish the phase diagram. To construct this phase diagram, we have considered the onset of the endotherm and the position of the second peak. An alternative procedure could consist of considering the position of both peaks. As usual, the extrapolation to 0 °C/min is linear, and the temperatures obtained are reported in the temperature–concentration phase diagram of Figure 9. Two features immediately emerge from this phase diagram:

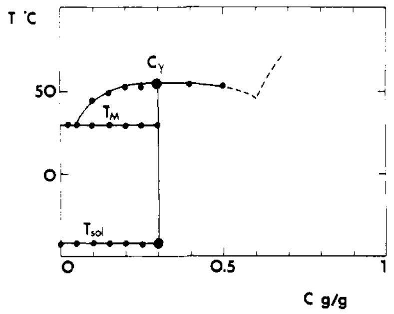

Figure 9. Temperature–concentration phase diagram (on melting) for *cis*-decalin/iPS gels prepared at 0 °C. T_M stands for the monotectic line. The monotectic concentration is located near $C_{pol} \simeq 5\%$. T_{sol} stands for the solvent melting temperature. Dotted lines represent the supposed continuation of the diagram. T_{sol} represents the solvent melting temperature as measured after the gel is formed.

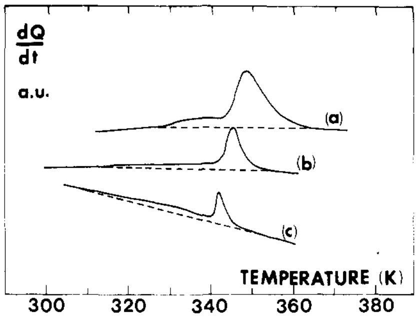

Figure 10. Typical endotherms recorded on heating at different heating rates for a *trans*-decalin/iPS gel formed at -5 °C for 30 min; $C_{pol} = 20\%$; (a) 40 °C/min; (b) 20 °C/min; (c) 10 °C/min.

(i) The onset of the melting endotherm is a constant independent of concentration (T_M in Figure 9). Thermodynamic considerations imply that this line be a monotectic line[12,15,16] (it cannot be a eutectic or a peritectic one), which arises from the effect of the liquid–liquid phase separation involved in the gelation process when the solutions are quenched to 0 °C (see for instance ref 10 or 11; monotectic transition = liquid 1 + solid → liquid 2 + solid with $C_{liquid\,1} < C_{liquid\,2}$).

(ii) The gel final melting point versus concentration exhibits a maximum in the vicinity of C_γ. Worth remembering is the similar shape found for the temperature–concentration phase diagram obtained from the cooling experiments (see Figure 3). Such a result is what is found with a congruently melting compound whose "stoichiometry" is defined at C_γ. We note that the concentration C_γ is obtained through three different ways: the maximum of the formation or melting enthalpies as a function of concentration, the maximum of the melting or the formation temperatures, and the crystallization of the solvent as a function of polymer concentration.[3]

The same type of result has already been obtained with thermoreversible gels of atactic polystyrene in carbon disulfide (CS_2) and also been interpreted as a stoichiometric compound.[13]

2. iPS/*trans*-Decalin Gels. The same type of study was carried out on gels prepared from *trans*-decalin. The results differ from those presented above.

Typical endotherms recorded at different heating rates are given in Figure 10. As can be seen, the shape of the endotherm varies with the heating rate. The main peak is more pronounced at high heating rates than at lower ones. There is thus a kind of superheating effect. At 10 °C/min the endotherm tails off over a larger range of temperatures than that observed in *cis*-decalin. Unlike gels from *cis*-decalin, it is difficult to see a first peak corresponding to the monotectic transition, although this transition is almost certainly present. The temperature–concentration phase diagram (Figure 11) does show that the extrapolated onset of the endotherm is virtually a constant as a function of polymer concentration. Due to the spread of the endotherm over a broader range of temperatures, the determination of the melting enthalpy is accordingly less precise. However, Figure 12 shows that extrapolating to zero heating rate provides values that are in agreement with those found for the cooling experiments. The spread over a broader range of temperature may indicate a significant degree of imperfection.

