It should be noted that the conclusions reached in the preceding paragraph, according to which anisotropy of mobility is dependent only on the static orientation function, are results of experimental observations for the polyisoprene network. The dynamic contributions to anisotropy of mobility may not be negligibly small for other polymer systems, in general. More conclusive discussion on this subject awaits further experimental work on different polymeric systems.

Conclusions

Comparison of the predictions of the theory with experimental data on mean mobility and anisotropy of mobility shows the following. (i) The mean segmental mobility in undeformed networks increases linearly with swelling in the range $v_2 > 0.85$ and according to the WLF law with temperature. (ii) The mean segmental mobility is proportional to the combination of first invariants of the molecular deformation tensor and the deformation tensor of constraint domains. Proportionality to the former reflects effects of rotational isomerization of a stretched chain on the mobility of its segments, whereas proportionality to the latter reflects effects of coupling of sequences of segments to their surroundings. Increase of mobility up to $\alpha = 4$ is indicative of the dilation of constraint domains upon stretching. Decrease of mobility for strains exceeding $\alpha = 4$ reflects the effect of increase of local constraints at high strains. On the other hand, isomerization of the stretched polyisoprene chain results in a decrease of mean segmental mobility at all levels of strain. (iii) Swelling of the network drastically decreases the effect of the constraints on segmental mobility, whereas the effect of isomerization is independent of swelling. (iv) The strain dependence of mean segmental mobility is not affected by temperature. (v) To the first-order approximation, within experimental accuracy, the anisotropy of mobility is proportional to the orientation function. It may be concluded that mobility of segments along the direction of stretch for the polyisoprene network is larger than those along lateral directions.

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Sol–Gel Transition and Phase Diagram of the System Atactic Polystyrene–Carbon Disulfide

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ABSTRACT: This paper deals with the determination of the phase diagram by means of calorimetry (DSC) of the physically gelling system atactic polystyrene (aPS)–carbon disulfide (CS_2). The investigation was carried out with different molecular weights. DSC results have been compared to those obtained by other techniques. The findings of Tan et al. are confirmed and particularly a gel formation exotherm is unmistakably shown as well as a broader gel melting endotherm. These thermal features are absent in solvents wherein physical gelation cannot take place. From the results, it is concluded that gelation in aPS–CS_2 solutions proceeds from a first-order transition that entails a mechanism of nucleation and growth. Accordingly, three-dimensional structures that possess a certain order are created. This is in total contradiction with the recent hypothesis of Boyer et al., who consider liquid-like contacts. In addition, both the phase diagram and the variation of either the formation or the melting enthalpies display a maximum near $C_{pol} \simeq 55\%$. After checking the absence of any artifact, we conclude that aPS and CS_2 form a polymer–solvent complex or a stoichiometric compound. This means that without solvent, physical links cannot be created, a statement in agreement with the fact that aPS cannot crystallize from the bulk.

Introduction

The occurrence of physical gelation of polymer solutions is generally thought to originate in chain crystallization and has been accordingly restricted to crystallizable polymers or at least stereoregular polymers. However, the propensity of *atactic polystyrene* (aPS) to form physical gels has been recently discovered by Tan et al.[1] and has received confirmation from rheological measurements.[2,3] In addition, the existence of aPS physical gelation has enabled Guenet et al. to provide a coherent explanation[4,5] for the so-called "enhanced low-angle scattering" (ELAS) observed in moderately concentrated solutions, which had been unaccounted for.

Once the principle of aPS physical gelation is accepted, the next step in gaining knowledge concerns the mechanism involved. If one considers that ELAS and gelation are simply different manifestations of the same phenomenon,[5] results gathered on semidilute solutions can be used to attempt to explain gelation. On this basis, Gan, François, and Guenet[5] recently suggested that ELAS is due

Table I

M_w	M_w/M_n	catalyst
1.05×10^3	1.2	
6×10^3	1.08	butyllithium
1.8×10^5	1.08	butyllithium
1.7×10^6	1.3	phenylethylpotassium
5.6×10^6	1.3	

to chain aggregation via some kind of "crystallites"[6] embodying polymer segments and solvent molecules. The physical links then exist due to a polymer–solvent complex or, more precisely speaking, to a stoichiometric compound. The exact sequences involved remain unclear at the moment. Yet, Gan et al.'s results clearly show that ELAS is observable in certain good solvents such as THF and tend to be absent in other ones. There is no correlation with Flory's interaction parameter χ but rather with solvation at the monomer unit level (number of solvent molecules adsorbed per monomer unit, which is not necessarily related to χ[5]).

