

Viscoelastic properties of thermoreversible gelation of atactic polystyrene

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The gelation of several samples of atactic polystyrene (aPS) in CS₂ is studied by rheological methods. The Young's modulus and the loss and storage moduli are measured as a function of temperature in the sol and gel phases. In the sol phase the concentration dependence of the plateau modulus, G_N , is found to be in good agreement with the theoretical predictions. The sol-gel transition is accompanied by an abrupt increase of G_N , which shows the formation of additional entanglements with respect to the sol. For temperatures, T , below the gelation temperature, T_{gel} , G_N does not vary with temperature and the gel seems to reach a final structure at $T = T_{gel} - 10^\circ\text{C}$. These behaviours, which are independent of the aPS molecular weight, are discussed in relation to other experimental investigations (phase diagram, anisotropic light scattering, neutron scattering).

(Keywords: atactic polystyrene; gelation; viscoelastic properties)

INTRODUCTION

The first observation of the ability of atactic polystyrene (aPS) solutions to form thermoreversible gels at low temperature was made by Tan *et al.*¹ This unexpected phenomenon was the subject of many further experimental investigations and controversial interpretations²⁻¹².

The overall picture that emerged was that gelation is due to intermolecular associations of chain segments in complex crystals, including syndiotactic segments and solvent molecules. This was deduced from calorimetric measurements performed with aPS samples of various tacticity in different solvents⁷. A recent systematic study of the aPS-carbon disulfide (CS₂) system by depolarized light scattering (H_v)¹³ has demonstrated that part of the chains is stiffened upon gelation. An abrupt jump of H_v is indeed observed at the gelation temperature (T_{gel}), indicating a cooperative process. Such a result has been interpreted by considering that some of the entanglements and contacts present in the semidilute solution above T_{gel} become locked into a parallel train of segments. In consequence, a model was proposed where a pair of p statistical segments was assumed to form locked entanglements with a total fraction of segments f participating in these crosslinks. In such a model, with p independent of the concentration c , the difference of H_v between the gel and the semidilute solution, ΔH_v , is expected to increase as $c^{2.25}$, according to the scaling concentration dependence of the number of polymer-polymer contacts in good solvents^{14,15}. Surprisingly, ΔH_v was found to decrease as $c^{-1.7}$ and it was suggested that the value of p decreases with concentration, owing to topological constraints and the limitation of suitable syndiotactic sequences.

At this stage of our knowledge, the total number of

long-lived crosslinks and entanglements in the gel, and their concentration dependence, are required in order to resolve this puzzling problem and to make the model more quantitative.

There is a lack of reliable data on the rheological behaviour of this system. The purpose of the investigation of Gan *et al.*³ using a ball rheometer was to verify the elastic behaviour at temperatures below T_{gel} , which had been previously studied only through visual observations. This paper presents a systematic study of the temperature, concentration and molecular weight dependences of the Young's modulus, E , and the dynamic storage and loss moduli, $G'(\omega)$ and $G''(\omega)$. The results show that the shear modulus of the gel and the plateau modulus of the semidilute solution have the same concentration dependence, close to the theoretical law of $c^{2.25}$. Their ratio is about 4, reflecting the formation of new long-lived crosslinks in the gel.

EXPERIMENTAL

Material and sample preparation

Five samples of aPS were used in this study. Samples B and D, supplied by Aldrich, were obtained by radical polymerization, while samples C, E and F were prepared by anionic polymerization. They were characterized by size exclusion chromatography in tetrahydrofuran, using aPS calibration. The two types of samples have polydispersity indices around 1.5 and 1.1, respectively, but such a difference cannot have any effect on the present studies, which were performed in the semidilute concentration regime.

Measurements of the intrinsic viscosity, $[\eta]$, were made at 25°C in CS₂, using an automatic capillary viscometer. The values of M_w , M_w/M_n and $[\eta]$ are reported in Table I. The solutions directly prepared by weighting, at the

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Table 1 Characteristics of the samples: weight average molecular weight, M_w , polydispersity index, M_w/M_n , intrinsic viscosity $[\eta]$ measured in CS_2 at $25^\circ C$

Sample	M_w	M_w/M_n	$[\eta]$ (ml g ⁻¹)
B	1.8×10^5	1.55	50.1
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
F	1.9×10^6	1.03	–

measurement concentrations, were homogenized for 2 days at room temperature. The concentration, c , was always higher than $1/[\eta]$, and corresponds to the semi-dilute regime.

