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Anisotropic Light Scattering Study of the Physical Gelation of Atactic Polystyrene in Carbon Disulfide

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ABSTRACT: The physical gelation of the solutions of atactic polystyrene (aPS) in carbon disulfide (CS_2) is studied from the excess of anisotropic light scattering, δH_v. An abrupt jump of δH_v at gelation temperature shows that a part of the chains is stiffened upon gelation. This effect which is independent of aPS molecular weight strongly decreases with concentration. The compatibility of this abrupt jump with the thermodynamic theories used to interpret the concentration and molecular weight dependence of the gelation temperature is discussed.

I. Introduction

The discovery of Tan et al.[1] that shows the ability of atactic polystyrene (aPS) solutions to give physical gels by cooling has given rise to several works aiming to elucidate the origin of this unexpected phenomenon.[2-12]

The occurrence of physical gelation in vinyl polymer solutions was generally thought to originate in chain crystallization and was accordingly restricted to stereoregular polymers (isotactic polystyrene[13]) or atactic crystallizable polymers [poly(vinyl chloride)[14]]. Because aPS is a stereoirregular polymer, crystallization was not expected to occur on cooling its solutions. Then it was proposed that gelation of aPS originates from a liquid-liquid demixing.[5,8,9] Such a model implies a relation between the thermodynamical quality of the solvent and the gelation temperature, the better solvent giving the lowest gelation temperature. This is consistent with the results of a comparison of the behavior of *cis*- and *trans*-decalin solutions of aPS.[9]

However, carbon disulfide (CS_2) was revealed to be the aPS solvent which promotes gelation at the highest temperature[1] while viscosity measurements show that it is unambiguously a good solvent in the temperature range of the sol–gel transition.[15] It turns out that gelation is not directly related to the thermodynamical solvent quality and is not the prerogative of poor solvents.

This observation as well as a series of other parallel studies led Gan et al.[6] to propose that gelation of aPS in CS_2 may be due to the intermolecular association of chain segments in "complex crystals", including syndiotactic sequences and solvent molecules. However, further investigations are needed to characterize the structure and the size of the cross-link domains.

Stiffening and association should lead to a large increase in the optical anisotropy of the cross-links in comparison with a single flexible chain.

It is indeed well-known that the light scattered by N uncorrelated anisotropic molecules at a right angle to the vertically polarized incident beam is depolarized and is characterized by two components: (1) the horizontal component H_v which is proportional to the square of the difference in principal polarizabilities $(\alpha - \beta)^2$, assuming cylindrical symmetry;

$$H_v \propto N[(3/5)(\alpha - \beta)^2] \tag{1}$$

(2) the vertical component V_v which contains in addition to the part proportional to the mean polarizability $\bar{\alpha} = (\alpha + 2\beta)/3$, a second term in $(\alpha - \beta)^2$:

$$V_v \propto N[\bar{\alpha}^2 + (4/5)(\alpha - \beta)^2] \tag{2}$$

For noninteracting molecules in solution the excess scattering with respect to the solvent writes directly by replacing $\bar{\alpha}$ by $\bar{\alpha} - \alpha_0 \propto \mathrm{d}n/\mathrm{d}c$, where α_0 is the polarizability of a volume of solvent proportional to that of the solute molecule and $\mathrm{d}n/\mathrm{d}c$ is the refractive index increment.

$$\delta V_v = V_v - V_{v,sol} = N[(\bar{\alpha} - \alpha_0)^2 + (4/5)(\alpha - \beta)^2] \tag{3}$$

$$\delta H_v = H_v - H_{v,sol} = N[(3/5)(\alpha - \beta)^2] \tag{4}$$

To first order, the excess δH_v only depends on the anisotropy of the solute. It is seen that the excess δV_v does not vanish for $\mathrm{d}n/\mathrm{d}c = 0$ as does the excess of the isotropic part.