This viewpoint is in total conflict with the recent explanation proposed by Boyer et al.[7] These authors suggest that gelation is a manifestation of a second-order transition occurring at T_{ll}, a few degrees above T_g and designated as the liquid–liquid transition. Their model consists of liquid-like contacts between monomers of different chains which are supposed to occur in poor or bad solvents. Such a view seems, however, hard to reconcile with the fact that the best solvent known hitherto for aPS gelation is carbon disulfide (CS_2), which happens to be a very good solvent even at very low temperatures.[8] In addition, if gelation is directly associated with the T_{ll} transition, this phenomenon should proceed from a *second-order transition* and should be nearly parallel to the variation of T_g with concentration.[9] Conversely, if the interpretation of Gan et al.,[5] which allows the formation of three-dimensional objects possessing a certain order, is relevant, one should observe a *first-order transition* both for the gel formation and the gel melting and no direct correlation with T_g. From the work of Tan et al.[1] an exotherm of gel formation can be seen in DSC experiments. Accordingly, in order to settle the above discrepancy, the aPS–CS_2 system has been studied by differential scanning calorimetry. The purpose of this paper is to report the results and to establish the temperature–concentration phase diagram which shows that the hypothesis of a stoichiometric compound is valid.

Experimental Section

(A) Materials. Five samples of atactic polystyrene were used in this study. Their characteristics are given in Table I. Tacticity determinations were achieved by ^{13}C NMR with a Brukker WH 90 spectrometer from 10% solutions in $CDCl_3$ at 30 °C. The usual results for aPS were found.

(B) Differential Scanning Calorimetry (DSC). A Perkin-Elmer DSC microcalorimeter equipped with the Thermal Analysis Data Station (TADS) was employed. The desired quantity of vitrified aPS was introduced into a weighed volatile sample pan. An estimated volume of CS_2 (high-purity grade) was added into the pan, which was then tightly sealed. The pans were annealed for several days at 40 °C and then for at least 2 months at room temperature to ensure a thorough homogenization. The weight of each pan was measured prior to taking any data in order to determine the concentration of the system (in g/g). Some DSC measurements were repeated a month later to test homogenization. These controls have shown the preparation procedure to be quite satisfactory. Cooling and heating rates ranging from 10 to 80 °C/min were used. In addition, in order to measure with sufficient accuracy and reliability very low ΔH_m values as well as to detect broad melting endotherms, a straight base line is required. This can be achieved by making use of the S.A.Z. correction available on the DSC II. This procedure consists of recording the thermogram from empty pans and then subtracting it from subsequent thermograms. As a result, all of the noise due to the apparatus, particularly at low temperatures, is considerably attenuated.

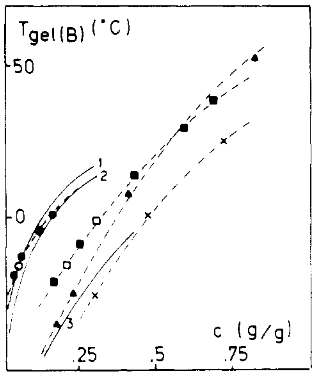

Figure 1. Plot of T_{gel}(B) vs. polymer concentration: filled symbols, ball drop method; unfilled symbols, sphere rheometer. (●, ○) aPS $M_w = 1.7 \times 10^6$; (■, □) aPS $M_w = 1.8 \times 10^5$; (▲) aPS $M_w = 5 \times 10^3$; (×) aPS $M_w = 6 \times 10^3$. Full lines represent the experimental results of Tan et al.:[1] (1) aPS $M_w = 2 \times 10^6$; (2) aPS $M_w = 10^6$; (3) aPS $M_w = 4 \times 10^3$.

(C) Ball Drop Method. To bridge the gap with previous experiments,[1,3] some measurements were performed with the ball drop technique. We used the method described by Takahashi et al.[10] Known quantities of polymer and solvent were introduced along with a steel ball (60 mg) in a glass tube, and the system was sealed from the atmosphere. These tubes were kept at 40 °C for 1 week to allow for homogenization prior to any measurements. The ball was then allowed to sink to the bottom of the tube, and the gel was formed by slowly cooling to -60 °C. The tube was then turned upside down after the gel formation. The temperature was raised at a rate less than 0.5 °C/min. A magnetic field was applied from time to time to make sure that the ball was still supported by a gel-like material and not by a viscous solution. The temperature at which the ball fell through the sample under a magnetic field was taken as the gel melting temperature.