Young's modulus measurements

The Young's modulus, E , was measured with a home-built apparatus working in uniaxial compression. It included an HBM (Hottinger Baldwin Messtechnik (GmbH) amplifier coupled to a force transducer connected to a measurement Teflon cylinder (diameter, $\phi_c = 15$ mm, height, $h = 20$ mm). The force transducer could move the cylinder to the gel surface by micrometric steps with the help of a microcontrol translator. In fact, this type of device is well adapted to chemically crosslinked gels, for which well-defined geometry can be prepared. Cylinders of diameter equal to that of the Teflon cylinder are usually used, and they are immersed in the solvent for the measurements. This is much more difficult to achieve with thermoreversible gels. The solutions or gels were confined to a cell of diameter larger than ϕ_c . By studying the elastic moduli of chemically crosslinked polyacrylamide gels, swollen in water, it was found that the wall effects for confined gels could be minimized if $\phi_c > 26$ mm. A cylindrical glass cell of $\phi_c = 26$ mm and $h = 8$ mm was used in this work. This cell was put into a well-adjusted double-walled brass cylinder, maintained at $\pm 1^\circ C$ by circulating isopropanol from a Haake cryostat. In order to avoid problems arising from water condensation at the surface of the gel, all mechanical parts of the device were put in a glove box under a dry nitrogen flow.

A typical measurement was conducted as follows: the aPS- CS_2 solution was introduced into the glass cell, which was immediately closed to avoid the evaporation of CS_2 . Then the temperature was lowered to $-25^\circ C$ (i.e. lower than T_{gel} of all the samples studied). The nitrogen glow was set and stopped during measurements. Then measurements were made by raising the temperature in steps of $5^\circ C$, the solution being kept at each temperature for 1.30 h. The statistical theory of rubber elasticity¹⁶⁻¹⁹ gives the following simple form for the stress-strain equation:

$$\sigma = \frac{E}{3(\lambda^2 - \lambda^{-1})} \quad (1)$$

where E is Young's modulus. The extension ratio λ is:

$$\lambda = 1 + \gamma_{uniax} \quad (2)$$

with γ_{uniax} the uniaxial deformation. For small deformations ($\gamma_{uniax} < 10\%$):

$$\sigma = E\gamma_{uniax} \quad (3)$$

As shown in Figure 1, the value of E is obtained from the slope of the plot of $\sigma = f(\gamma_{uniax})$, using a least square analysis.

Rheological measurements

The dynamic storage and loss moduli, G' and G'' , were measured with a stress-controlled rheometer (Carrimed CSL 100) equipped with a cone cylinder geometry as a function of the frequency ($10^{-2} < \omega < 62.8$ rad s⁻¹). The magnitude of the shear strain was set at values lower than 0.1. The device could be thermostatically controlled by isopropanol circulation at $\pm 1^\circ C$. Water condensation on the metallic parts was avoided by means of a dry nitrogen flow. A thin layer of low viscosity silicon oil was put at the gel surface in order to reduce the CS_2 evaporation. We had previously checked the immiscibility of the silicon oil in CS_2 . Therefore, the oil stayed away from the gel-cylinder surfaces and could not perturb the measurements. Moreover, the measurements made just before and just after deposition of the oil layer were quite similar. The concentration was found to vary by less than 2% during all the measurement cycles. The measurements were performed over the temperature range $-30^\circ C$ to $+30^\circ C$, and the results were reduced to $20^\circ C$ using time-temperature superposition²⁰, for the semidilute solutions. Figure 2 gives typical isotherms and master curves for G' and G'' .

RESULTS

Semidilute solutions were prepared in the concentration range between c^* and 0.30 g cm⁻³. T_{gel} was measured by the ball-drop method, as described in ref. 13.