$$\delta I_{iso} = (V_v - V_{v,solv}) - (4/3)(H_v - H_{v,solv}) \tag{5}$$

Similarly

$$\delta I_{aniso} = (7/3)(H_v - H_{v,solv}) \tag{6}$$

For interacting molecules the excess isotropic scattering is affected by the correlations in position as expressed by the pair correlation function $g(r)$, while the anisotropic scattering is affected by the orientational correlations $g(r,\omega)$.[16]

$$\delta I_{iso} \propto N(\bar{\alpha} - \alpha_0)^2 \left[1 + \frac{N}{V} \int [g(r) - 1] \exp(iqr)\, 4\pi r^2\, \mathrm{d}r \right] \tag{7}$$

$$\delta I_{aniso} \propto N(\alpha - \beta)^2 \left[1 + \frac{N}{V} \int \frac{(3\cos^2\omega - 1)}{2} [g(r,\omega) - 1] 2\pi r^2\, \mathrm{d}r \sin\omega\, \mathrm{d}\omega \right] \tag{8}$$

The existence of strong positional correlations in the semidilute regime leads indeed to a concentration dependence of δI_{iso} (at zero scattering angle) in $c^{-1/4}$ for good solvents, while δI_{aniso} is expected to be proportional to c in the absence of orientational correlation.

At the gelation point, however, if physical cross-links result as previously proposed from a locally stiff parallel arrangement of chains, one expects to detect the strong orientational correlation and to observe an increase in δI_{aniso}.

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Table I. Weight-Average Molecular Weights M_w and the Polydispersity Indices M_w/M_n Obtained by Size-Exclusion Chromatography in Tetrahydrofuran[a]

sample	M_w	M_w/M_n	$[\eta]$, mL/g
A	2500	1.01	4.49
B	1.8×10^5	1.55	50.15
C	2×10^5	1.14	56.95
D	1.5×10^6	1.55	358.95
E	2×10^6	1.15	396.95

[a] $[\eta]$ is the intrinsic viscosity measured in CS_2 at 25 °C.

As the aPS/CS_2 system has a small refractive index increment (−0.03 mL g^{-1}), the isotropic contribution to light scattering is expected to be small enough for an accurate determination of the anisotropic contribution in the semidilute and gel states.

This paper presents a systematic study of the temperature and concentration dependence of the anisotropic light scattering of aPS/CS_2 solutions. It indeed reveals an abrupt change at gelation, the amplitude of which gives new ideas upon the gelation process.

II. Experimental Section

(A) Materials. Five aPS samples were used in this study. Samples B and D from Aldrich were obtained by radical polymerization and samples A, C, and E were prepared in our laboratory by anionic polymerization. Their characteristics are given in Table I.

(B) Light Scattering. The measurements of the isotropic and anisotropic scattered light intensities were made with a Wippler–Scheibling type photogoniodiffusometer[17] operating with a vertically polarized blue laser beam (λ = 488.5 nm). The scattering cell can be thermostated by an isopropyl alcohol circulation bath at ±1 °C. As shown in Figure 1, the temperature of the sol–gel transition is generally lower than 0 °C and the light scattering apparatus was modified in order to avoid all the problems arising from the water condensation on the metallic and glass parts. For this purpose, all the devices except the laser source were put into an airtight Plexiglas box under a dry nitrogen flow. An analyzer is introduced into the scattered beam between the cell and the photomultiplier. It can be turned by an angle of 90° in order to measure H_v and V_v, the horizontal and vertical components of the scattered light, respectively. Then the intensities of the isotropic, I_{iso}, and anisotropic, I_{aniso}, scattered light can be deduced according to eqs 5 and 6.

The value found for the depolarization factor ($\rho_v = H_v/V_v$) of benzene is 0.27, close to the literature data (0.266). For pure CS_2, the values obtained for the Rayleigh ratios associated with V_v and H_v are 187×10^{-6} and 84.2×10^{-6} cm^{-1}, respectively, and the value of ρ_v is 0.45 independent of temperature. The aPS solutions were prepared directly at the measurement concentration and kept at room temperature for at least 48 h in order to ensure good homogeneity. Then they are centrifuged at 14 000 rpm for 4 h at 5 °C because of the low boiling point of CS_2, and the concentration of the solutions was controlled after centrifugation, by measuring the dry content. The solutions were then introduced in tightly closed scattered cells.