Results and Discussion

Hitherto, gelation has been essentially studied by the ball drop method,[1] which is sensitive to the change of macroscopic viscosity of the system but cannot precisely show a viscous–elastic transition. Surprisingly, we have shown[3] that gelation temperatures obtained by this technique are in good agreement (within 2-3 °C) with those determined by means of a sphere rheometer,[3,11] a more sophisticated apparatus that allows the differentiation of a viscous solution from a gel (provided that the system is far away from its T_g) and the performance of the experiment in a system totally sealed from the atmosphere.

Such a comparison was achieved for concentrations lower than 30%. It appeared to be of interest to extend the ball drop method to higher concentrations and to compare the results with DSC data, thereby allowing an estimation of the reliability of each technique and what phenomenon they actually measure.

(A) Ball Drop Method. The values of T_{gel}(B) obtained from the ball drop method with the aPS–CS_2 system are given in Figure 1. They are in good agreement with those published by Tan et al.[1] and those determined from rheological measurements[3] for the range of moderately concentrated solutions. as already pointed out,[1] T_{gel}(B) increases as a function of molecular weight at a given concentration. Yet, for very low molecular weights, T_{gel}(B) for $M_w = 5 \times 10^3$ is higher than for $M_w = 6 \times 10^3$. The fact that these samples were prepared with different catalysts by anionic polymerization (α-methylstyrene for $M_w = 5 \times 10^3$ and butyllithium for $M_w = 6 \times 10^3$) may play a role. The butyl group may constitute a destabilizing

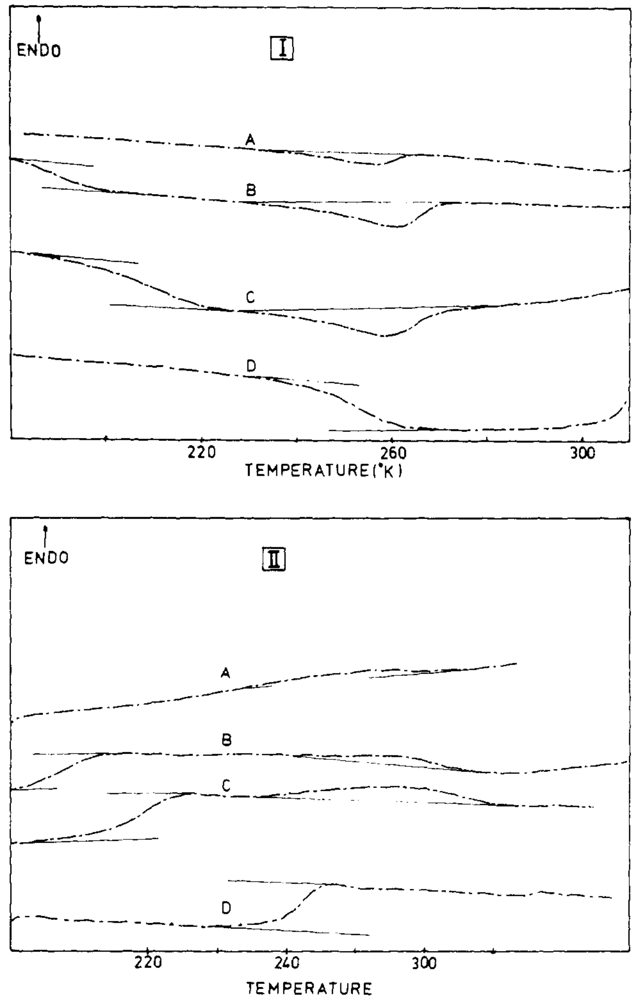

Figure 2. DSC thermograms for $M_w = 1.8 \times 10^5$ at different polymer concentration ((A) 30.3%; (B) 47.8%; (C) 58.8%; (D) 74.7%): (I) cooling; (II) heating.

factor of the gel—hence a lower gelation temperature. Finally, whatever the molecular weight, the ball drop method shows that T_{gel}(B) increases monotonically with polymer concentration in the range of compositions studied.

In order to test the analogy between the T_{ll} transition and gelation proposed by Boyer et al.,[7] we have studied the system aPS–dinonyl phthalate, which shows a liquid–liquid transition at room temprature.[9] One might then expect the same behavior as in CS$_2$. However, no gelation was observed, yet demixing takes place in this system.