Young's modulus measurements

Figure 3 shows that in a typical uniaxial compression experiment (aPS- CS_2 solutions, $c \approx 0.25$ g ml⁻¹), $T = T_{gel} - 30^\circ C$, the variation with time (t) of the stress relaxation at constant deformation obeys a classical law, $\sigma \propto t^{-m}$. Because it is difficult to completely avoid evaporation in our device, the measurements were limited to times lower than 1000 s. The value of the exponent m (0.09–0.12) is larger than that generally found for chemical networks ($m \approx 0.01$)²¹. Similar values of m have been obtained for isotactic polystyrene (iPS) by Guenet and

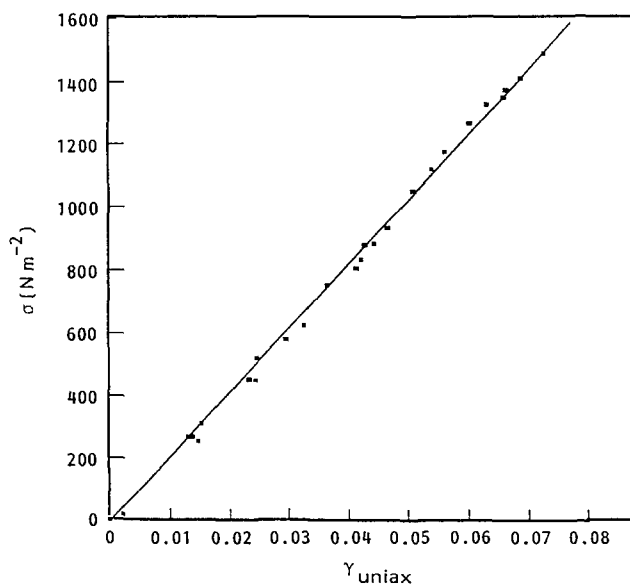


Figure 1 Typical uniaxial compression experiment: plot of the stress, σ , versus the uniaxial deformation, γ_{uniax} (sample E in CS_2 , $c = 0.33$ g ml⁻¹)

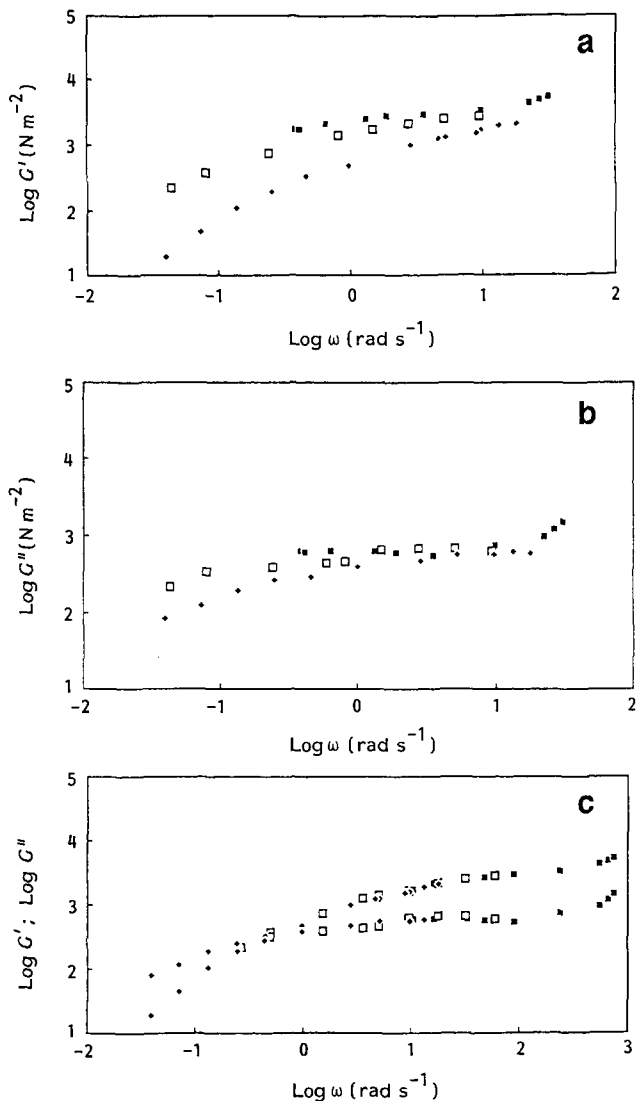


Figure 2 (a) Dynamic storage modulus and (b) dynamic loss modulus at various temperatures: \blacklozenge , 20°C ; \square , 15°C ; \blacksquare , 10°C . (c) Master curves (reduced at $T = 25^\circ\text{C}$) for sample C, $c = 0.22 \text{ g ml}^{-1}$