(C) Ball Drop Method. The phase diagrams of Figure 2 were obtained by the ball drop method described by Takahashi et al.[18] Known quantities of polymer and solvent were introduced along with a steel ball in a glass tube, and the system was sealed from the atmosphere. The tube was kept at room temperature for 48 h. The ball was then allowed to sink to the bottom of the tube, and the gel was formed by slowly cooling under the expected gelation temperature. The tube was then turned upside down after the gel formation. The temperature was raised by steps of 1 °C, and the temperature at which the ball fell through the sample was taken as the gel melting temperature.

III. Results

(A) Semidilute Solutions. Isotropic Scattering. The angular dependence of $c/\delta I_{iso}$ for different concentrations is given in Figure 1a. The scaling theory predicts that the isotropic scattering is controlled by the screening

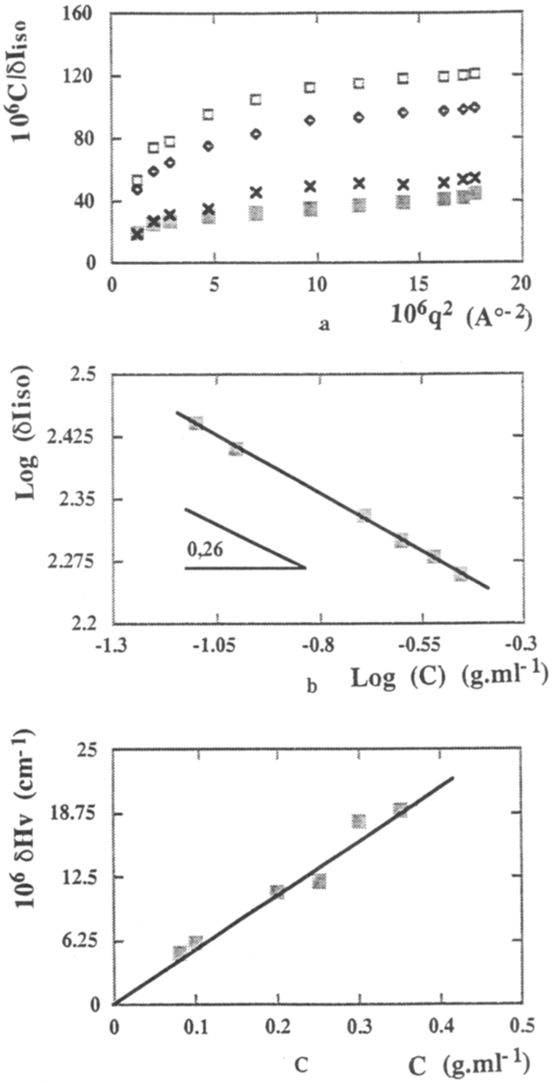

Figure 1. Light scattering experiments on semidilute solutions of sample D in CS_2 at T = 20 °C. (a) Plot of $c/\delta I_{iso}$ (arbitrary units) vs q^2. Polymer concentration c = 0.08 (□), 0.1 (×), 0.2 (◇), 0.25 g/mL (□). (b) Variation of log $\delta I_{iso}(q{=}0)$ (arbitrary units) vs log c (g/mL). (c) Variation of δH_v at θ = 90° vs c at T = 20 °C.

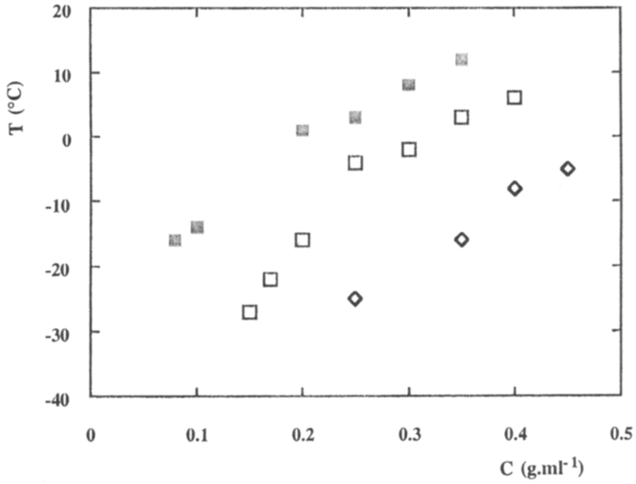

Figure 2. Plot of T_{gel} (obtained by the ball drop method) vs polymer concentration for sample A (M_w = 2500) (◇), sample B (M_w = 1.8×10^5) (□), and sample D (M_w = 1.5×10^6) (■).