(B) Differential Scanning Calorimetry (DSC). General Characteristics of the DSC Traces. Figure 2(I) displays DSC traces recorded under cooling conditions for aPS–CS$_2$ systems of various concentrations. The curves reveal both the glass transition and an exotherm, the latter being in the expected gelation temperature range. From these curves, the important experimental fact is that an enthalpy of gel formation can be observed, which clearly confirms previous findings by Tan et al.[1] Repeated experiments showed the absence of any artifacts and excellent reproducibility. It is important to emphasize that both the method of sample preparation (in situ) and the use of the S.A.Z. correction contribute to the success of the investigation. Similarly, under heating conditions, Figure 2(II) shows typical DSC traces which are characterized by the presence of an endotherm. Although this endotherm is broad, it can be unmistakably shown. Before proceeding further with the discussion and description of the system, we mention two important experimental results that give credit to the above findings:

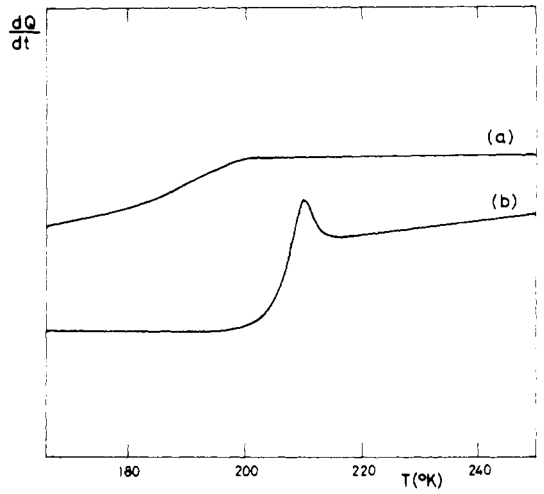

Figure 3. DSC thermograms for aPS solution in methylene chloride (a) with $C = 45.6\%$ and in dinonyl phthalate (b) with $C = 47.5\%$.

(i) A blank sample containing only CS$_2$ does not display any of the characteristics of Figure 2.

(ii) A comparison of the thermal properties has been carried out with solvents wherein gelation is absent (methylene chloride and dinonyl phthalate). As shown in Figure 3, DSC traces obtained in these solvents do not show the same features observed for the aPS–CS$_2$ system but only the occurrence of T_g. The case of dinonyl phthalate is interesting due to the presence of a stress relaxation peak. Comparison with Figure 2 shows that there cannot be any confusion between this peak and the melting endotherm. These experiments clearly demonstrate the existence of some kind of ordered structures that are responsible for the cohesion of the network. Conversely, as stressed above, a liquid–liquid transition, which is of second order and analogous to T_{ll} in the bulk,[12] should be revealed by a change of slope in DSC experiments, but never as an exo- or endotherm. Moreover, such a transition should be observed in all of the solvents approximately 40 °C above T_g over the whole concentration range.[12]

From Figure 2(II) another interesting fact emerges: the melting endotherm of the gel tends to vanish above room temperature. This gives further support to the assumption put forward by Guenet et al.[4] and Gan et al.[5] according to which some remnants of the gel are still present in solutions above C^* and that the "enhanced low-angle scattering" and gelation are different manifestations of the same phenomenon. Thereby, investigations of semidilute solutions at room temperature can provide valuable information on the gel formation mechanism.[5]

Once it is possible to show the exo- and endotherm and to measure their area (proportional to ΔH), the temperature–concentration phase diagram can be established.

Phase Diagram of aPS–CS$_2$ Systems. The phase diagrams obtained from DSC are reported in Figure 4 for different molecular weights. They show the following features:

Glass Transition Temperature (T_g). In the molecular weight range investigated, T_g increases slightly with molecular weight, as expected. Values reported here are in good agreement with those of ref 13, considering the differences in the experimental methods. The authors of ref 13 determined T_g by refractometry at very low heating rates, i.e., under quasi-equilibrium conditions, as opposed to our DSC experiments, which were performed at 20