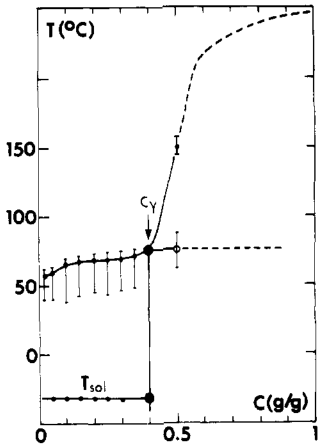

Figure 11. Temperature–concentration phase diagram (on melting) for *trans*-decalin/iPS gels prepared at -5 °C. Dotted lines represent the supposed continuation of the diagram. T_{sol} has the same meaning as in Figure 9.

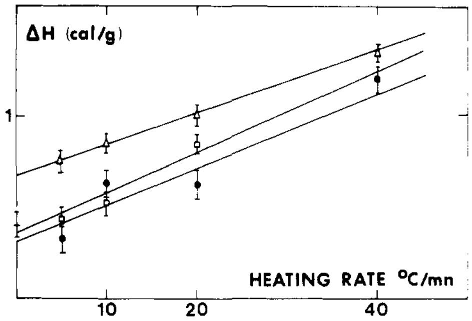

Figure 12. Melting enthalpies (per gram of gel) as a function of the heating rate for *trans*-decalin/iPS gels. Bars at zero heating rate stand for the values found for the gel formation enthalpies at respectively 15% and 20%: (△) FK2, 40%; (●) FK2, 15%; (□) FK2, 20%.

Interestingly, for $C_{pol} \simeq 50\%$, the melting point increases up to $T \simeq 150$ °C. According to phase diagram rules, the species melting at this temperature are no longer those previously obtained at lower concentrations. In other words, beyond $C_\gamma = 40\%$, two types of structures coexist. Optical microscopy indeed reveals birefringent structures in 50% gels that were absent at lower concentrations (Figure 13). From the resolution, it cannot be concluded whether lamellae or fibers are seen. An electron microscope investigation is required, which is not the purpose of this paper. The structures that melt at $T \simeq 150$ °C and are birefringent are certainly crystals constituted of 3_1 helices. To confirm this point, we carried out X-ray diffraction experiments at 20 °C on the nascent 50% samples placed in a 1-mm-diameter sealed glass capillary. Although weak, the two main reflections due to crystals containing the threefold helical form are unmistakably observed (reflections from the 110 and 220 planes). The low pro-

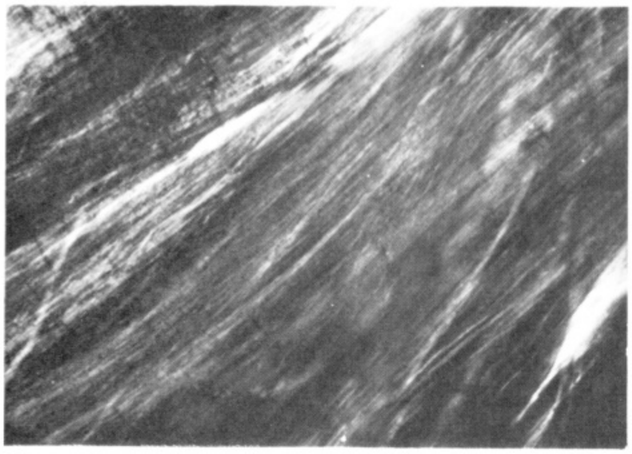

Figure 13. Optical micrographs of a 50% *trans*-decalin gel (FK2) quenched to −5 °C. The birefringent structures are either lamellae or fibers constituted of "3_1 crystals".

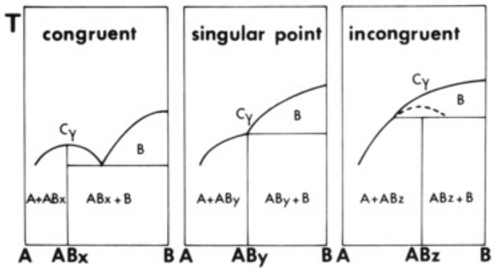

Figure 14. Theoretical temperature–concentration phase diagram for various types of compounds: (A) congruently melting compound; (B) singular point; (C) incongruently melting compound.

portion of "3_1 crystals" accounts for the low diffracted intensity.

The phase diagram of Figure 11 is similar to that obtained on cooling (see Figure 3), which indicates the consistency of the results. According to phase diagram nomenclature, the iPS/*trans*-decalin system is characterized by a singular point (see ref 12, for instance). This means, in particular, that this system is intermediate between a congruently melting compound and an incongruently melting compound (see Figure 14, where three phase diagrams corresponding to each type of compound are drawn).