length ξ defined by Edwards.[19] For a good solvent with excluded-volume exponent ν

$$\xi \propto R_g(c/c^*)^{-\nu/(3\nu-1)} \tag{9}$$

$$\delta I_{\rm iso}(q) = \delta I_{\rm iso}(q{=}0)\,[1 + \xi^2 q^2]^{-1} \tag{10}$$

where R_g is the radius of gyration, c the polymer concentration, c^* the overlap concentration, and q the scattering vector ($q = (4\pi/\lambda)\sin(\theta/2)$ with θ the scattering angle).

Since the osmotic pressure varies with c according to

$$\pi \propto \xi^{-3} \propto c^{-3\nu/(3\nu-1)} \tag{11}$$

$$\delta I_{\rm iso}(q{=}0) \propto c/({\rm d}\pi/{\rm d}c) \propto c^{(3\nu-2)/(3\nu-1)} \tag{12}$$

A value of $\nu = 0.6$ is deduced for aPS in CS$_2$ from both the measurements of R_g and ξ by neutron and light scattering[20,21]

$$R_g = 0.121M^{0.6} \tag{13}$$

$$\xi/R_g \propto (c/c^*)^{-.74} \tag{14}$$

In the range of concentration and scattering vectors $\xi q \ll 1$ investigated, no angular dependence should be observed by light scattering.

The enhanced low-angle scattering reported in Figure 1a is a common feature of many semidilute solutions in good solvent.[22] Its origin has been the subject of many controversies. It is generally attributed to heterogeneities. Since the values of $c/\delta I_{\rm iso}$ in Figure 1a tend to become q independent within experimental error at high q, the value at the highest q available has been taken as a good approximation for $\delta I_{\rm iso}(q{=}0)$ and plotted logarithmically as a function of c in Figure 1b. The scaling exponent -0.26 is close to the theoretical prediction for $\nu = 0.6$.

Anisotropic Scattering. The concentration dependence of δH_v is reported in Figure 1c, for sample D. As expected δH_v is a linear function of c throughout the semidilute regime. The value of $\delta H_v/c$ is in good agreement with that obtained by one of us[22] in the dilute regime. This indicates that no strong intermolecular orientational correlation results from the entanglements and polymer–polymer contacts, in the semidilute regime. The same straight line was obtained for the other polymers except for the sample of lower molecular weight ($M_w = 2500$). In this case, the slope of δH_v vs c is 3 times higher. One of us already observed that $\delta H_v/c$ decreases with increasing M_w and reaches a plateau for $M_w > 5000$.[23] This decrease is easily understood in term of the persistence length of the aPS chain.

(B) Sol–Gel Transition. The variations of the sol–gel transition temperature with concentration as obtained by the ball drop method in this work are reported in Figure 2. The agreement with previously published data is very good.[1,4] These results confirm the gelling ability of solutions of aPS samples with molecular weight much smaller than the value M_c requested for the formation of entanglements at the given concentration. Figure 2 shows that gelation occurs at -25 °C for a concentration as low as 0.25 g/mL, when $M_w = 2500$. As shown by Boyer et al.[5] physical entanglements present at higher molecular weights and higher concentrations stabilize the gel but are not necessary to the gelation which can occur through simple chain–chain contacts. These authors have distinguished three distinct regimes: regime I which corresponds to nongelling solutions, $c < c^*$, regime II where gelation occurs without entanglements, $c^* < c < c_{\rm ent}$, and regime III where entanglements enhance the gel stability and $c_{\rm ent}$ is the critical entanglement concentration. Even with the condition for gelation $c > c^*$, gelation for $M = 2500$ at $c = 0.25$ g/mL may be surprising if one considers the value obtained from the classical relation:

$$c^* = \frac{M}{(4/3)\pi N_a R_g^{\,3}} \tag{15}$$

where R_g is given by eq 13: $c^* = 0.42$ g/mL. However, eq 13 is not valid for the low molecular weight range ($M < 10\,000$) since it is well-known that the molecular weight dependencies of R_g or $[\eta]$ exhibit a crossover for a critical number of segments, N_c, when the chain passes from Gaussian statistics ($N < N_c$) to excluded-volume statistics ($N > N_c$).[24-26] For polystyrene, N_c was found to be close to 100. The extrapolation of eq 13 established for $M > 10\,000$ at lower molecular weight leads to an underestimation of R_g and then an overestimation of c^*. Another classifical expression of c^* is $c^* = 1/[\eta]$. From the value of $[\eta]$ given in Table I, for $M = 2500$, one obtains $c^* = 0.22$ g/mL. It is no more surprising to observe gelation with this sample, at $c > 0.25$ g/mL.

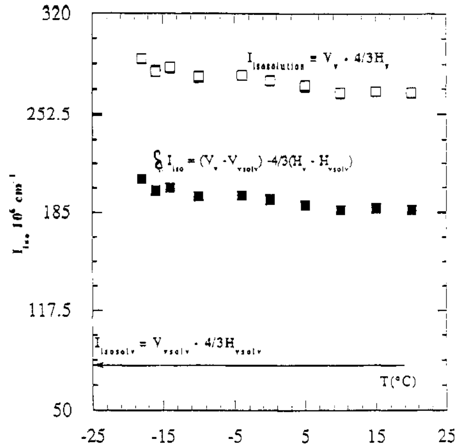

Figure 3. Variation of $I_{\rm iso}$ at $\theta = 90°$ vs temperature for sample D, $c = 0.25$ g/mL.

Light Scattering. Measurements of δH_v and δV_v were made upon cooling at various concentrations for each PS sample. The striking result is an abrupt jump of δH_v and δV_v at the gelation point. Their increments ($\Delta V_v = \delta V_{\rm v,gel} - \delta V_{\rm v,sol}$, $\Delta H_v = \delta H_{\rm v,gel} - \delta H_{\rm v,sol}$) are in the ratio 4/3 which is in agreement with eqs 4 and 5 provided the isotropic part has no discontinuity at the gelation point and only the anisotropic part is affected.

Figure 3 shows that there is indeed no change in the isotropic scattered intensity (at 90°) at the gelation temperature, T_g. Besides, the shape of $Kc/\delta I_{\rm iso} = f(q^2)$ curves at small angles does not significantly change: this means that the large-scale inhomogeneities of the semidilute solutions are not amplified by the gelation process. In fact, in the semidilute solutions above T_g the enhanced small-angle light scattering implies the presence of regions of concentration fluctuations of sizes much higher than the molecular dimensions. This result shows that only those short-range orientational correlations which affect $I_{\rm anis}$ are abruptly modified at the gelation point.

In Figure 4 are plotted the variations of δH_v as a function of temperature for different concentrations of sample D. They cannot be due to changes in the anisotropic properties of the solvent which are rather independent of temperature. The excess of H_v with respect to the pure solvent is also largely out of the experimental error range. The temperature range where the transition occurs is very narrow and the scattered intensity stabilizes very quickly

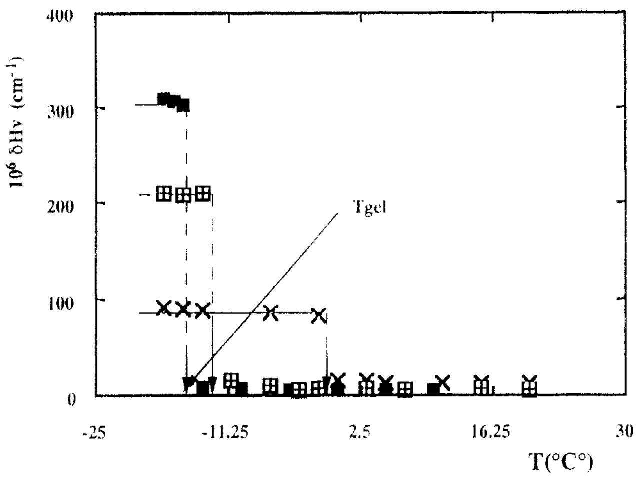

Figure 4. Variation of δH_v vs T at different concentrations (g/mL) for sample D. c = 0.08 (■); c = 0.10 (□); c = 0.20 (×). The arrows indicate the gelation temperature obtained by the ball drop method.