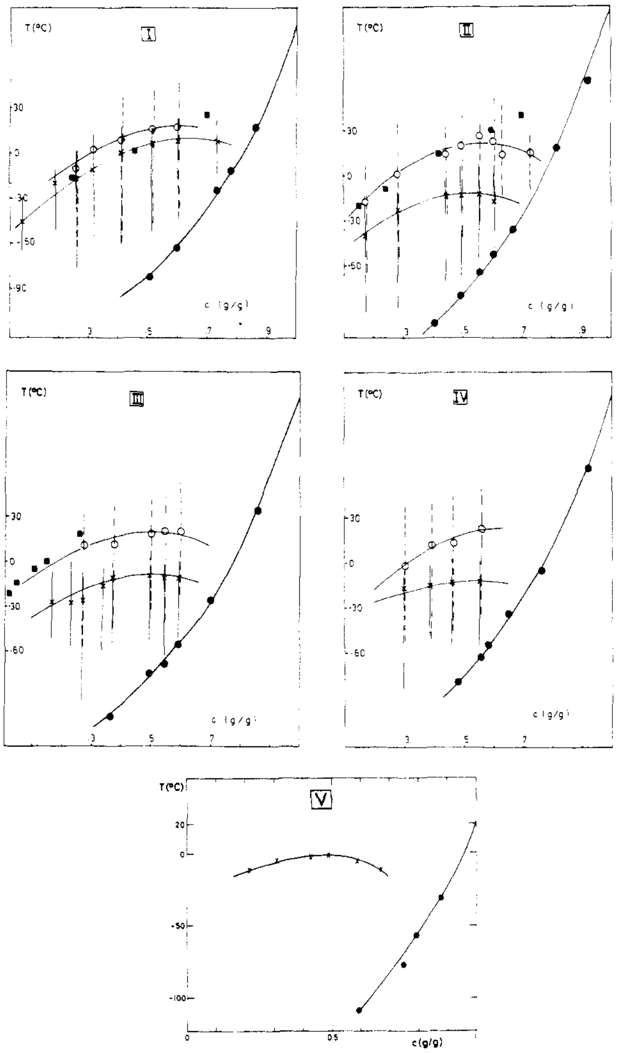

Figure 4. Temperature vs. concentration phase diagrams determined by DSC at 20 °C/min for different molecular weights: (I) $M_w = 6 \times 10^3$; (II) $M_w = 1.8 \times 10^5$; (III) $M_w = 1.7 \times 10^6$; (IV) $M_w = 5 \times 10^6$; (V) $M_w = 1.05 \times 10^3$. (●) T_g; (○) T_{gel} measured on heating; (×) T_{gel} determined on cooling. Broken line, temperature range of the endotherm; full line, temperature of the exotherm. (■) T_{gel}(B) measured by the ball drop method.

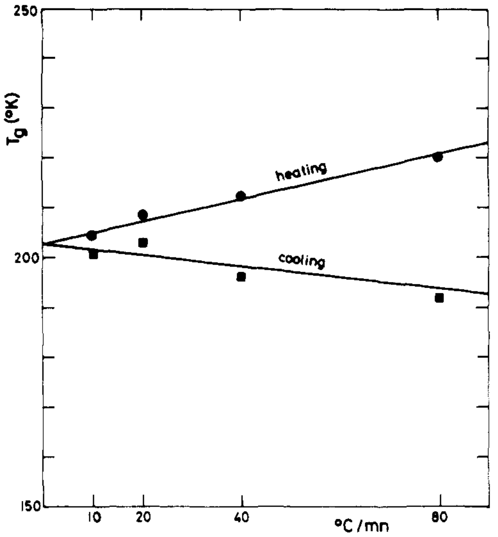

Figure 5. Variation of T_g with heating and cooling rates for $M_w = 1.8 \times 10^5$ and $C = 50.9\%$ in CS_2.

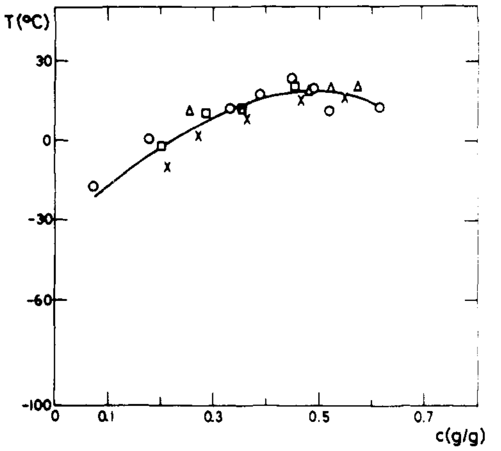

Figure 6. Melting points of the gels as determined by DSC for all the different molecular weights: (○) $M_w = 1.8 \times 10^5$; (△) $M_w = 1.7 \times 10^6$; (×) $M_w = 6 \times 10^3$; (□) $M_w = 5.6 \times 10^6$. The full line is a guide line for the eyes and shows the absence of a molecular weight effect.