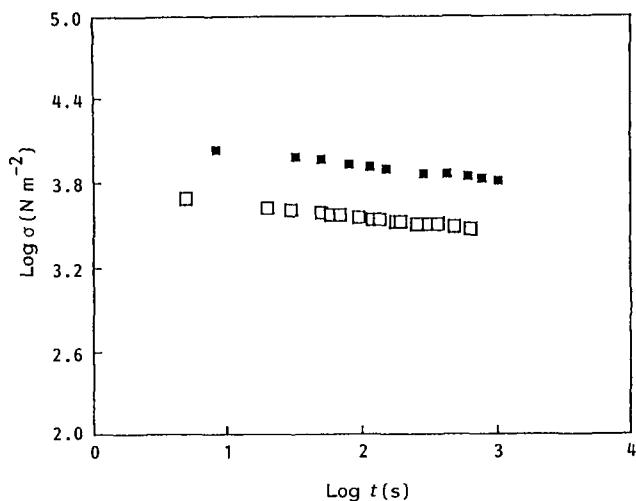


Figure 3 Uniaxial stress relaxation, sample C: $c = 0.22 \text{ g ml}^{-1}$ (\square), 0.27 g ml^{-1} (\blacksquare); $T = -25^\circ\text{C}$

McKenna²², who considered that gels of iPS in *cis*-decalin do not display true solid-like behaviour but flow slowly. This result can be related to the limited lifetime of the physical crosslinks.

For all the following results, measurements of σ were made at the same time interval after changing the deformation, in order to avoid stress relaxation effects; the linearity of the plot of σ versus γ_{uniax} , as shown in Figure 1, confirms the validity of the method.

An example of the temperature dependence of E is given in Figure 4 (sample F at $c = 0.27 \text{ g ml}^{-1}$). An abrupt jump of E is observed at $T = 4^\circ\text{C}$, close to the T_{gel} value obtained by the ball-drop method ($T_{\text{gel}} = 5^\circ\text{C}$). Besides, E is independent of T in the gel state ($T < T_{\text{gel}}$). The values of E obtained in the gel state for the four aPS samples at different concentrations are reported in Table 2. The data can be fitted by the following scaling law:

$$E = 5.8 \times 10^5 c^{2.13 \pm 0.08} (\text{N m}^{-2}) \quad (4)$$

where c is in g ml^{-1} , as shown in Figure 5.

G' and G'' measurements

Semidilute solutions, $T > T_{\text{gel}}$. The viscoelastic behaviour of these systems in the sol phase, for $T > T_{\text{gel}}$, is shown in Figure 2. They exhibit behaviour typical of semidilute polymer solution²³⁻²⁶, with three characteristic frequency zones. In the low frequency range, below a characteristic frequency ω_c , G'' and G' increase like ω

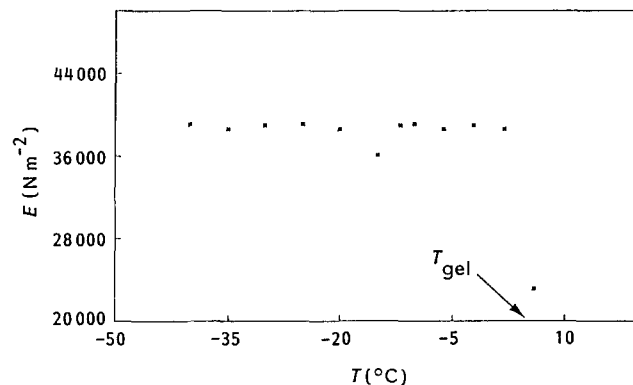


Figure 4 Young's modulus E versus temperature, sample F, $c = 0.27 \text{ g ml}^{-1}$

Table 2 Variation of G_N , E and M_e with polymer concentration, c , at $T = -25^\circ\text{C}$ ($< T_{\text{gel}}$)