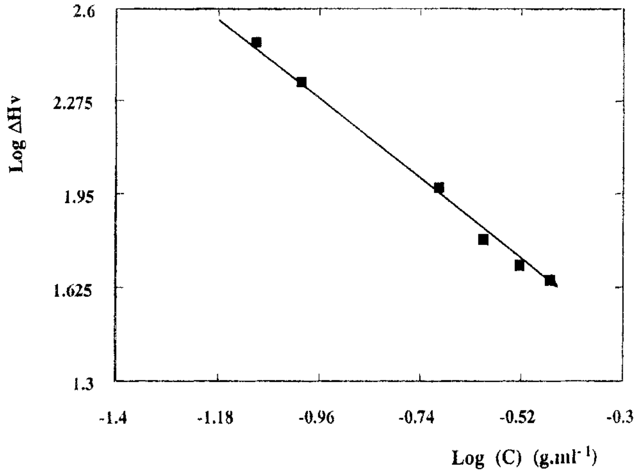

Figure 5. Logarithmic plot of ΔH_v at the sol–gel transition vs c for sample D.

after the change of temperature. When temperature cycles are applied to the gels, the results were well reproducible.

Interestingly enough, the jump is much larger at low concentration. As seen in Figure 5, the excess of anisotropic scattering $\Delta H_v = (\delta H_{v,gel} - \delta H_{v,sol})$ in the gel state with respect to the semidilute solution decreases with c according to a power law $c^{-1.7}$. The jump clearly confirms our starting hypothesis, but the peculiar concentration dependence of δH_v in the gel state has to be further understood.

Despite the difference in gelation temperature, the change in $\delta H_v/c$ in the semidilute and gel states at a given concentration does not depend on molecular weight, at least for $M_w > 2500$, as shown in Figure 6. In the case of the lower molecular weight sample, the value of δH_v in the gel state does not differ significantly from those obtained with the other polymers, but since the δH_v value in the sol state is much higher, the stiffening of the segments is less modified by the gelation.

IV. Discussion

The variation of the anisotropic light scattering as a function of temperature clearly demonstrates that at least a part of the polymer segments is stiffened upon gelation as obtained from ref 8. This supports the overall picture according to which some polymer–polymer contacts and/or entanglements become locked in a locally parallel train of segments. It may be surprising to observe such a stiffening only at the sol–gel transition defined from a rheological point of view. A parallel rheological study[29] has, however, revealed that the shear modulus of the gels below T_{gel} are about 4 times as high as the plateau modulus of the corresponding semidilute solutions above T_{gel}. This suggest that what we see in the anisotropic scattering experiments reflects the formation of new permanent physical cross-links. But it seems to conflict with the interpretation of the phase diagrams, as well as with the DSC[7] and neutron scattering measurements[11,12] which indicate that segment–segment association takes place in a broad range of temperature around T_{gel}. The variations of T_{gel} with M and c have been interpreted by Boyer et al.[5] in the framework of the classical Ferry–Eldridge approach.[27] The gelation is assumed to be due to a binary association of chain segments ruled by an equilibrium law, the sol–gel transition occurring for a cross-link concentration equal to $c/2M$, according to Stockmayer.[28] In a first approximation, this leads to the following relation between concentration and temperature at the sol–gel transition:

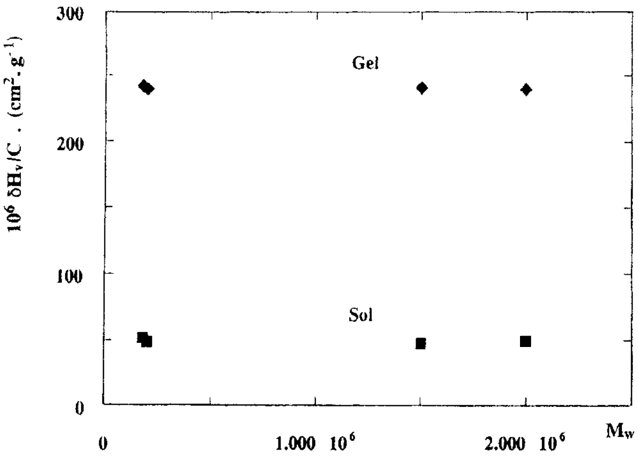

Figure 6. Variation of $\delta H_v/c$ vs the polymer molecular weight for c = 0.25 g/mL below (◆) and above (■) the gelation temperature.

$$\log c = \frac{\Delta H_0}{2.303RT} + \text{constant}(M) \qquad (16)$$

Then the slope of the plot of log c versus $1/T$ gives the enthalpy ΔH_0 associated with the formation of the cross-links. ΔH_0 was found to depend on M by Boyer et al.[5] Such a dependence is considered as an indication of a difference between cross-links formed from entanglements and those obtained from simple chain–chain contacts and is at the origin of the three regimes previously defined below, between, and above the overlap and entanglement concentration c^* and c_{ent}. Figure 7 represents such a diagram where the limiting lines are calculated as described elsewhere,[29] showing that most of our experiments have been carried out in regime III, i.e., starting from entangled solutions, but for the lower molecular weight.

In such a picture, one can consider that, at each temperature and each concentration, the same number of segment–segment associations is formed, dependent on M, provided the system belongs to the same regime, II or III. These associations take place in a broad range of temperature, and inside this domain, gelation occurs at a temperature which increases with increasing M. This description is well consistent with the results of DSC experiments carried out by Gan et al.,[4] who have found very broad DSC traces. In a first approximation and due to the relatively poor precision on these measurements (ΔH_0 very low), ΔH_0 was considered as roughly dependent

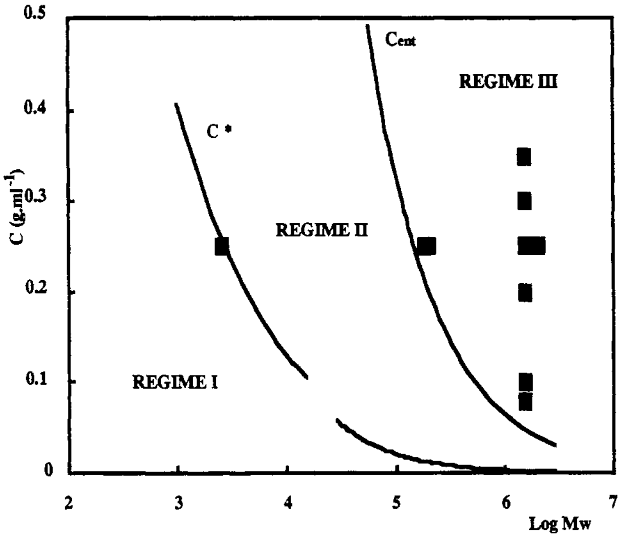

Figure 7. Molecular weight dependence of the overlap and entanglement concentration defining the three regimes I–III (see text). The concentrations at the gelation point (■) are all in regime III, but for the M_w = 2500 sample.

on M, except for a very low molecular weight sample (M = 1000) for which ΔH_0 was found to be significantly lower. In fact, the DSC results are quite compatible with two different values of ΔH_0 for entanglements and simple contacts as proposed by Boyer et al.[5] from the analysis of the phase diagrams.