°C/min. When a systematic study of the T_g variation is carried out as a function of the heating and cooling rates, values extrapolated at zero rate are the same (Figure 5) and are in better agreement with those of ref 13.

It is important to emphasize that even when the thermograms display both the exo- or endotherm related to the gel and the glass transition jump, T_g values are correctly determined.

Sol–Gel Transition. In addition to the maxima and minima measured for the endotherm and the exotherm in Figure 4, the temperatures of the sol–gel transition determined by the ball drop method are reported. This leads to several comments. For *moderately concentrated* solutions, T_{gel} as determined by the maximum of the melting endotherm corresponds to T_{gel} within a few degrees as measured by the ball drop method. This indicates that the DSC endotherm is unambiguously associated with the sol–gel transition. In addition, this confirms the statement of Gan et al.[5] which considers that the gel melting temperature deduced by this latter method only corresponds to the loss of three-dimensionality of the system as opposed to the sudden disappearance of all the entities ensuring the stability of the network. Contrarily to what is observed by the ball drop method, T_{gel} values obtained on heating do not depend markedly on molecular weight. As a matter of fact, the maximum of the DSC endotherm is slightly higher for low molecular weights and slightly lower for high molecular weights than what is obtained by the ball drop technique. Moreover, for *high polymer concentrations* there is definitely a mismatch between both techniques. While T_{gel}(B) monotonically increases with concentration, T_{gel} from DSC exhibits a slight, but unmistakable fall-off. This result confirms what was suspected by Boyer et al.:[7] the ball drop method is subject to chain entanglements. This effect manifests itself more readily the higher the molecular weight or the concentration. Conversely, the phase diagram from DSC is virtually independent of molecular weight, and a "master curve" can even be drawn as shown in Figure 6.

The phase diagrams drawn in Figure 4 have been obtained for heating and cooling rates of 20 °C/min. There is a difference between the values of T_{gel} determined either way. This discrepancy tends to increase slightly with polymer concentration and molecular weight. Unlike the T_g results, a study at different heating and cooling rates reveals a systematic shift when extrapolated to zero rate (Figure 7). For instance, taking the maximum and minimum of the endotherm and the exotherm, one finds about a 30 °C difference. Together these results suggest that a

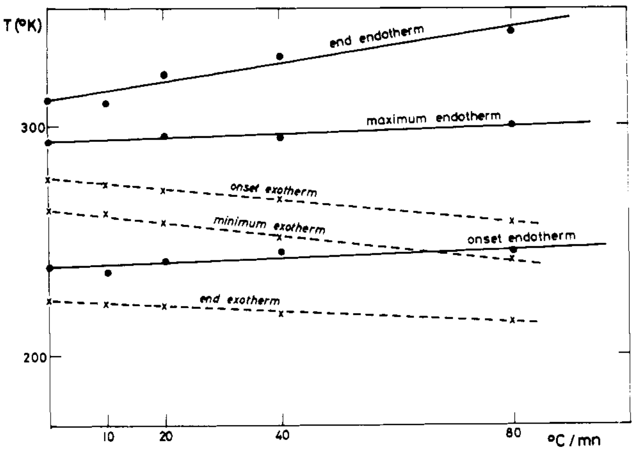

Figure 7. Variations of the characteristics of the endotherms and the exotherms with heating rate (endotherm) and cooling rate (exotherm). $M_w = 1.7 \times 10^6$, $C = 33.6\%$.

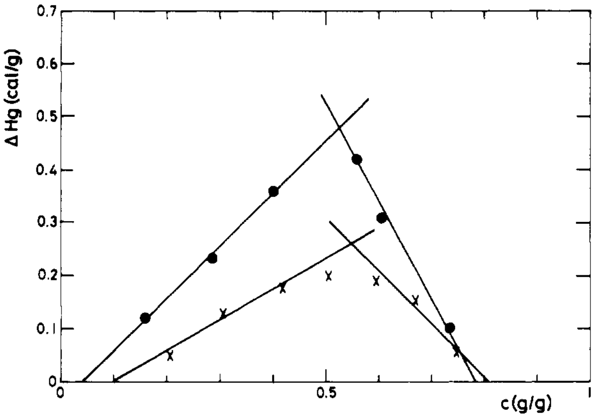

Figure 8. Variation of ΔH_{gel} (cal/g) as a function of polymer concentration on cooling: (●) $M_w = 6 \times 10^3$; (×) $M_w = 1.05 \times 10^3$.

mechanism of nucleation and growth, reminiscent of "crystallization", is taking place. Note that if the physical cross-links are not punctual but three-dimensional as expected with structures possessing a certain degree of order, such a mechanism is compulsory. We note further that the undercooling is far less pronounced for $M_w = 6 \times 10^3$, which is not surprising with a lower molecular weight.