Sample	c (g ml^{-1})	G_N (N m^{-2})	E (N m^{-2})	M_e
C	0.08	—	2755	1.7×10^5
	0.141	3162	—	9×10^4
	0.15	—	9660	9.4×10^4
	0.25	—	31622	4.9×10^4
D	0.06	363	—	3×10^5
	0.105	—	4581	1.4×10^5
	0.126	1513	—	1.7×10^5
	0.13	—	6936	1.2×10^5
	0.16	—	12067	8.2×10^4
	0.20	—	18954	6.5×10^4
	0.22	8913	23316	5.1×10^4
	0.275	—	37250	4.6×10^4
0.302	—	47985	3.9×10^4	
E	0.05	264	—	3.9×10^5
	0.09	832	—	2×10^5
	0.12	—	5861	1.3×10^5
	0.18	—	15136	7.4×10^4
	0.225	—	25942	5.4×10^4
F	0.046	199.5	—	4.7×10^5
	0.066	398	—	3.4×10^5
	0.07	—	2400	1.8×10^5
	0.085	—	2979	1.7×10^5

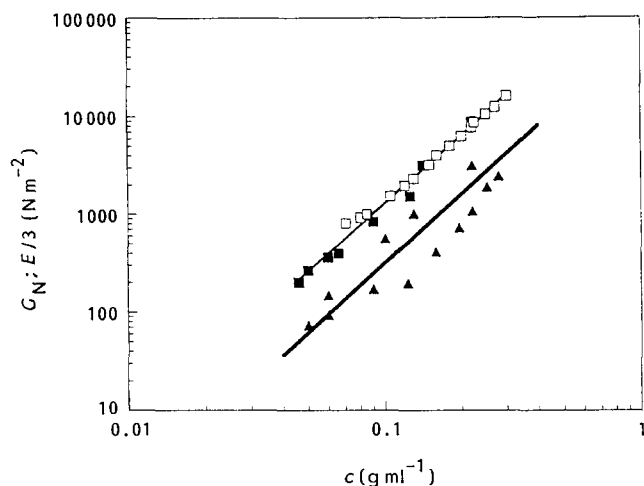


Figure 5 Logarithmic plots of the Young's modulus $E/3$ (□), the plateau modulus G_N in the sol phase (▲) and in the gel phase (■) versus concentration, c

and ω^2 , respectively (terminal zone of a viscoelastic liquid). The isotherms of *Figure 2* show that ω_c decreases with decreasing temperature. In an intermediate frequency range G' and G'' are almost independent of the frequency (plateau zone) and G' becomes higher than G'' . For still higher frequencies, G' and G'' increase again.

The plateau modulus (G_N) can be defined as the value of the dynamic storage modulus, G' , at the frequency corresponding to the minimum of the dynamic loss modulus, G'' . It is reported as a function of concentration in *Figure 5* and, despite the scatter of the results, a least square analysis was made, which leads to a concentration dependence with an exponent close to 2.

This result is consistent with experimental and theoretical results from the literature^{14,23-27} and confirms that this system does not present any particular behaviour.

Gels, $T < T_{gel}$. *Figure 6* shows the evolution of the curves $G' = f(\omega)$ when temperature decreases, for a solution of sample C (0.28 g ml^{-1}). For $T = 5^\circ\text{C}$, which is close to the T_{gel} value (4°C) obtained by the ball-drop method, G_N is found to increase abruptly and level off for $T < T_{gel}$. This result means that the number of long-lived crosslinks in the gel is independent of temperature and higher than the number of entanglements in the solution. For the lowest temperatures, corresponding to $-40^\circ\text{C} < T - T_{gel} < -20^\circ\text{C}$, the system exhibits a nearly elastic behaviour, at least in the frequency range investigated (see *Figure 7*). For temperatures closer to T_{gel} , a terminal zone is observed at frequencies lower than ω_c , at which the rubber plateau is reached. As for the solutions, ω_c decreases with decreasing temperature, but the slope of the plot $\log(1/\omega_c) = f(1/T)$ seems to be significantly higher in the gel phase. This reveals a more pronounced increase of the lifetime of the crosslinks in the gel when temperature decreases.

In the concentration range studied, the characteristic moduli are independent of the molecular weight. The results obtained for the different samples are given in *Table 2* and the variation of G_N with c is shown in *Figure 5*.

According to the classical relation ($E = 3G_N$) between the plateau modulus and Young's modulus, in an elastic incompressible material, the experimental values of $E/3$ are plotted in *Figure 5* and both sets of experiments

appear to be in good agreement. A unique scaling law for the variation of $E/3$ and G_N is obtained:

$$E/3 = G_{N_{gel}} = 2.6 \times 10^5 c^{2.3} \quad (\text{N m}^{-2}) \quad (5)$$

Almost the same exponent for the concentration dependence of G_N is found in the sol and gel phases, which is consistent with the observed absence of syneresis effect upon gelation.