Concluding Remarks

Comparison between the phase diagrams obtained either on cooling (Figure 3) or on heating (Figures 9 and 11) reveals the difference between gels from *cis*-decalin and those from *trans*-decalin. First, although the melting domain is larger in *trans*-decalin, the final melting is located at higher temperature than that of *cis*-decalin. Second and most important, the shape of each phase diagram is quite distinct, which indicates the existence of two different types of compounds.

These results, as well as previous results,[3] can be interpreted in terms of solvated structures. The fact that the threefold helical form reappears in *trans*-decalin but not in *cis*-decalin indicates that the solvent plays an important role. Since *cis*-decalin and *trans*-decalin exhibit the same thermodynamic quality toward polystyrene (χ parameters are virtually the same), the reason for such a difference must be sought elsewhere. Solvation generally conveys the idea that the solvent involved in the solvated structures is characterized by a lesser mobility. Yet, recent NMR investigations,[17] which indicate that the solvent is virtually as mobile in the gels as in the pure solvent liquid state, suggest that the solvent kinetic behavior is different from what would be expected with solvated structures.

Finally, it is worth examining the present results in the light of recent findings by Arnauts and Berghmans.[18] From investigations on atactic polystyrene/decalin solutions, these authors claim that polystyrene gelation results from solution vitrification. The liquid–liquid phase separation occurring in these systems when quenched to low temperatures leads to the formation of a concentrated phase that lies below its T_g. As a result, the solution looks like a gel but is in fact a glass. One may wonder whether this process is involved here too. The existence of a hysteresis between the formation temperatures and the melting temperatures indicate a nucleation and growth process. Such is not the case for a glass transition that is of second order. As a result, although there might be interferences between both processes when the systems are quenched to very low temperatures, the driving process remains the polymer–solvent compound formation. In addition, it is worth dwelling upon the fact that the glass transition mechanism does not necessarily hold for other atactic polystyrene–solvent systems either. It has been clearly shown by Francois, Gan, and Guenet[13] that the gelation temperature and the glass transition temperature are quite distinct in atactic polystyrene/CS_2.

Acknowledgment. G.B.McK. is indebted to the CNRS for a grant in aid during his stay at the ICS. Thanks are also due to Prof. B. Wunderlich for helpful discussions concerning the gel melting behavior.

Registry No. iPS, 25086-18-4.

References and Notes

(1) Girolamo, M.; Keller, A.; Miyasaka, K.; Overbergh, N. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 39.
(2) Atkins, E. D. T.; et al. *Colloid Polym. Sci.* **1984**, *262*, 22.
(3) Guenet, J. M. *Macromolecules* **1986**, *19*, 1961.
(4) Guenet, J. M.; McKenna, G. B. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 2499.
(5) Natta, G. *J. Polym. Sci.* **1955**, *16*, 143.
(6) Utiyama, H. *J. Phys. Chem.* **1965**, *69*, 4138.
(7) Guenet, J. M.; Gallot, Z.; Picot, C.; Benoit, H. *J. Appl. Polym. Sci.* **1977**, *21*, 2181.
(8) Berry, G. C. *J. Chem. Phys.* **1966**, *44*, 4450.
(9) Orofino, T. A.; Ciferri, A. *J. Phys. Chem.* **1964**, *68*, 3136.
(10) Wellinghoff, S. J.; Shaw, J.; Baer, E. *Macromolecules* **1979**, *12*, 932.
(11) Guenet, J. M.; Lotz, B.; Wittmann, J. C. *Macromolecules* **1985**, *18*, 420.
(12) Reisman, A. *Phase Equilibria*; Academic: New York, 1970.
(13) Francois, J.; Gan, Y. S.; Guenet, J. M. *Macromolecules* **1986**, *19*, 2755.
(14) Yang, Y. C.; Geil, P. H. *J. Macromol. Sci., Phys.* **1983**, *B22*(3), 463.
(15) Carbonel, L.; Rosso, J. C.; Ponge, C. *Bull. Soc. Chim. Fr.* **1972**, *3*, 941.
(16) He, X.; Herz, J.; Guenet, J. M. *Macromolecules* **1987**, *20*, 2003.
(17) Perez, E.; Vanderhart, D. L.; McKenna, G. B., to be submitted for publication.
(18) Arnauts, J.; Berghmans, H. *Polym. Commun.* **1987**, *28*, 66.