Another interesting result lies in the fact that an exotherm can still be seen with a molecular weight as low as $M_w = 1.05 \times 10^3$. This shows that ordered structures can grow for a broad range of molecular weights.

As to the enthalpies involved in either the formation or the fusion of the gels, their variation with concentration is worth looking at. For instance, the formation enthalpies of the samples prepared with $M_w = 6 \times 10^3$ or $M_w = 1.05 \times 10^3$ increase up to $C_{\text{pol}} \simeq 55\%$ and then decrease to zero for $C_{\text{pol}} \simeq 80\%$ (Figure 8). Taking into account all the results, we note again a maximum near $C_{\text{pol}} \simeq 55\%$ (Figure 9) in spite of the experimental scatter.

The occurrence of the maximum in the phase diagram as well as in the enthalpy variation at virtually the same concentration ($C_{\text{pol}} \simeq 55\%$) is certainly not fortuitous. This may find its origin in a possible experimental artifact. The use of finite heating and cooling rates with a system close to its T_g may bias the results. It can accordingly be suggested that the formation of the ordered structures was hampered by too rapid a quench, resulting in an artificial decrease of both the gel melting point and the enthalpy. Experiments performed with $M_w = 1.8 \times 10^5$ at $C_{\text{pol}} = 55\%$ indeed show a dependence of ΔH with the cooling rate, which tends, however, to level off for rates equal to or lower than 20 °C/min (see Table II). Thus, a cooling rate of 20 °C/min is not rapid enough at this concentration to freeze in the system and prevent "crystallization". For the same molecular weight with $C_{\text{pol}} = 73\%$, an additional test has been carried out so as to confirm the falloff of T_{gel} and ΔH. This solution has been cooled at a very slow rate (1.25 °C/min) from +35 to −80 °C and then heated at 20 °C/min while the DSC spectrum was recorded. No noticeable change was detected compared to a sample cooled at 20 °C/min. Other experimental facts enable one to dismiss an artifact: (i) the maximum of T_{gel} and ΔH(formation) can be observed for $M_w = 1.05 \times 10^3$, for which the T_g is at far lower temperatures; (ii) the melting points are not molecular weight dependent at 20 °C/min.

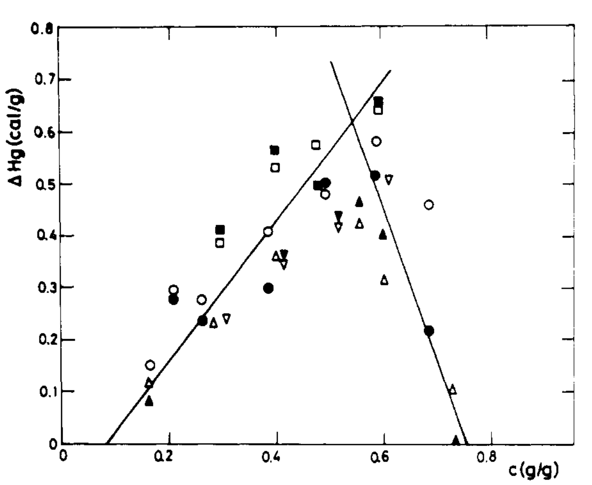

Figure 9. Bulk of the results on the enthalpies of formation and of fusion for different molecular weights (ΔH in cal/g). Open symbols stand for enthalpies determined on cooling and full symbols for those measured on heating. (●, ○) $M_w = 1.7 \times 10^6$; (■, □) $M_w = 5.6 \times 10^6$; (▲, △) $M_w = 1.8 \times 10^5$; (▼, ▽) $M_w = 6 \times 10^3$. Variation as a function of polymer concentration.

Table II[a]

cooling rate, °C/min	ΔH, cal/g
80	0.27
40	0.35
20	0.42
10	0.43
5	0.47

[a] $M_w = 1.8 \times 10^5$, $C = 55.8\%$.

Since the maximum both in the phase diagram and in the variation of the enthalpies as a function of concentration is genuine, this entails that the ordered structures consist of an aPS–CS$_2$ stoichiometric compound. In other words, the polymer "crystallizes", thanks to the incorporation of solvent. When the solvent is progressively removed, the structures collapse and amorphous polystyrene is retrieved. This agrees with the fact that aPS cannot crystallize from the bulk (here the word crystallize is used in the proper way).