If each of the segment–segment associations involves a locally stiff arrangement of parallel trains of segments, a gradual increase of δH_v is expected in the whole domain of temperature covered by the DSC traces. The abrupt change at T_{gel} of both δH_v and the (plateau) shear modulus implies that, among all the segment–segment associations revealed by DSC, a few of them adopt a special structure at T_{gel} and a correspondingly long lifetime requested for the formation of the gel. It is enough that the number of such tight associations is proportional to the total number of segment–segment associations to keep the Ferry–Eldridge interpretation of the phase diagram valid. This is well supported by the fact that the concentration dependence of the shear and (plateau) moduli below and above T_{gel} scale both with $c^{2.2}$ with a shift by a factor on the order of 4, implying that a number of new cross-links nearly equal to 3 times the number of entanglements (which is itself proportional to the number of simple contacts) is formed.

One is then left with the interpretation of the jump of δH_v at the gel point which can be understood as follows.

The theoretical expression of δH_v for a solution of n chain molecules made of N repeat units, with orientational correlations, is written as

$$\delta H_v \propto n(\alpha - \beta)^2 \sum_i^n \sum_j^N [(3 \cos^2 a_{ij} - 1)/2] \qquad (17)$$

where a_{ij} is the angle between the axes of the polarizability ellipsoids of the segments i and j. In dilute solutions, there is no orientational correlation between segments belonging to different chains and eq 15 writes

$$\delta H_v \propto nN(\alpha - \beta)^2 \sum_{i-j}^N [(3 \cos^2 a_{ij} - 1)/2] \qquad (18)$$

The sum has been shown to converge over distances on the order of the persistence length[30] so that a long chain of N correlated segments can be replaced by a chain of N' uncorrelated statistical elements with the corresponding polarizabilities α' and β':

$$\delta H_v \propto nN'(\alpha' - \beta')^2 \qquad (19)$$

Since $nN' \propto c$, $\delta H_v/c$ should be independent of concentration through c^* as long as no new orientational correlations result from intermolecular contacts and entanglements. This is what is found above T_{gel}.

Inversely, we can assume that, below the gelation temperature, some contacts become locked into a locally parallel ($\cos^2 a_{ij} = 1$) train of p statistical segments. If f is the total fraction of segments participating in locked contacts, the value of δH_v for gel becomes

$$\delta H_{v,gel} \propto nN'(\alpha' - \beta')^2[1 + 2fp] \qquad (20)$$

and the ratio

$$\frac{\delta H_{v,gel} - \delta H_{v,sol}}{\delta H_{v,sol}} = \frac{\Delta H_v}{\delta H_v} = 2fp \qquad (21)$$

Since δH_v in the semidilute solution is proportional to c (see Figure 1c), the data of Figure 5 show that $\Delta H_v/\delta H_v$ varies as $c^{-2.7}$.

$$fp \propto c^{-2.7} \qquad (22)$$

If we take into account the fact that the number of stiff associations, given by f/p scales as the total number of contacts

$$f/p \propto c^{2.2\pm0.2} \qquad (23)$$

we get

$$f \propto c^{-0.25\pm0.2} \quad \text{and} \quad p \propto c^{-2.5\pm0.4} \qquad (24)$$

We then deduce that the total fraction of segments which participate in stiff associations is nearly independent of concentration and that the length of such associations decreases rapidly with concentration.

It is difficult at this point to find an explanation for such a decrease. One can think that topological constraints limit the extension of such parallel arrangements when the distance between entanglements decreases. One must also recall that the gelation properties are strongly dependent upon the microstructure and that the formation of stiff associations can be related to the pairing of stereosequences. The recent synthesis of syndiotactic PS, allowing the preparation of epimerized samples with varying high content of syndiotactic sequences, should help to clarify this issue. Moreover, it has been suggested[7] that CS_2 participates in these associations. Their formation may then be controlled by a multiple equilibrium involving the decreasing concentration of CS_2 with increasing polymer concentration (the molar ratio monomer/polymer equals 2 at an aPS concentration of 0.30 g/mL).

V. Conclusion

The results of a systematic study of the aPS/CS_2 system as a function of temperature by anisotropic light scattering clearly demonstrate that a part of the chains are stiffened upon gelation. A simple model in which some chain–chain contacts transform in long-lived associations of parallel segments belonging to two chains seems to explain the experiments provided the length of these associations decreases with concentration. Further investigations using polymer of different microstructure as well as more detailed correlations with DSC, spectroscopic, or recent neutron scattering data[11,12] are requested.

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