DISCUSSION

Theoretical expression of G_N in semidilute solutions

It is well known that the dynamic storage modulus at the rubber plateau, G_N , can be expressed by:

$$G_N = (cRT/M_e) \quad (6)$$

where R is the gas constant, T is the absolute temperature and M_e is the entanglement molecular weight. This quantity is related to the number of entanglements per

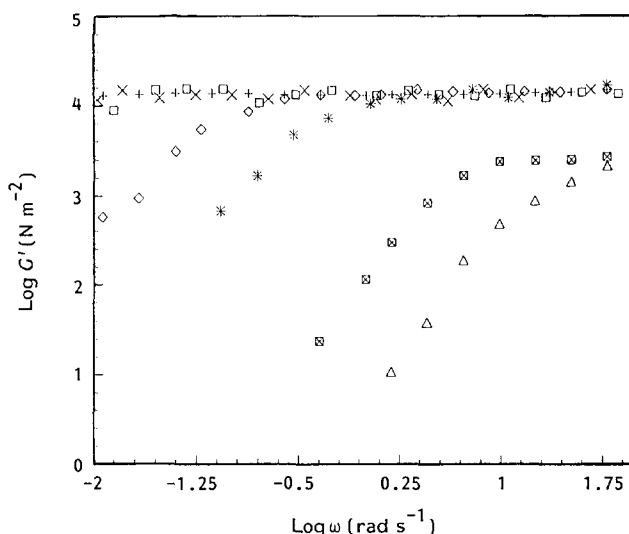


Figure 6 Variation of G' as a function of ω at various temperatures, sample C, $c = 0.28 \text{ g ml}^{-1}$. Temperature ($^\circ\text{C}$): □, -35; ×, -25; +, -15; ◇, -2; *, 5; ⊠, 10; △, 20

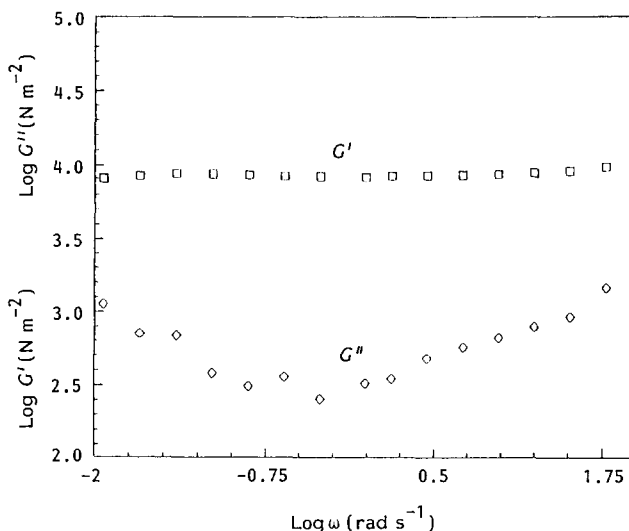


Figure 7 Examples of double logarithmic plot of the dynamic storage and loss moduli, G' and G'' for a gel, sample C, $c = 0.2 \text{ g ml}^{-1}$, $T = -25^\circ\text{C}$

molecule, N , through:

$$N = (M/M_e) \quad (7)$$

The problem is to determine the concentration dependence of M_e by using the framework of the polymer semidilute solution theories. The theory of ref. 27 leads to the following relation between M_e and the blob molecular weight M_b :

$$(M_e/M_b) = (18\pi^2)^{1/2} \quad (8)$$

On the other hand, it is known that²⁸:

$$(M_b/M)^\nu = (\xi_b/R_{g0}) \quad (9)$$

R_{g0} , the radius of gyration at infinite dilution varies as aM^ν , where ν is the excluded volume exponent.