Melting Behavior of the Solvent (CS$_2$) in the Gel. As already stressed in a previous paper,[5] the melting behavior of the solvent in the gel can yield additional information. For aPS–CS$_2$, the melting temperature of CS$_2$ is constant within 4 °C with polymer concentration. Such an invariance is a further confirmation that the system consists of two phases, one of which possesses a certain degree of order. In addition, the variation of ΔH_m of the solvent is linear with concentration and extrapolates to zero for $C_{\text{pol}} \simeq 40\%$. Beyond this concentration all the solvent is bound. The T_g value (once extrapolated to zero rate) for this concentration is close to the solvent melting temperature.

Concluding Remarks

All of the DSC experiments are consistent with the existence of structures possessing some degree of order in the aPS–CS_2 gels. Such a conclusion is shared by other authors.[14] However, the work presented here shows that the structures responsible for the gel physical cross-links owe their existence to the formation of a stoichiometric compound.

There is virtually no molecular weight effect on the melting points determined by DSC, unlike those measured mechanically. Consequently, the values of the gel melting enthalpies as obtained from the Ferry–Eldrige equation are certainly misleading.[1] From the melting enthalpies measured here, an estimate of the amount of material participating in the links can be attempted. On an average basis of 10 cal/g (a value that represents the order of magnitude usually encountered in nonpolar organic systems) the gel would contain 5–10% of these structures. Such figures seem reasonable in view of the atactic character of this polymer, which cannot contain long stereoregular sequences. Recent statistical calculations[15] carried out to estimate the content of syndiotactic sequences possessing a subsequent length can account for the above figures.

Finally, a possible structure could resemble a ladder, the rungs of which would be the CS_2 molecules. Such a picture has been recently proposed for iPS physical gels on the basis of DSC and neutron diffraction experiments.[16] If such a model turned out to be correct, the same structures would be obtained by different mechanisms (in good solvent for aPS; in a phase-separating system for iPS).

Registry No. aPS, 9003-53-6; CS_2, 75-15-0.

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Self-Diffusion Measurements in Polymer Solutions at the Θ Temperature by Forced Rayleigh Light Scattering

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ABSTRACT: Using forced Rayleigh light scattering technqiues (FRS), we have measured the self-diffusion coefficient, D_{self}, of polystyrene chains in cyclopentane at the Θ temperature as a function of both molecular weight M and polymer concentration c. For entangled solutions at the Θ temperature, the FRS signal shows a strong amplification as compared to the dilute, Θ, or semidilute good solvent cases. We show that this effect can be attributed to the formation in the sample of an index of refraction grating, due to monomer–photoexcited label interactions. The long-time relaxation of the FRS signal yields the self-diffusion coefficient of the labeled chains, and we obtain $D_{\mathrm{self}} \sim M^{-2\pm0.1}c^{-3.1\pm0.2}$, in agreement with reptation and scaling predictions, assuming the tube width to be equal to the correlation length of the Θ solution, $\xi \sim c^{-1}$.

Introduction

The self-diffusion coefficient (D_{self}) of polymer chains has proven to be a quite interesting parameter to characterize individual chain motions in entangled solutions or melts.[1]

Several techniques have been used in recent years to measure D_{self},[2-8] and in the case of long enough chains in good solvent conditions, a good agreement was observed[2,9] between measurements and theoretical predictions from the reptation model[10] and the scaling approach to polymer solutions.[11,12] The case of Θ solutions, however, is far less clear from a theoretical point of view: due to the exact compensation between two-body monomer–monomer and monomer–solvent interactions, the correlation length of the monomer density is proportional to the average distance between three monomer contact points and should scale like $\xi \sim c^{-1}$.[13] However, the chains are real chains that cannot cross each other, and individual chain motions may be restricted by the two monomer contact points (average distance $d \sim c^{-1/2}$).[14] If such is the case, simple reptation arguments are not easy to develop, as they lead to a tube width, d, different from the screening length of the hydrodynamic interactions ξ.

From quasi-elastic light scattering measurements, Amis and Han[15] have obtained a characteristic time for the slow mode obeying simple scaling laws. It is not clear, however, that these slow modes may be attributed to center-of-mass translational diffusion of the chains.[16]

In order to better understand the dynamic properties of entangled Θ solutions, we have undertaken systematic

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