Experimentally, the blob length ξ_b cannot be directly obtained. Scattering experiments allow the measurement of the screening length, ξ , introduced in the semidilute polymer solution theory of Muthukumar and Edwards²⁹. Broseta *et al.*³⁰ have obtained a relation between ξ and ξ_b , through the mean field approximation:

$$\xi = 2^{1/2}(2\pi)^{-3/4}\xi_b \quad (10)$$

and

$$\frac{\xi}{R_{g0}} = 2(2\pi)^{-3/4}(c/c^*)^{\nu/(1-3\nu)} \quad (11)$$

From equations (6), (8)–(11), and the expression of c^* :

$$c^* = \frac{3M}{4\pi N_a R_{g0}^3} \quad (12)$$

the concentration dependence of the entanglement molecular weight M_e and the plateau modulus G_N are obtained as follows:

$$M_e = (18\pi^2)^{1/2}(2)^{1/2\nu}(4/3\pi N_a a^3)^{-1/(3\nu-1)}c^{-1/(3\nu-1)} \quad (13)$$

and

$$G_N = (18\pi^2)^{-1/2}(2)^{-1/2\nu}(4/3\pi N_a a^3)^{1/(3\nu-1)}RT10^6 c^{3\nu/(3\nu-1)} \quad (14)$$

Comparison with experimental data

The general validity of relations (13) and (14) has been checked using the results of Osaki *et al.*^{23–26} on the viscoelastic properties of aPS in the good solvent chlorinated biphenyl, Aroclor 1248. They represent the only extensive set of results concerning the variation of M_e and G_N with c . Their experimental expressions are, for $c < 0.1 \text{ g ml}^{-1}$:

$$M_e = 7.3 \times 10^3 c^{-1.4} \quad (15)$$

$$G_N = 3.44 \times 10^5 c^{2.4} \quad (16)$$

The two concentration exponents fit with $\nu=0.57$, in fair agreement with the viscosity of aPS in Aroclor:

$$[\eta] = 1.5 \times 10^{-2} M^{0.70} \quad (\text{ml g}^{-1}) \quad (17)$$

From relations (13) and (14), where a is deduced from $c^* = 1/[\eta]$, we have calculated the prefactors:

$$M_e = 8 \times 10^3 c^{-1.4} \quad (18)$$

$$G_N = 3 \times 10^5 c^{2.4} \quad (19)$$

in excellent agreement with experiments.

For the aPS-CS₂ system, values of $\nu=0.58$ and $a=0.122 \times 10^{-8} \text{ cm}(\text{g mol})^{-\nu}$ have been measured by

neutron scattering by Rawiso *et al.*³¹; they lead to the following concentration dependences of M_e and G_N :

$$M_e = 2.1 \times 10^4 c^{-1.35} \quad (20)$$

and

$$G_N = 0.7 \times 10^5 c^{2.35} \quad (21)$$

In Figure 5, the three experimental variations of $E/3$, $G_{N\text{sol}}$ and $G_{N\text{gel}}$ can be compared with the calculated law, equation (21). For the sol phase, the calculated curve lies between the experimental points. It is then clear that gelation introduces an excess of crosslinks with respect to the entanglements present in the semidilute solution.

CONCLUSION

The concentration dependence of the viscoelastic properties of aPS-CS₂ semidilute solutions is consistent with the theoretical predictions. At gelation point, an abrupt change in the plateau modulus, G_N , is observed but the exponent of its concentration dependence is almost unmodified. If for each blob, a chain-chain contact was transformed in a new long-lived crosslink, the ratio $G_{N\text{gel}}/G_{N\text{sol}}$ should be, according to ref. 30, $(18\pi^2)^{1/2}$, which is much higher than the experimental value of around 4. The viscoelastic properties of the gel are weakly perturbed by cooling below T_{gel} and are independent of aPS molecular weight.

These results are consistent with the previously observed jump in anisotropic light scattering at gelation point, which can be interpreted by a model implying the formation of stiffened segments. This seems to contradict both the interpretation of the molecular weight of T_{gel} in terms of a simple segment-segment association, and the conclusion of neutron scattering studies by Izumi *et al.*^{11,12} on deuterated aPS in CS₂. The first problem has been addressed in ref. 13. For the second, the evidence of a maximum in the Kratky representation of the scattered intensity is interpreted by Izumi *et al.* in terms of the formation of highly branched molecules or star molecules with a high number of branches, reaching 400 at low temperature. However disputable this interpretation may be, it should be stressed that short-lived segment-segment associations may introduce spatial correlations capable of influencing neutron scattering, while they will not affect the rheological behaviour, as long as the lifetime is much smaller than the terminal time of the semidilute solution.

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